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<td>8.20-9.00</td>
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<td>PL3 - Balsara</td>
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<td>9.00-9.30</td>
<td>K1 - Cui</td>
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<td>9.30-10.00</td>
<td>I1 - Tominaga</td>
<td>I7 - Popovic</td>
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<td>10.50-11.20</td>
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<td>I9 - Teeters</td>
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ISPE-XV – Welcome back to Uppsala!

Some 20 years after the ISPE-5 was held here in 1996, we can finally wish you welcome back! The ISPE community has of course developed a lot since then, but we do recognize more than a few that was around also last time. But more important is that this meeting brings in young researchers and PhD students to hopefully allow ISPE at least another 20 years of success. In total we are this time gathering 176 attendees from over 26 countries – indeed broadcasting how widespread the interest in polymer electrolytes is globally. All of you are welcome to ISPE-XV to contribute to the rich discussions that the ISPE meetings are so well-known for.

During our five days of conferencing at “Uppsala Konsert & Kongress” we will offer you quite a varied “smorgasbord” of science – following the development of the field at large and thus you will find presentations of polymer electrolytes, alternative electrolyte systems, electrochemical applications, and presentations dwelling on the fundamental understanding of ion transport, structure, and dynamics. As well you will find ISPE-XV to include a wealth of related soft matter; ionic liquids, hybrid concepts, gels, and glasses, and aiming at a wide range of applications such as lithium- and sodium-ion batteries, fuel cells, photo-electrochemical systems, supercapacitors, sensors & actuators, etc.

As we sincerely think that science is a social activity there will also be time to socialize at the poster sessions, the conference excursion – to Stockholm including the Nobel museum, and of course at the conference dinner at a typical Uppsala student place: “Norrlands Nation”.

We hope and think that this layout and not the least all your contributions, scientific and social, will make this ISPE conference at least as excellent as all previous ISPEs.

As for the history of the ISPE series it was inaugurated in 1987 in the UK (St. Andrews), and has since then seen Italy (Siena, 1989), France (Annecy, 1991), USA (Newport, 1994), Sweden (Uppsala, 1996), Japan (Hayama, 1998), Australia (Noosa, 2000), USA (Santa Fe, 2002), Poland (Mragowo, 2004), Brazil (Foz do Iguacú, 2006), Portugal (Ofr, 2008), Italy (Padova, 2010), Iceland (Selfoss, 2012), and Australia (Geelong, 2014).

The conference is this time co-organized by the two polymer electrolyte research groups at Chalmers University of Technology and Uppsala University – and we are sincerely grateful to both universities for their ample financial support. The same big thanks goes to our exhibitors and corporate sponsors, please visit them during the conference, and last but not the least to the Swedish Research Council (“Vetenskapsrådet”) and “Stiftelsen Lämnanska Kulturfonden”.

Finally we hope you will enjoy Sweden and the pleasant atmosphere of summertime Uppsala.

Prof. Patrik Johansson
Chalmers University of Technology

Prof. Daniel Brandell
Uppsala University

Chairmen of ISPE-XV
Important Information

Get-together Party (and Registration) at Linnéträdgården
The conference will kick-start with a mingle event 17-20 at “Linnéträdgården” on Sunday Aug 14th. “Linné” is more famous as Linnaeus and “trädgård” means garden. The garden, in the city centre of Uppsala, was the first botanical garden in Sweden, founded in 1655 by Rudbeck the elder. It is laid out in the French style and restored following Linnaeus’ and Carl Härleman’s design from 1745. Today approximately 1300 species are grown here – all known to have been cultivated by Linnaeus and arranged according to his own system.

Uppsala Konsert & Kongress (UKK) – the Conference Venue
The conference venue UKK is a landmark in Uppsala inaugurated in 2007. It is a modern eight-storey building for meetings, concerts, etc with expressful architecture and the view over Uppsala from level 6 is fantastic.
All activities Monday-Friday, excepted the excursion and the banquet, will take place at UKK.

Conference Excursion – Stockholm or Uppsala
Uppsala has many things to offer – but it does not have a Nobel museum!
For those of you that have signed up for Stockholm, tour buses will leave from UKK on Wednesday Aug 17th at 12.30 (sharp!) to bring you to Stockholm’s Old Town (“Slottsbacken”).
A small packed lunch will be provided and the ride lasts ca. 1h20.

In Stockholm guides will meet you for both a walking tour of the Old Town, from the 13th Century, and the Nobel museum where you will learn more about the Nobel Prize and its founder, as well as the Nobel Laureates and their creative endeavors. The Nobel Museum opened in 2001 and is situated in one of Stockholm’s most beautiful 18th Century buildings.

After the tour you will have some extra time to see other sights of Stockholm – the buses will leave for Uppsala again at 21.00 (sharp!) from where you disembarked. If you, however, like to go back earlier (or later) – there are both trains and buses, tickets are approx. 90-130 SEK.

For those of you preferring to stay in Uppsala, a limited number of people will be provided a shorter guided tour focused on the local but rich history of chemistry.

Conference Banquet at Norrlands Nation
On Thursday Aug 18th, starting at 18.30, you will be welcomed into a student nation – Norrlands – for a dinner. Student nations are regional corporations of students, in medieval times common all across Europe but now largely restricted to the older universities of Sweden and Finland – such as Uppsala. In Uppsala the nations, there are 13 of them and the oldest “Västgöta Nation” started already in 1639, often have impressive beautiful buildings and handle all kinds of social activities such as pubs, clubs, theatre companies, orchestras, sports societies, etc. Norrlands is primarily for students from the northern part of Sweden.
International Scientific Advisory Board for the International Symposium on Polymer Electrolytes

The International Scientific Advisory Board for ISPE-XV consists of the following members:

- Fannie Alloin, LEPMI Grenoble, France
- C. Austen Angell, Arizona State University, USA
- Michel Armand, CIC Energigune, Spain
- Nitash Balsara, University of California Berkeley, USA
- Daniel Brandell, Uppsala University, Sweden
- Peter G. Bruce, University of Oxford, UK
- Guanglei Cui, Chinese Academy of Sciences, China
- Joseph Dura, NIST Center for Neutron Research, USA
- Maria Forsyth, Deakin University, Australia
- Roger Frech, University of Oklahoma, USA
- Diana Golodnitsky, Tel Aviv University, Israel
- Steve G. Greenbaum, City University of New York, USA
- Michael Hickner, Penn State, USA
- Patrik Johansson, Chalmers University of Technology, Sweden
- Whan Gi Kim, Konkuk University, South Korea
- Klaus-Dieter Kreuer, Max Planck Institute Stuttgart, Germany
- Douglas MacFarlane, Monash University, Australia
- Louis Madsen, Virginia Tech, USA
- Joachim Maier, Max Planck Institute Stuttgart, Germany
- David Mecerreyes, Polymat, Spain
- Vito Di Noto, University of Padova, Italy
- Hiroyuki Ohno, Tokyo University of Agriculture and Technology, Japan
- Stephen J. Paddison, University of Tennessee, USA
- Stefano Passerini, Helmholtz Ulm, Germany
- Agnieszka Pawlicka, University of Sao Paolo, Brazil
- Emanuel Peled, Tel Aviv University, Israel
- Michael Popall, Fraunhofer Institute Würzburg, Germany
- Jean-Yves Sanchez, Charles III University of Madrid, Spain
- Bruno Scrosati, Sapienza University of Rome, Italy
- Maria Manuela Silva, University of Minho, Portugal
- Robert Slade, University of Surrey, UK
- Eugene Smotkin, Northeastern University, USA
- Masayoshi Watanabe, Yokohama National University, Japan
- Wladislaw Wieczorek, Warsaw University of Technology, Poland
- Thomas A. Zawodzinski, University of Tennessee, USA
- Verónica de Zea Bermudez, University of Tras-os-Montes and Alto Duro, Portugal
Local scientific committee

Daniel Brandell
Patrik Johansson
Kristina Edström
Aleksandar Matic
Tim Bowden
Johan Scheers

Local organizing committee

Daniel Brandell
Patrik Johansson
Kristina Edström
Steffen Jeschke
Viktor Nilsson
Manfred Kerner
Mahsa Ebadi
Tim Nordh
Ronnie Mogensen
Stéven Renault
Matthew Lacey
Burak Aktekin
Habtom Desta Asfaw
Fabian Jeschull
Erik Björklund
Andreas Bergfelt
Reza Younesi
Programme
Sunday Aug 14th

17.00-20.00  Registration and Get-together Party at Linnéträdgården

Monday Aug 15th

08.00- Registration

08.10-08.20  Welcome Address
Patrik Johansson & Daniel Brandell – Chairmen of ISPE-XV

Session 1  Chairperson: Maria Forsyth

08.20-09.00  PL1
C. Austen Angell: Flexible Inorganic SPEs of a Novel Type: Anhydrous Fuel Cell
Membranes and the Possibility of Protic Ionic Liquid and Alkali-ion-conducting
Cousins

09.00-09.30  K1
Guanglei Cui: Safety-reinforced and High-voltage Poly(propylene carbonate)-
based All-solid-state Polymer Electrolyte for Ambient-temperature Solid
Polymer Lithium Batteries

09.30-10.00  I1
Yoichi Tominaga: Poly(ethylene carbonate) and its Derivatives for Solid Polymer
Electrolytes

10.00-10.20  Coffee Break

Session 2  Chairperson: Jelena Popovic

10.20-10.50  I2
Grażyna Z. Żukowska: Influence of the architecture of the solid phase on the
conductivity: Concentrated electrolyte systems doped with salts bearing Hückel
anions

10.50-11.20  I3
James Snyder: Multifunctional Electrolytes for Structural Batteries &
Supercapacitors Using Additive Manufacturing

11.20-11.40  O1
Trang N. T. Phan: Polystyrene block copolymers bearing sulfonimide and PEG
side chain for improved conductivity and mechanical performance
11.40-12.00  O2  
Basile Commarieu: Lithium battery with solid polymer electrolyte based on comb-like copolymers

12.00-13.30  Lunch Break

Session 3  Chairperson: Klaus-Dieter Kreuer

13.30-14.00  K2  
Stefano Passerini: Ionic Liquid-Based Electrolytes for Alkaline-ion Batteries

14.00-14.30  I4  
Masahiro Yoshizawa-Fujita: Improvement of Charge/Discharge Properties of Cells with Various Electrolyte Materials by Zwitterion Additives

14.30-15.00  I5  
Ludvig Edman: On the Application and Design of Electrolytes for Efficient, Large-Area and Conformable Light-Emitting Devices

15.00-15.20  Coffee Break

Session 4  Chairperson: Michael Popall

15.20-15.50  I6  
Adam S. Best: Lithium polysulfides and ionic liquid based electrolytes – is this the solution?

15.50-16.10  O3  
Steve Greenbaum: Multinuclear NMR Studies of Ion Solvation and Association in Glyme Solvents

16.10-16.30  O4  
Noriyoshi Matsumi: Crystalline Organoboron Compound as Scaffold for Ion Conductive Path via Boron-Anion Interaction

16.30-16.50  O5  
Takahito Itoh: Solid Polymer Electrolyte Based on Poly (2,2-dimethyl-oxytrimethylene carbonate)

Session 5  Chairperson: Tim Bowden

16.50-17.20  Short presentations  
Jürgen Wackerl, Adrien Lassagne, Oxana Ivanova, Jiangshui Luo, Naveeda Firdous, Jan Swenson, Xiaoen Wang, Nadhratun Naiim Mobarak

17.20-19.30  Poster session 1
Tuesday Aug 16th

Session 6  Chairperson: Masayoshi Watanabe

08.20-09.00  PL2
Michel Armand: Advanced Anions for Polymer Electrolytes and ILs

09.00-09.30  K3
Alexei P. Sokolov: From Fundamentals of Ionic Conductivity to “Superionic” Polymer Electrolytes

09.30-10.00  I7
Jelena Popovic: Charge carrier chemistry in liquid/solid lithium electrolytes

10.00-10.20  Coffee Break

Session 7  Chairperson: Eugene Smotkin

10.20-10.50  I8
Michael Popall: Inorganic-organic hybrid materials and their niche in energy storage applications

10.50-11.20  I9
Dale Teeters: Enhanced Ionic Conduction and Battery Fabrication Using Polymer Electrolyte, Ionic Liquids and Polymer Electrolyte/Ionic Liquid Mixtures in Ceramic Interpenetrating Networks

11.20-11.40  O6
Claudio Gerbaldi: Lignocellulosic Materials for the Next-Generation of Eco-Friendly Polymeric Energy Storage Devices

11.40-12.00  O7
Michał Marzantowicz: Polymer electrolytes comprising oligomeric lithium borate salts and poly(ethylene oxide)

12.00-13.30  Lunch Break
Session 8  
Chairperson: Anna Martinelli

13.30-14.00  K4
Patric Jannasch: Synthetic approaches towards anion-exchange membranes with high alkaline stability and OH conductivity

14.00-14.30  I10
Jean-Yves Sanchez: Revisiting Single-Cation conducting Polymer Electrolytes through Bottom-up syntheses of Poly(oxyethylene)-based Ionomers

14.30-15.00  I11
Renaud Bouchet: From neutral to single-ion block copolymer electrolytes

15.00-15.20  Coffee Break

Session 9  
Chairperson: Patric Jannasch

15.20-15.50  I12
Fannie Alloin: N-methylphenothiazine based organic materials for lithium battery

15.50-16.10  O8
Zhigang Xue: Solid polymer electrolyte based on Comb-like SPEEK-g-PEG for lithium ion batteries

16.10-16.30  O9

16.30-16.50  O10
Luca Porcarelli: Single-ion Conducting Block Copolymer Electrolytes for Solid State Lithium Batteries

Session 10  
Chairperson: Daniel Brandell

16.50-17.20  Short presentations
Azizan Ahmad, Jessica Lefevre, Jiangshui Luo, Ramesh Subramaniam, Graeme Nawn, Giulia Piana, Michael Zimmerman, Dorota Gladka, Wan M. Khairul

17.20-19.30  Poster session 2
Wednesday Aug 17\textsuperscript{th}

\textit{Session 11} \quad Chairperson: Vito di Noto

\textbf{08.20-09.00} PL3  
Nitash. P. Balsara: \textit{Toward Complete Characterization of Polymer Electrolytes}

\textbf{09.00-09.30} K5  
Oleg Borodin: \textit{Modeling Lithium Battery Electrolytes and Solid Electrolytes Interphases}

\textbf{09.30-10.00} I13  
Monika Schönhoff: \textit{Ion Mobilities and Correlated Motion in Ionic Liquids Analyzed by Electrophoretic NMR}

\textbf{10.00-10.20} Coffee Break

\textit{Session 12} \quad Chairperson: Stefano Passerini

\textbf{10.20-10.50} I14  
John R. Owen: \textit{Reactant Concentration and Transference Number Effects in Electrolytes for Battery Cells}

\textbf{10.50-11.20} I15  
Nicolaas Stolwijk: \textit{Analysis of Ionic Transport in Polymer/Ionic-Liquid Systems}

\textbf{11.20-11.40} O11  
Sabina Abbrent: \textit{Effect of polymer network structure on physical and chemical properties of resulting gel polymer electrolyte materials}

\textbf{11.40-12.00} O12  
Lars Wadsö: \textit{Sorption calorimetry: measuring the thermodynamics of interactions between charged polymers and water}

\textbf{12.30-} \quad Conference Excursion
Thursday Aug 18th

Session 13  Chairperson: Oleg Borodin

08.20-09.00  PL4
Klaus-Dieter Kreuer: Ion Conducting Membranes for Fuel Cells and Batteries: A Combined Bottom-up / Top-down Approach

09.00-09.30  K6
Vito Di Noto: Conductivity and Relaxation Phenomena in Proton and Anionic Exchange Membranes by Broadband Electric Spectroscopy

09.30-10.00  I16
Eugene S. Smotkin: A local symmetry description of the Nafion exchange site environment vs. state-of-hydration

10.00-10.20  Coffee Break

Session 14  Chairperson: Masahiro Yoshizawa-Fujita

10.20-10.50  I17
Yossef A. Elabd: Polymerized Ionic Liquid Block Copolymers for Alkaline Fuel Cells

10.50-11.20  I18
Anna Martinelli: From neat ionic liquids to hybrid ionogels: challenges and progresses

11.20-11.40  O13
Michael A. Hickner: Crosslinked Anion Exchange Membranes with Complex Structures

11.40-12.00  O14
Masamichi Nishihara: Alternative polymer electrolyte membranes consisting with supramolecular charge-transfer complex structure for high temperature operation

12.00-14.00  Lunch Break + Scientific Advisory Board Meeting

Session 15  Chairperson: Alexei Sokolov

14.00-14.30  I19
Tom Zawodzinski: High Performance Electrolytes for Flow Batteries and Other Open Electrochemical Systems
14.30-15.00  I20  
Federico Bella: Faster Than Light: The Evolution Of Polymer Electrolytes For New Generation Solar Cells In The Last Five Years

15.00-15.20  Coffee Break

Session 16  Chairperson: Adam Best

15.20-15.50  I21  
Amita Chandra: Polymer Electrolyte Complexes/Composites: Organic-Inorganic Route for EMI Shielding

15.50-16.10  O15  
Mohamed A. Careem: Prototype solar panels with polymer electrolyte based dye sensitized solar cells

16.10-16.30  O16  
Dominic Bresser: Nanostructured Liquid-Crystalline Single-Ion Conductors for Lithium Battery Electrolytes

16.30-16.50  O17  
Lorenz Gubler: Ion-Conducting Membranes with Vanadium Barrier Motif for Redox Flow Battery Applications

Session 17  Chairperson: Patrik Johansson

16.50-17.00  Y1  
Bing Sun: Ion Transport in Polycarbonate-Ester Based Solid Polymer Electrolytes

17.00-17.10  Y2  
Jae-Kwang Kim: Hybrid solid electrolyte for high safety solid-state lithium ion batteries

17.10-17.20  Y3  
Siti A.M. Noor: Properties of High Na-Ion Content Solid-State N-Propyl-N-Methylpyrrolidinium Bis(Fluorosulfonyl)Imide Ionic Liquid Gel Electrolytes

17.20-17.30  Y4  
Krzysztof A. Bogdanowicz: Can only proton cations pass selectively through a non-ionomeric membrane? From polymer design to a fuel cell

18.30-  Conference Banquet at Norrlands Nation
Friday Aug 19th

Session 18  
Chairperson: Ludvig Edman

08.20-09.00 PL5  
Maria Forsyth: Novel Solid Electrolyte composites materials enabling Li and Na metal devices

09.00-09.30 K7  
Masayoshi Watanabe: Polymer Electrolytes Containing Glyme-Based Solvate Ionic Liquids: A New Approach to Achieve High Ionic Conductivity, Thermal Stability and Wide Potential Window

09.30-10.00 I22  
Jean Le Bideau: Confined ionic liquids within Silica Based Host Networks: Systematic Study of the Effect of Pore Size

10.00-10.20 Coffee Break

Session 19  
Chairperson: Fannie Alloin

10.20-10.50 I23  
Louis A. Madsen: Combining a Rigid-Rod Polyelectrolyte and an Ionic Liquid to form Thermally Stable Ion Gels with Tunable Modulus and Anisotropy

10.50-11.20 I24  
Hajime Matsumoto: Zero-Solvent Electrolyte for Lithium Secondary Batteries

11.20-11.40 O18  
Rebeca Marcilla: Polymer Electrolytes based on Ionic Liquids and their combination with Multifunctional Electrodes in Electric Double Layer Capacitors

11.40-12.00 O19  
Mohd. S. Su’an: Novel Bio-Based Polyurethane Polycation for Solid-State Electrochemical Devices Application

12.00-12.15 Concluding Remarks  
Daniel Brandell & Patrik Johansson – Chairmen of ISPE-XV
Thank you to the ISPE sponsors!
Plenary & Keynote Presenters
Plenary Speakers

Austen Angell

Austen Angell obtained his bachelor’s and Masters’ degrees from the University of Melbourne, Australia, and his Ph.D. from Imperial College of Science, University of London. He is currently Regents’ Professor of Chemistry at Arizona State University, Tempe, AZ, having moved to ASU in 1989 after 23 years at Purdue University. From an original interest in glassforming liquids with emphasis on aqueous solutions, he moved to solid electrolytes and later to the study of flexible polymer electrolytes, enduring the frustration of inadequate conductivities or other inadequacies over many years. With focus more recently on practical power systems, he has turned to polymer gels and recently has had some success with an all-inorganic anhydrous gel membrane for fuel cells that will be given some attention in the present lecture. He has published > 500 research and review papers, nearly 80 of them cited >100x, averaging 72x/paper over the past 20 years, for a WebOfScience H index of 88 this year (97 on Google scholar). His research efforts have been recognized by internationally-contested awards from four different Technical Societies (ACERS-Morey 1989 for glassformer studies, ACS-Hildebrand 2004 for liquids and the fragilities thereof, MRS-Turnbull 2006 for the glass transition, and ECS-Bredig 2010 for ionic liquid studies).

Michel Armand

Michel Armand, born in France (1946), graduated from Ecole Normale Supérieure (rank 1st); Master in inorganic and organic chemistry (Paris 1968); Ph.D. in Physics (1978); Fulbright Fellow at Stanford University in 1970-1. Directeur de Recherche at Centre National de la Recherche Scientifique (CNRS) since 1989. Invited professor at Lawrence Berkeley Laboratory (1982-83). Professor at University of Montreal (Canada) (1995-2004). Director of the Joint CNRS-UdM International Laboratory on Electroactive Materials (2000-2004). Resumed as Directeur de Recherche at CNRS in Amiens (France). Michel Armand has authored or co-authored 230 publications; 225 presentations at conferences, of which 185 were invited, 157 patents delivered or pending. He has been or is the Ph.D. advisor for 23 students.
Nitash P. Balsara

Nitash P. Balsara is a chemical engineer with a bachelor’s degree from IIT Kanpur, a master's degree from Clarkson, and a PhD from RPI. He did post-doctoral research at the University of Minnesota, and at Exxon Research and Engineering Company in Annandale, New Jersey. In 1992, he joined Polytechnic University in Brooklyn as an assistant professor of Chemical Engineering, New York. In 2000 he accepted a joint appointment as professor of Chemical Engineering at the University of California, Berkeley, and faculty scientist at Lawrence Berkeley National Laboratory. He has managed to hang on to both jobs. He also co-founded two battery start-ups: Seeo, Inc., and Blue Current.

Klaus-Dieter Kreuer

After receiving his Diploma in Mineralogy at the University of Cologne (1979), Klaus-Dieter Kreuer did a PhD in the department of Chemistry at the University of Stuttgart (1982). As a fellow of the “Studienstiftung des Deutschen Volkes” he benefited from a research stay at the California Institute of Technology (1978) (group of R. Vaughan) and a Max-Planck award allowed him to join the Massachusetts Institute of Technology as a visiting scientist (1983-84). Later, Klaus-Dieter Kreuer built an R&D group within a Swiss-German company (Endress & Hauser) (1985-1991) before joining the Max-Planck-Institute for Solid State Research, where he assisted J. Maier in building his new department. Since 1990 Klaus-Dieter Kreuer is lecturing at the University of Stuttgart from which he received his Habilitation degree.

Maria Forsyth

Professor Maria Forsyth (FAA) is an Australian Laureate Fellow, an Alfred Deakin Professorial Fellow at Deakin University. She is the Associate Director in the ARC Centre of Excellence in Electromaterials Science (ACES) and Deputy Director of the Institute for Frontier Materials (IFM) at Deakin University in Australia, where she leads the research effort in energy storage and corrosion science. Specifically, her work has focused on understanding the phenomenon of charge transport at metal/electrolyte interfaces and within novel electrolyte materials. Such materials have included a range of novel ionic liquids, polymer electrolytes and plastic crystals. NMR techniques have featured strongly in Professor Forsyth’s research where she has applied pulsed field gradient NMR to measure diffusion of ionic species in electrolytes, variable temperature solid state wide line NMR and MAS to investigate structure and dynamics in solids and, most recently, NMR imaging of...
electrochemical processes. She leads collaborative projects in lithium and sodium battery technologies funded through recent Australian Research Council grants. Professor Forsyth is a co-author of over 400 journal and conference publications attracted more than 11000 citations. She has delivered more than 25 invited and plenary talks in the past 5 years.

**Keynote Speakers**

**Cui Guanglei**

Professor Dr. Cui Guanglei was selected as a scientist of “CAS Hundred Talents Program” in 2008. Prof. Cui obtained his Ph.D. degree at the Institute of Chemistry, CAS. From 2005 to 2009, he had worked at Max-Planck-Institute for Polymer Research and Max-Planck-Institute for Solid State research as a postdoctoral scientist on Ener. Chem. Project. Then he joined the Qingdao Institute of Bioenergy and Bioprocess Technology, CAS as full professor from 2009. His research interests include low-cost and highly efficient energy-storage materials, electrode materials and polymer electrolyte for lithium batteries and lithium ion capacitors. Prof. Cui has published more than 100 papers on peer-reviewed journals of Adv. Mater., Angew. Chem. Int. Ed., Coordin. Chem. Rev., Energy Environ. Sci., Chem. Mater. and 5 invited review articles such as Coordin. Chem. Rev., Progress. Polym. Sci.. These papers have been cited for more than 2500 times by other groups. Notably, Prof. Cui has been invited to review the progress about transition metal nitride, functional lithium borate salts, biomass-derived materials for electrochemical energy storages, and highly safe and flame-retardant separators for power lithium ion batteries owing to his contributions to this area.

**Stefano Passerini**

Prof. Passerini is working on the development of materials and systems for electrochemical energy storage for almost 30 years. Co-Founder and co-Director of MEET (Muenster Electrochemical Energy Technology), the battery research Centre at the University of Muenster, in 2014 he was appointed a Professor at the Karlsruhe Institute of Technology as a member of the Helmholtz Institute Ulm, Germany. Co-author of over 300 peer-reviewed publications (H Index of 52), and several book chapters and patents, he received the Research Award of the Battery Division of the Electrochemical Society. From January 2015 he is Editor-in-Chief of the Journal of Power Sources after three years as European Editor.
Alexei Sokolov

Dr. Alexei Sokolov received his PhD in Physics from Russian Academy of Sciences in 1986. He continued his work at the Russian Academy of Sciences till 1991. Then he worked in Germany as a Humboldt Fellow, and a Max-Planck Fellow and at the end of 1998 he became a Professor at the Department of Polymer Science, The University of Akron, USA. In 2009 he accepted the Governor’s Chair position at the University of Tennessee and Oak Ridge National Laboratory, where he currently leads the Soft Matter group. His current research interest focuses primarily on Dynamics of Soft Materials, including topics of the glass transition, polymer dynamics and dynamics of biological macromolecules, composite materials and materials for energy applications. He has published more than 240 peer-reviewed papers.

Patric Jannasch

Patric Jannasch received his Ph.D. degree in Chemical Engineering from Lund University in 1996. After postdoctoral studies at Risø National Laboratory in Denmark, he joined the Department of Chemistry at Lund University in 1998 to build up a research group on polymers for energy technologies. He was appointed to Full Professor in Polymer Technology in 2010. His current research interests cover synthesis and properties of electrolyte and membrane materials for separation and energy applications, as well as biopolymers from renewable resources.

Oleg Borodin

Dr. Borodin currently works as a research scientist at the Electrochemistry Branch of the US Army Research Laboratory, focusing on multiscale modeling of materials for energy storage applications such as batteries and capacitors. His expertise include quantum chemistry calculations and high throughput screening of electrochemical reactions in electrolytes and electrode - electrolyte interfaces, force field development and molecular dynamics simulations of liquid, ionic liquid, polymeric and solid electrolytes for lithium battery applications, solid electrolyte interphase (SEI) components, electric double layer structure and capacitance. Before joining ARL in 2011 he worked at the University of Utah, Wasatch Molecular Inc and held a Guest Faculty appointment at ANL. His research was supported by DOE, NSF, NASA, DOD and private industry and published in 135 papers and 6 book chapters.
Vito Di Noto
Prof. Vito Di Noto is a Full Professor of Chemistry for Energy and Solid State Chemistry in the Department of Industrial Engineering of the University of Padova, Italy. He is a solid-state electrochemist with more than 30 years of experience and is the founder and the team leader of the Chemistry of Materials for the Metamorphosis and the Storage of Energy group (CheMaMSE). Currently, the research activity of Prof. Di Noto is focused on the synthesis and the studies of the structure, relaxation phenomena and electrochemistry of ion-conducting, dielectric and electrode materials for application in: (a) primary and secondary batteries; (b) fuel cells; (c) electrolysers; (d) supercapacitors; (e) electrochemical sensors; (f) photo-electrochemical devices; (g) actuators. Prof. Di Noto is also a member of the executive committee of the Energy Technology Division of the Electrochemical Society (ECS). Prof. Di Noto was the Conference Chairman of the 12th International Symposium on Polymer Electrolytes (ISPE-12) and was one of the co-organizers of ISPE-13. He also organized the 7th German-Italian-Japanese Meeting of Electrochemists, and is the chairman of the forthcoming 21st International Conference on Solid State Ionics (SSI-21). He is author or co-author of more than 230 publications on “peer-reviewed” journals and 20 patents.

Masayoshi Watanabe
Masayoshi Watanabe is a Professor of Yokohama National University. He received his Ph.D. (1983) degrees from Waseda University. After a visiting scientist with Professor Royce W. Murray at University of North Carolina (1988–1990), he joined Yokohama National University in 1992 and was promoted to a full Professor in 1998. Prof. Watanabe’s research interest has been mainly concerned with “ionics” and “nano-structured materials”. Ionics has become an important scientific area for the realization of key materials for advanced electrochemical devices, which supports a sustainable society. He is one of research leaders in the fields of ionic liquids and polymer electrolytes in the world. Recent research activity has been expanded to nano-structured materials, including block copolymer assembly in ionic liquids. He has published more than 325 original research papers and 185 books and reviews in these and relating fields. Number of Citations > 18000, h-index = 66.
Plenary Presentations
Flexible Inorganic SPEs of a Novel Type: Anhydrous Fuel Cell Membranes and the Possibility of Protic Ionic Liquid and Alkali-ion-conducting Cousins

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The field of polymer electrolytes is commonly thought of as (i) the study of ionic transport in materials made of chain polymers acting as electrolyte solvents, or alternatively (ii) the study of polymers that are polyionic and ion-conducting themselves - in either case providing tough flexible ion transporting materials. More recently the advantages of using chain polymers to support gel structures, within which a higher-conducting solution component can be supported, has been found successful. Indeed, it is now incorporated in the current lithium ion battery electrolyte technology. Here we overview the different possibilities for introducing matrices of characteristics dimensions as supports for liquid electrolytes, and then describe a method for making inorganic polymers of 3D character that are flexible and nanoporous, and that incorporate conducting media into their nanoporous structures as they form.1 When the occluded medium is orthophosphoric acid, the material can be used as a fuel cell medium of high performance and unusually robust character, especially when a fibreglass mesh is included to provide a dual length scale matrix in the gelating medium. While the initial observations have been published there are many degrees of freedom, both compositional and structural, waiting to be explored.

Figure 1. LHS. Cartoon of 3D polymer net with occluded communicating H₃PO₄ molecules. RHS. Polarization and power curves for fuel cell working with this electrolyte.

It is hoped to be able to give a fuller report on this sort of inorganic polymer gel electrolyte - which can support unusually high temperature operation - and its relation to more conventional polymer gel electrolytes - at the time of ISPE-16.

1. Ansari, Y. et al. A flexible all-inorganic fuel cell membrane with conductivity above Nafion, and durable operation at 150°C. J. Power Sources (2016) 303, 142-149,
Advanced Anions for Polymer Electrolytes and ILs

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The cations solely exchanged at the electrodes being either Li⁺ or Na⁺, the counter-negative charge is the only variable in the design of new solutes for battery electrolytes. LiPF₆ has emerged as the dominant salt for liquid electrolytes batteries but it is not suitable for ILs and polymer electrolytes due to a strong structuring effect (T_M, ∂T_g/∂c) and for the latter, destruction of the ether linkage. Designing new anions must put as priorities i) the dissociation and ii) the voltage stability window. Delocalization is of utmost importance in the absence of electron pair acceptors (high AN) solvents, which like water, exert a leveling effect on dissociation. The tool box is based on the consideration that in almost all cases, an anion oxygens can be replaced, in the order of delocalization extension and/or electron-withdrawing ability, by: =NCN, =C(CN)₂ and =NSO₂R. In addition, the negative charge stabilization on a five-membered ring give a series of its own, the best example of which is TDI (2-trifluoromethyl-4,5-dicyano-imidazolide) with 10 π electrons, stable to +4.6 V. Possibly, this series could be completed by tetracyanopyrrole, a fully aromatic 14 π electrons system, if a simple synthesis were to be found. The “pseudo oxygen” strategy on the other hand is likely to give an even wider range of possible combinations. From triflate, CF₃SO₃⁻ the =NSO₂CF₃ substitution has led in the 80’s to TFSI (CF₃SO₂NSO₂CF₃⁻) which has become the workhorse of polymer electrolytes and ILs. Beyond the extension from 3 to 5 of the negative charges “relays”, this introduces the S–N–S “hinge” with low configuration change energy inducing the smallest ∂T_g/∂c for polymers and high fluidity for ILs. The lighter FSI (FSO₂NSO₂F⁻) pushes this even further, with the added advantage of usually forming a friendly SEI at the lithium interface. Yet, CF₃SO₂NCN⁻ and CF₃SO₂C(CN)₂⁻ have also proven to give good conductivities in PEO and low viscosity ILs, so would FSO₂NCN⁻ and FSO₂C(CN)₂⁻.

The latest development in terms of anion design indeed pushes the “pseudo oxygen” concept further than TFSI, by substituting from the latter another oxygen by =NSO₂CF₃ to extend delocalization to 5 oxygens and 2 nitrogens (Fig 1):

![Figure 1. The structure of the “super TFSI” anion.](image)

This anion can be considered as the first member of the “super TFSI” family (s¹TFSI), where the replacement of oxygens by =NSO₂CF₃ can be iterated at will to further extend the charge dispersion. Interestingly when reaching 4 sulfur centers (s²TFSI), intrinsic charge chirality appears, something hitherto unknown and of great potential interest in cationic polymerization and asymmetric synthesis. Li[s¹TFSI] has two S–N–S hinges, which lowers the T_M to 118°C ≈ 100°C below that of LiTFSI and reaching one of the lowest recorded for a Li salt. Though a synthesis strategy has not been devised yet, the corresponding s¹FSI [FSO₂NS(O)(F)NSO₂CF₃⁻] substitution should lead to even lower T_M and possibly to bridge the gap between conventional organic ILs and alkali salts. Further, the very small =NCN group, adding a minimum volume increment, adds more delocalization and affixes a hinge.

Following the strategy for reaching t = 1 in polymer electrolytes, which was to tether the -SO₂N⁺(CF₃)₂ to a styrene moiety and polymerization + alloying or copolymerization to include PEO segments, the -SO₂N⁺(S(O)(CF₃))₂NSO₂CF₃⁻ was attached to polystyrene and blended with PEO resulting in 5x increase in conductivity despite the remaining rigidity of the polystyrene.
Toward Complete Characterization of Polymer Electrolytes

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Connecting continuum-scale ion transport properties such as conductivity and cation transference number to microscopic transport properties such as ion dissociation and ion self-diffusivities is an unresolved challenge in characterizing polymer electrolytes. Better understanding of the relationship between microscopic and continuum scale transport properties would enable the rational design of improved electrolytes for applications such as lithium batteries. We present measurements of continuum and microscopic ion transport properties of nonflammable liquid electrolytes consisting of binary mixtures of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) and perfluoropolyethers (PFPE) with different end groups: diol, dimethyl carbonate, ethoxy-diol, and ethoxy-dimethyl carbonate. The continuum properties conductivity and cation transference number were measured by ac impedance spectroscopy and potentiostatic polarization, respectively. The ion self-diffusivities were measured by pulsed field gradient nuclear magnetic resonance spectroscopy (PFG-NMR), and a microscopic cation transference number was calculated from these measurements. The measured ion self-diffusivities did not reflect the measured conductivities; in some cases, samples with high diffusivities exhibited low conductivity. We introduce a non-dimensional parameter, beta, that combines microscopic diffusivities and conductivity, which interestingly, depends on end group functionality. In the ethoxylated electrolytes, beta is close to unity, the value expected for electrolytes that obey the Nernst-Einstein equation, the microscopic and continuum transference numbers are in reasonable agreement. PFPE electrolytes devoid of ethoxy groups exhibit values of \( \beta \) that are significantly lower than unity. In these cases, there is significant deviation between microscopic and continuum transference numbers.
Ion Conducting Membranes for Fuel Cells and Batteries: 
A Combined Bottom-up / Top-down Approach

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Most electrochemical conversion and storage devices, such as certain types of fuel cells, alkaline ion and redox-flow batteries, rely on the amazing properties of ion conducting polymer membranes. These devices function only if the corresponding membranes effectively separate the electrochemically active masses (electrodes) and mediate the electrochemical reactions taking place at anode and cathode though conducting specific ions. These may be protons or hydroxide ions in the case of PEM-fuel cells, Li⁺ in lithium ion batteries or specific anions or cations in the case of redox-flow batteries [1]. Apart from these key properties, many other especially stability requirements render the development of such membranes a formidable one! This lecture provides insights into membrane structure and dynamics as well as stability issues which are discussed on different length scales [2-6]. The resulting understanding not only provides a framework for better describing the properties of well-established membrane materials such as Nafion® (bottom-up), it also consolidates the basis for the development of new alternative membranes for specific applications (top-down) [1].


Novel Solid Electrolyte composites materials enabling Li and Na metal devices

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The holy grail of energy storage is battery technology based on Lithium metal anodes, with Sodium metal being a close second contender with the advantage of lower cost and possibly greater safety. However, a significant problem with both metals is the ability to cycle the electrode without creating either dendritic morphology or 'dead' metal, which can cause rapid failure of a battery. Polymer electrolytes, and more recently ionic liquid and organic ionic plastic crystal (OIPC) based systems, have shown great promise for stable cycling of Li and Na. For example mixtures of lithium or sodium salts of FSI, TFSI or BF\textsubscript{4} anions with phosphonium based OIPC show high ionic conductivity and stable electrochemical cycling of Na or Li metal as well as good device performance. NMR techniques are used to probe ionic structure and dynamics in these systems and correlate this with the conductivity and electrochemical performance. This talk will summarise our work on OIPC materials and their composites, from fundamental understanding to their behaviour as battery electrolytes.
Keynote Presentations
Safety-reinforced and High-voltage Poly(propylene carbonate)-based All-solid-state Polymer Electrolyte for Ambient-temperature Solid Polymer Lithium Batteries

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Solid polymer electrolyte is regarded as a perfect way to handle the potential safety issues of lithium batteries. Herein, we reported a new class of safety-reinforced, wide voltage window and ambient temperature polymer-based solid polymer electrolyte for high-performance all-solid-state lithium batteries. It was demonstrated that such solid polymer electrolyte exhibited comprehensive performance in terms of higher ionic conductivity ($4.3 \times 10^{-4}$ S cm$^{-1}$) at 25 °C, wider electrochemical window (> 4.6 V), better mechanical strength (25 MPa) and superior rate performance (3 C) at ambient temperature than those of pristine poly (ethylene oxide) solid polymer electrolyte. In addition, LiFePO$_4$/Li cell employing this solid polymer electrolyte can charge and discharge normally even at 120 °C, which indicating remarkably improved reliability and thermal stability of such solid polymer electrolyte. Moreover, the aluminum-pouch-type lithium cells assembled with such solid polymer electrolyte could light a red light emitting diode (LED) lamp and without suffering from internal short-circuit failures even after cutting off the part of lithium batteries. There is no doubt that the development of highly safe and ambient temperature polymer-based all-solid-state polymer electrolyte would provide a prospective scope for high-performance lithium batteries.

**Figure 1.** (a) Typical charge/discharge profiles of LiFePO$_4$/Li cells using PEO-SPE and CPPC-SPE at varied rates ranging from 0.1 to 3 C. Temperature: 20 °C. b) Cycling stability of LiFePO$_4$/Li cell using CPPC-SPE at 0.5 C. Temperature: 20 °C. The inset is SEM image of the lithium anode after 1000 cycles. c) Nyquist plots for LiFePO$_4$/Li cells using CPPC-SPE after the first cycle and after 1000 cycles. d) Illustration of solid-state soft-package lithium battery using LiFePO$_4$ as the cathode and lithium metal as the anode for lighting LED lamp labelled with “SPE”. Temperature: 20 °C.

**References**
Ionic Liquid-Based Electrolytes for Alkaline-ion Batteries

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Li-metal batteries have known a continuous development since the introduction of PEO based electrolytes [1]. Indeed, if the focus has been directed toward Li-ion batteries since 1991, following the commercial success of Li-ion batteries for portable devices, 2012 have seen the coming on the market of a Li-metal polymer powered car with 250 km driving range (BlueCar). Moreover, most of the ’next generation’ batteries such as Li-S or Li-air are based on Li-metal negative electrodes. If the present Li-metal electrolytes are based on polymer electrolytes, ionic liquids (ILs) based electrolytes such as LiFSI-PYR14FSI [2] or crosslinked PEO-PYRnTFSI-LiTFSI [3] have demonstrated very reversible lithium plating/stripping and, due to their high stability in oxidation and toward O₂⁻, to be good candidate for Li-air applications [4]. IL-based electrolytes are showing promising performance in novel energy storage systems such as Na/seawater batteries [5].

A review of our results on the use of ionic liquid-based electrolytes for lithium, sodium and divalent alkaline cations will be presented.

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References:
From Fundamentals of Ionic Conductivity to “Superionic” Polymer Electrolytes

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Use of polymer electrolytes instead of traditional liquid electrolytes offers an elegant solutions to many problems in current battery technology. However, a major obstacle in use of polymer electrolytes is their low ionic conductivity. Classical theories suggest that structural (segmental) relaxation controls ionic conductivity in polymers. This is indeed observed in materials such as polyethylene oxide (PEO), the classical polymer electrolyte. However, the mechanism of ionic conductivity in polymers remains poorly understood. In this talk we present an overview of traditional mechanisms of ionic conductivity with emphasis on ‘superionic’ behavior in some materials. Based on this understanding we demonstrate that only strong decoupling of ionic conductivity from segmental dynamics can lead to a ‘superionic’ behavior of a polymer and might provide sufficiently high conductivity required for many applications at ambient temperature. Using the knowledge on diffusion and decoupling phenomena developed in the field of soft materials we suggest the way to design of polymeric structures with strongly decoupled ionic conductivity [1,2]. Our experimental studies demonstrate feasibility of the proposed approach and reveal ‘superionic’ behavior in several new polymers. The polymer specific decoupling of ionic conductivity is especially well illustrated by a comparison of ionic liquids with their polymerized analogs [3]. Our detailed studies of polymerized ionic liquids (PolyILs) helped to unravel mechanisms controlling ion diffusion in this promising class of polymer electrolytes [3,4]. We present a model that predicts the glass transition temperature and decoupling of ion conductivity from segmental dynamics in PolyILs based on knowledge of their chemical structure. Ways to further enhancements of ionic conductivity in PolyILs and their possible limitations are discussed at the end.

References
Synthetic approaches towards anion-exchange membranes with high alkaline stability and OH\(^-\) conductivity

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Different synthetic approaches targeted towards cationic polymers for anion exchange membranes (AEMs) with high alkaline stability and OH\(^-\) conductivity are presently intensively investigated. The general objective is to identify and prepare materials with the necessary properties for long-term operation in alkaline membrane fuel cells and electrolyzers [1].

The standard and straightforward pathway to AEMs typically involves attachment of quaternary ammonium (QA) groups in benzylic positions on aromatic polymers such as polystyrenes, polysulfones and poly(phenylene oxide)s (PPOs) [1]. However, QA groups in these positions have in many cases proven to be quite sensitive toward nucleophilic attack, and also seem to activate the cleavage of adjacent ether links in the polymer backbones [1,2]. Several studies of cationic model compounds have shown that QA groups attached to benzene rings via alkyl spacer chains have a high stability in alkaline solutions at elevated temperature [3]. Thus, there is a current need for new synthetic strategies to efficiently attach QA groups to suitable aromatic polymers via alkyl chains [1].

We have recently developed a straightforward synthetic route involving bromoalkylation and quaternization by which QA groups are attached to PPO via flexible and stable alkyl spacer units [4,5]. AEMs based on these polymers show efficient phase separation, significantly enhanced hydroxide ion conductivity and far superior alkaline stability in relation to corresponding polymers with QA groups placed in benzylic positions directly on the backbone. Using the spacer concept, we have prepared and studied PPOs with different side chain configurations, different QA groups, side chains containing multiple QA groups, as well as covalently crosslinked AEMs. In the current presentation we will discuss molecular design principles, synthetic procedures and important structure-property relationships of new AEM materials.

References
Modeling Lithium Battery Electrolytes and Solid Electrolytes Interphases

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Tailoring electrolyte electrochemical properties is critical for stabilizing the electrode – electrolyte interfaces and enabling novel electrochemical couples in lithium batteries. The rational design of an electrolyte requires not only the knowledge of the limits of electrolyte electrochemical stability and electrolyte decomposition reactions that might or might not occur at the surface of the electrode but also understanding of the structure and transport properties of the passivation film formed at the anode and/or cathode surfaces.[1] I will discuss application of the distributed multi-scale computing framework for high-throughput screening of solvent and salt electrochemical stability and decomposition reactions in the multicomponent electrolyte as shown in the Figure below.[2] When combined with accurate predictions of the electrolyte structure and transport obtained from molecular dynamics simulations, such calculations provide insight into the mechanism of the in-situ formation of anode passivation layer and electrolyte stabilization at the electrode surface. A particular example of molecular modeling the initial stages of the protective anode passivation layer formation will be discussed.[3] An unusual structure of the highly concentrated aqueous electrolytes predicted from molecular dynamics simulations will be related to its transport properties as a function of concentration and temperature. The implication of the double layer structure of concentrated electrolytes at carbon electrodes obtained from molecular dynamics simulations to interfacial transport and electrochemical stability will also be discussed.

References
Conductivity and Relaxation Phenomena in Proton and Anionic Exchange Membranes by Broadband Electric Spectroscopy


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Ionically conducting materials (ICM) are of great importance for the fabrication of portable batteries for electronic devices such as computers, tools, video and still cameras, and for the development of fuel cell and battery-powered electric vehicles, dye-sensitized solar cells, supercapacitors and sensors [1]. It has been suggested that conductivity in ICMs occurs via a number of different processes. The predominant conductivity processes are attributed to: a) the charge migration of ions between coordination sites in the host materials [2-5] and b) the increase of conductivity due to relaxation phenomena involving the dynamics of the host materials [2-5]. Ions “hopping” to new chemical environments can lead to successful charge migration only if ion-occupying domains relax via reorganizational processes [2-5], which generally are coupled with relaxation events associated with the host matrix.

Here, it will be described in a concise fashion, the instruments used to comprehensively study the electric response of ionic conductors. To provide the reader with the basic tools necessary for understanding broadband electric spectroscopy [6-8], the first part will review the general phenomena and basic theory behind each type of electric response that materials may exhibit when they are subjected to static or dynamic electric fields. This will be achieved by focusing on the practical use of equations, while referring to specialized texts for detailed explanations of the equations. Then, an overview of the application of BES in the study of the charge transfer mechanisms pristine and hybrid inorganic-organic proton-conducting and anion-conducting membranes and the models adopted for the interpretation of conductivity mechanisms are described and a unified conductivity mechanism is proposed.

References

Acknowledgements
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Polymer Electrolytes Containing Glyme-Based Solvate Ionic Liquids: A New Approach to Achieve High Ionic Conductivity, Thermal Stability and Wide Potential Window

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Solvate ionic liquids (SILs) belong to a new class of ionic liquids and are defined as the mixture of a salt and a ligand that strongly coordinates with the cation or/and anion of the salt.\textsuperscript{1} Recently we reported the equimolar mixtures of lithium bis(trifluoromethane sulfonyl)amide ([Li(TFSA)]) and triglyme (G3) or tetr glyme (G4) are liquids at room temperature, consisting of [TFSA] anion and the complex cation [Li(glyme)]\textsuperscript{+} by the coordination of the glymes to the Li\textsuperscript{+} ion and behave like typical ionic liquids (Figure 1).\textsuperscript{2,3} Due to the coordination of the glymes to the Li\textsuperscript{+} ion, evaporation of the glyme molecule is greatly suppressed, and the oxidation stability of [Li(glyme)][TFSA] is also improved.\textsuperscript{4,5} In addition, the high Li\textsuperscript{+} ion concentration (ca. 3 mol dm\textsuperscript{-3}) for [Li(glyme)][TFSA] is one of the noteworthy property as a Li\textsuperscript{+}-conductor. Therefore, the glyme-Li salts SIL have attracted considerable attention as electrolytes for lithium batteries.

In this study, we investigated the coordination environment and transport properties of Li\textsuperscript{+} in the binary system of a SIL and ABA-triblock copolymers.\textsuperscript{6,7} We prepared three kinds of copolymers consisting of incompatible A segment (polystyrene, PST) and compatible B segment; poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), and poly(butyl acrylate) (PBA). The mixtures of the SILs and copolymers form ion gels with physically cross-linked network structures by self-assembly of the PST segment (Figure 1).\textsuperscript{4} The preservation of the complex cation in the ion gel was explored by pulsed-field gradient spin-echo NMR, Raman spectra, and thermogravimetric analysis. From the comparison of physicochemical properties of these ion gels, it is revealed that the [Li(glyme)]\textsuperscript{+} complex cation is broken by the ligand exchange between the glyme and PEO, whereas the complex cation remains the coordination structure in the PMMA- and PBA-based ion-gels. The difference in battery performances when these ion gels are applied as electrolytes of lithium batteries will be presented.

Figure 1 Preparation of polymers electrolytes containing glyme-based solvate ionic liquids.

References
Invited Presentations
Poly(ethylene carbonate) and its Derivatives for Solid Polymer Electrolytes

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Since ionic conduction in novel polymer electrolytes consisting of alternating copolymers of CO₂ with glycicyl ethers and LiTFSI was first reported in 2010 [1], we have been focusing on polycarbonates (poly(ethylene carbonate) (PEC) and its derivatives) and studying their unique ionic-conductive properties. The chemical structure of polycarbonates, which have one alternating carbonate group (-O-(C=O)-O-) in each repeating unit of the main chain, can be suitable for the electrolyte matrix because of its large dipole moment to dissolve many types of metal salts. These polymers also have methylene-methylene (-CH₂-CH₂-) or methylene-methine (-CH₂-CH(-R)-, R means side groups) units in the main chain, and this therefore gives rise to lower glass transition temperature for showing better conductivity in the solid state. In this study, we used commercial PEC [2-4] and many polycarbonates having different side groups [1,5-7] synthesized in our laboratory. We found that the conductivity of some PEC-Li salt electrolytes increases with increasing salt concentration and the Li transference numbers (t-Li) are extremely higher than those of typical polyether system. A PEC-LiF composite filled with nano-ordered TiO₂ particulates also showed very high t-Li more than 0.8, and excellent Li-ion conductivity to be 0.4 mS/cm at 60 °C [3]. Recently, polycarbonates having short oxyethylene (OE₁, n=1~3) side chains were synthesized, and we revealed that the LiF electrolytes having OE₁ and OE₂ groups decrease at low salt concentration but then increase dramatically with increasing salt concentration [7]. On the other hand, we have studied dielectric behavior of PEC-based electrolytes using broadband dielectric spectroscopy, and it was revealed that the mobility of PEC segment at high salt concentration is enhanced by two factors; one is the decrease in intermolecular interactions by the existence of many ion pairs and aggregated ions around saturated PEC domains where the dissociated ions are highly concentrated, and the other is the intramolecular interactions between C=O and CH₂ are lowered by the ion-dipole interaction [8]. Moreover, we have demonstrated battery performance of a Li|PEC-LiFSLiFePO₄ cell and obtained a reversible charge-discharge capacity around 120 mAh/g at 30 °C and C/20 rate [9].

References
Influence of the architecture of the solid phase on the conductivity. Concentrated electrolyte systems doped with salts bearing Hückel anions.

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Solid polymer electrolytes (SPEs) with high cation conductivity, as a safe material for lithium battery applications, are still very desirable. Conducting properties of such systems strongly depend on the phase composition. Presence of the low-melting phase seems to be useful on the grounds of the lowering of the temperature window of operation. Recently, salts based on cyano substituted heteroaromatic rings, e.g. 2-trifluoromethyl-4,5-dicyanimidazolates (LiTDI, NaTDI)\textsuperscript{1-5}, 2,4,5-tricyanomimidazolates (LiTIM, NaTIM) and tetracyanopropyrlates (NaTCP) attracted attention due to their excellent conducting properties as well as thermal and electrochemical stability. The performed structural studies on the solvates revealed variety of structural motifs but also indicate on the low ability to aggregate, which make them interesting alternatives for commercial salts.

Herein we present a study on the structure of SPE’s based on the salts with Hückel anions with wide range of ether oxygen to lithium (or sodium) molar ratios. The phase composition was characterized in details with thermal, diffraction and spectroscopic techniques and its influence on conductivity behavior was examined. Detected two crystalline phases of LiTDI-PEO were simulated with computational methods. The thermal stability of the samples was checked to prove safety of electrolytes.

Figure 1. Conductivity as a function of temperature of the LiTDI-PEO electrolytes (a) Optimized structures of crystalline phases of PEO-LiTDI complexes (b)

References
Multifunctional Electrolytes for Structural Batteries & Supercapacitors Using Additive Manufacturing

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There is an increasing need for mass- and volume-saving techniques for mobile energy storage. Lighter, more energy dense material solutions are typically pursued in order to make Army systems as efficient as possible. Instead of improving system performance through materials substitution at the subcomponent level, in the present work we seek to combine energy storage and structural functions into a single material in order to increase overall system capability. One effort has capitalized on commercial glass and epoxy materials as dielectrics to successfully develop highly efficient structural capacitors that also perform well for ballistic protection. Batteries and supercapacitors have more complex operating behaviors such that we spent several years developing the frontiers of materials science in the material subcomponents, with integration and testing of structural devices only recently becoming the primary focus. Critical to this effort is development of structural electrolytes with appropriate mechanical and electrochemical properties. In polymer based electrolytes these properties rely on competing mechanisms, demanding complex solutions. In our current work we are using additive manufacturing to control microstructure and interfaces to enable bulk performance. We are using finite element modeling to guide selection and understanding of target structures. One measure of success is development of structural batteries that are a feasible alternative to conventional structures and energy storage. To quantify progress towards this goal as well as value of alternative approaches we developed a metric to assess multifunctional performance of structural batteries and supercapacitors for a broad range of technologies and applications that explicitly correlates to properties of the structural electrolyte and structural electrodes. Our efforts were designed with flexibility in order to facilitate progress through collaboration and easy insertion of next generation subcomponent materials.
Improvement of Charge/Discharge Properties of Cells with Various Electrolyte Materials by Zwitterion Additives

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Lithium-ion batteries (LIBs) have been widely used in power devices. For further expanding usage of LIBs, improving safety and energy density are required. We have focused on zwitterions, which have positive charge and negative charge in the same molecule, as new electrolyte materials (Figure 1) [1,2]. Lithium-ion transport was improved by adding a zwitterion to polymer gel electrolytes [3]. Recently, we found that adding a small amount of zwitterion improved not only the electrochemical stability of oligo-ether electrolytes up to about 5 V [4] but also the charge-discharge cycle stability of cells with oligo-ether electrolytes [5]. We also investigated the effect of zwitterions on electrochemical properties of ionic liquid (IL) electrolytes. Li|electrolyte|LiCoO₂ cells containing IL electrolytes with a zwitterion exhibited high capacities in the cut-off voltage range of 3.0-4.6 V [6]. The increase in interfacial resistance between the electrolyte and the cathode with cycles was suppressed. In the cyclic voltammograms of cells employing a graphite electrode, current peaks corresponding to the intercalation/deintercalation of lithium ions were observed even in the presence of zwitterion. Graphite|electrolyte|Li cells containing IL electrolytes exhibited stable charge/discharge cycle behaviour over 50 cycles [6]. Zwitterions will be useful additives in lithium-ion batteries.

![Figure 1. Schematic overview of zwitterion additives.](image-url)

References
On the Application and Design of Electrolytes for Efficient, Large-Area and Conformable Light-Emitting Devices

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The concept of a future light-emitting device that can be extremely thin, lightweight, flexible and low-cost is tantalizing, and one technology that promises to bring this vision to reality is the light-emitting electrochemical cell (LEC). A characteristic and enabling feature of the LEC, which distinguishes it from other emissive devices, is the existence of mobile ions in the active material. These ions redistribute in an intricate manner during the initial LEC operation, so that a light-emitting p-n junction doping structure can form in-situ. As such, the ion redistribution allows for efficient electron injection, transport and recombination, which are fundamentally important features of light-emission devices.[1]

Unfortunately, the electrolyte also present challenges, and the workhorse in the field – a lithium salt dissolved in a high-molecular-weight poly(ethylene oxide) ion transporter -- suffers from limited electrochemical stability window, phase separation when blended with a light emitter, and ambient-temperature crystallization. To address these issues, we have designed and synthesized a series of ion transporters based on the trimethylolpropane ethoxylate (TMPE) core, into which an alkali-metal salt is dissolved.[2,3] To date, the best performance is attained from an LEC, based on an alkyl-carbonate capped TMPE ion transporter (Fig. 1, left panel), which delivers fast turn-on, a long operational lifetime of 1400 h at >100 cd m⁻², and a record-high power conversion efficiency of 18 lm W⁻¹.[4]

![Image](tmpe.png)

**Figure 1.** (left) Chemical structure of our state-of-the-art ion transporter, (center) a large-area LEC fabricated by spray-sintering, and (right) a LEC fabricated on a fork substrate and driven to light-emission by a battery.

We also report a new easily adoptable and scalable fabrication technique, which effectivly resolves previous problems with non-homogenous light-emission from large-area LEC devices.[5] The merit of the technique is demonstrated in the form of homogenous light emission from large-area (>100 cm²) devices and via the realization of light-emission from highly complex-shaped objects, such a kitchenware fork (Fig. 1, middle and right panels).[5] We further report that it is possible to attain high-quality white emission from a single-emitter LEC,[6] and that bilayer LECs, fabricated with a mask-free and additive process, can deliver static messages with a high resolution of 170 ppi.[7]

**References**

LITHIUM POLYSULFIDES AND IONIC LIQUID BASED ELECTROLYTES – IS THIS THE SOLUTION?

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The drive to identify high energy batteries remains an on-going challenge. Whilst companies and researchers continue to pursue intercalation materials that can operate high voltages (5 V vs Li|Li⁺), these materials and devices don’t offer the step change in energy density that a battery hungry world requires.

Although a 10 fold increase in specific energy is possible with recent advances in Li-Sulfur (2567 Wh per kg) technologies, there are several challenges in the development of these devices. The most vexing of these challenges is the generation of lithium polysulfides which are highly prone to irreversibly move into the electrolyte media. These can have deleterious effects on the performance of the device such as reduced capacity and cycle-life. The electrolyte plays an important role in the device and, to this end, numerous research teams have investigated many different materials to determine how they influence polysulfide formation, the performance of the lithium anode and the overall cycle life of the device.

At CSIRO, we have been looking at a range of different methodologies to understand the formation of polysulfides both in the electrolyte and the cathode and then examine various methods to keep them electrically connected within the cathode. In this presentation, we will highlight our work methods to prevent polysulfide dissolution, changes to the electrolyte and the effect on cycling and in-situ studies at the Australian Synchrotron.

Charge carrier chemistry in liquid/solid lithium electrolytes

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High lithium transference number electrolytes are greatly beneficial as they may solve the major issue of salt concentration gradients limiting lithium battery cell lifetime and energy density. In “soggy sand” electrolytes (oxide particles dispersed in lithium salt containing aprotic solvent), lithium conductivity is enhanced in the space charge zones due to the coupled effects of anionic adsorption and association-dissociation equilibrium. [1] Lithium can be transported through the pores when a suitable network of mesoporous SiO₂ particles is formed. [2] A convenient way of circumventing particle network reproducibility and stationarity problem is infiltration of hierarchically porous SiO₂ or Al₂O₃ monoliths with 1 M LiTf/PEGDME-150 leading to liquid/solid composite electrolytes with very high lithium transference number (0.75 to 0.89) without compromising high room temperature ionic conductivity (0.32 to 0.48 mS cm⁻¹). [3] Charge carrier chemistry at liquid/solid interface will be discussed in terms of various SiO₂ surface modifications. Additionally, importance of indirect (vehicular) transport mechanism of lithium and concentration dependent deconvolution of contributions of free ions, ion pairs and dimers to the overall conduction in LiTf/PEGDME-150 liquid electrolyte by a combination of experimental techniques (impedance spectroscopy, dc polarization, pulse field gradient NMR) will be discussed. [4] The pertinence of liquid/solid electrolytes is remarkable as they could make lithium battery separators dispensable offering form stability as well as excellent contact with high power nanostructured electrodes.

References

Inorganic-organic hybrid materials and their niche in energy storage applications

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Since three decades several teams work on the use of (hetero)polysiloxane based inorganic-organic hybrid materials (ORMOCER®s, ORMOLYTEs, ORMOSILs) for the use as polymer ionic electrolytes. These sol-gel processing based materials offer on the one hand easy tuning towards different applications because of playing with inorganic and organic chemistry. On the other hand the polycondensation reactions need careful management of remaining silanol units and solvated protons if lithium batteries are the focus. Within the last 10 years, the analytical technologies drastic improved and a new insight into conductivity mechanisms and needed properties by function and network for better electrochemical properties allowed focused tuning. The talk will highlight the improved tuning of network towards a) electrolytes for lithium metal batteries and an b) artificial SEI for cathodes for higher voltage use.

The electrolytes were obtained by a simple synthetic process, consisting of a sol-gel reaction followed by polymerization of cross-linkable moietyes. Properties were studied by differential scanning calorimetry, rheological analysis and by impedance spectroscopy, respectively. The materials are characterized by high thermo-mechanical stability based on the hybrid network, and by conductivity, higher than $10^4$ S cm⁻¹ at room temperature induced by the presence of siloxane clusters and by a high polyether chains segmental mobility.

An artificial SEI for positive electrode materials of lithium-ion batteries arise from coating with such sol-gel hybrids. Here the network was tuned towards dense polysiloxane clusters with long-chain and partly cross-linked organic modifications. This structure shows again conductivity of $10^4$ S/cm, high thermal stability, but also a high elasticity of $E = 63$ kPa and a high electrochemical stability of 5.0 V vs. Li/Li⁺. Based on the flawless and nanostructured coating, its specific properties and its resistance during the classical electrode production, it is possible to improve electrode materials regarding cycle life and high voltage stability. The expected mechanism for the improved electrode function by the hybrid polymer is the formation of a protection layer in the form of a Li⁺ conducting membrane, which protects the electrode against undesired reactions with the electrolyte.
Enhanced Ionic Conduction and Battery Fabrication Using Polymer Electrolyte, Ionic Liquids and Polymer Electrolyte/Ionic Liquid Mixtures in Ceramic Interpenetrating Networks

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Solid polymer electrolytes are of increasing importance in Li-ion battery technology. However, the biggest challenge in their use is raising ionic conduction needed for practical applications. A relatively new area of work involves the use of interpenetrating networks where one phase is the ion conducting phase while the other non-conducting phase can provide mechanical support, promoting dimensional stability of the polymer electrolyte composite. The non-conducting phase can enhance conduction as is observed for micro and nanoscale filler materials. A polymer electrolyte contained in a non-conducting nanochannel geometry in a non-conducting membrane is interesting for several reasons. Not only has it been found that ion conduction is increased upon confinement, but the channel geometry facilitates ion conduction along the long axis of the channels in the membrane, i.e. perpendicular to the membrane surface and perpendicular to battery electrodes, which is the desired configuration for battery systems. In this work several systems of interest to the polymer electrolyte field will be discussed in terms of a nanoconfined electrolyte material. Poly(ethylene oxide), PEO, complexed with lithium salts; pyrrolidinium-based and imidazolium-based ionic liquids complexed with lithium salts; and mixtures of PEO polymer and ionic liquids complexed with lithium salts will be discussed. These electrolyte systems were placed in nanoporous alumina membranes with 200 nm channels, which are aligned perpendicular to the surface of the membrane. AC impedance spectroscopy confirmed the enhancement of ionic conduction by, in some cases, more than four orders of magnitude compared to non-confined systems. In addition to SEM studies, X-ray diffraction, infrared spectroscopy and thermal analysis will also be used to characterize the degree of crystallinity and alignment of nanostructures in the polymer electrolyte. The enhanced ionic conduction observed will be discussed in terms of contribution from alignment of the polymer backbone and crystalline regions, from reduction in crystallinity of the polymer electrolyte or from an augmented interfacial conduction mechanism. Prototype battery systems using these composite electrolyte materials will be discussed.

Figure 1. SEM images of the top of alumina nanoporous membranes. Pores ~ 200 nm in diameter can be seen.
   On the left are empty pores while the right shows the pores after filling with electrolyte.
Revisiting Single-Cation conducting Polymer Electrolytes through Bottom-up syntheses of Poly(oxyethylene)-based Ionomers.

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Solvent-free polymer electrolytes for lithium and post-lithium batteries must fulfill severe conditions to get significant market shares in EV and smart grids e.g. sufficient cationic conductance, easy upscaling, moderate cost, recyclability and above all safety. Improvement of their cationic conductance requires both high cationic conductivity and high mechanical strength [1] to thin down the polymer electrolyte. In solvent-free polymer electrolytes the cationic transference numbers of alkaline cations, T⁺, are low and significantly lower than in aprotic polar liquid electrolytes. This is generally ascribed to the high solvating ability of the polyether chains versus cations (high DN) and its low one versus anions (low AN). Furthermore, the cation’s mobility through entangled polymer chain’ motions is much lower than in liquid solvents, where both solvated ions can move easily. It can be assumed that an increase in anion size should decrease its mobility (steric hindrance) and therefore increase T⁺, while decreasing the overall conductivity. As a matter of fact, increasing anion’s bulkiness was found to have no influence on the anionic mobility [2] leading to fairly low T⁺.

Moving from polymer electrolytes made of salts dissolved in macromolecular solvents to single-cation conducting polymers leads to a sharp conductivity decrease. Part of this decrease is obviously expected as the anion contribution to conductivity is suppressed. Additionally, the mobility of negatively and positively charged aggregates is impossible suppressing, too, their contribution to conductivity. Our previous works dealt with single-cation conducting polyethers (i.e. POE) obtained by ring-opening polymerization, ROP, of iononic oxirane [3] free-radical polymerization of ionic alkenes [3] or chemical modifications of a polyether [4]. The RO copolymerization of the ionic oxiranes with ethylene oxide led to fairly low incorporation of the ionic oxirane leading to concentration limited to ~ O/Li = 40. The ionic alkenes were integrated to unsaturated poly(oxyethylene) taking advantage of the free-radical cross-linking step. In that case the concentration in single-cation conducting moiety can be much higher. Nonetheless, it remains unreacted ionic monomer that implies an extraction step in order to preserve T⁺ = 1; this solvent extraction leads also to uncross-linked chain’s removal that decrease the solvating units density. As for the chemical modification, it was based on the grafting of ether-sulfate anions, more dissociated than sulfonates but much less than triflate or imide anions.

The new single-cation conducting poly(oxyethylene) were prepared by step-growth polymerization of a new aryl ionic monomer with a current and inexpensive PEG (PEG-1000) and a dichloro-isobutene. The obtained pre-ikanomers were subjected to ultrafiltration with a cut-off at 3,000 g/mole to eliminate the contribution of unentangled POE chains. The purified pre-ionomers were then cross-linked. The ionic monomers consisted either of a perfluorosulfonate anion (triflate-like) or of a perfluorosulphonimide one (Rf-SO₂-N-SO₂-CF₃, TFSI like) where Rf is a perfluoroalkylene. Although, non-optimized they demonstrate promising performances.

References
From neutral to single-ion block copolymer electrolytes

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Today the environment is a major society concern and the polluting fossil energy consumption, more and more expensive, is a drag on our economy, thereby the development of alternative transportation such as electric or hybrid vehicles, has become a key need for a sustainable long term development\(^1\). The increase of energy density necessary to promote this future revolution imposes to develop “new” chemistries for both the active electrode materials and electrolyte\(^2,3\). However, for high scale applications a safety issue comes from the liquid electrolytes as they embedded organic solvents that can likely leak or generate flammable reactions. The use of a solid polymer electrolyte (SPE) could solve most of the safety issues encounter with liquid electrolyte. However, the development of SPE has been hampered by two hurdles i/ the inability to design a SPE that has both a high ionic conductivity and good mechanical properties\(^3\) and ii/ the motions of lithium ions carry only a small fraction of the overall ionic current which leads during battery operation to the formation of strong concentration gradient with highly noxious effects like favored dendritic growth\(^4\) and limited energy density, especially when power increases. In this context, we are developing nanostructured multifunctional block copolymer electrolytes (BCE), B-A-B comprising a central A block based on poly(ethylene oxide) (PEO) that brings ionic conductivity and a B block that brings other functionalities like mechanical properties, electrochemical stability, increase of transport number etc. We will present our approach in improving the performances of BCEs starting from neutral BCEs like PS-POE-PS\(^5,6\) laden with a lithium salt to the single-ion BCEs (SIEL) comprising grafted lithium trifluoromethanesulfonylimide (TFSILi)\(^7\) on the B block. Especially, we analyse the impact of the BCEs architecture (composition (ie proportion of PEO), chemistries of the A (linear vs comb PEO) and B (nature of the anions and of the main chain) blocks) on the physical properties such as the morphology, the thermodynamic transitions, the mechanic stability and the ion transport. At last, for a complete analysis, the results obtained with several prototypes of batteries will be presented.

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5. E. Beaudoin, T. N. T. Phan, M. Robinet et al., Langmuir 2013, 29, 10874–10880
N-methylphenothiazine based organic materials for lithium battery

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The N-methylphenothiazine (MPT) is a prime target with the aim of developing innovative redox organic materials useful as positive electrode of lithium-ion battery [1]. These organic materials are today a credible alternative to inorganic materials by their lower cost and toxicity, furthermore due to their versatility versus cation species, organic materials can be also used for sodium, magnesium batteries technologies. The N-methylphenothiazine has two reversible systems but only the first one can be exploited in the electrolyte potential stability window.

The chemical modification of the MPT molecule, by the incorporation of donating electron groups, helps to reduce the potential values of two systems. These chemical developments thus allow improving notably the MPT derivative theoretical capacities accessible in lithium-ion technology. The effect of different moieties in regard to the MPT derivatives redox couples was investigated.

It is in this context that MPT-based redox polymers have been synthesized and characterized. Their electrochemical properties have been investigated in solution using model molecules and in lithium cells. The main point to be overcome is to obtain insoluble species even in their oxidized states. In this context, two strategies were investigated i) polymerization of the phenothiazine derivative and ii) the use of polyphosphazene backbone. The figure 1 shows the electrochemical responses obtained by cyclic voltammetry and galvanostatic cycling of MPT based polyphosphazene in LP30 (EC/DMC (1/1) LiPF6 1M).

Figure 1. a) Cyclic voltammetry at 0.1 mV/s and b) Galvanostatic cycle at C/10 of the AminoMPT based polyphosphazene on the first redox system

References

Ion Mobilities and Correlated Motion in Ionic Liquids Analyzed by Electrophoretic NMR

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The characterization of transport processes in Ionic Liquids (IL)-based electrolytes is very important for their potential application in energy storage devices, especially to elucidate mechanisms of Li⁺ transport. Commonly determined transport coefficients are conductivity, viscosity and diffusion coefficients. Using multinuclear Pulsed-Field-Gradient (PFG)-NMR, diffusion coefficients can be obtained specifically for each ion species. However, to identify the conductivity contribution of a specific ion species remains a challenge, since from diffusion coefficients Li transference number can only be obtained under the assumption of completely uncorrelated ion motion. In order to determine true transference numbers, and thus the species’ contribution to the overall current, the electrophoretic mobility µ has to be known.

Electrophoretic NMR (eNMR) is one of the few methods to measure the electrophoretic mobility µ of non-metal ions. During a diffusion experiment (Pulsed Field Gradient (PFG)-NMR) an electric voltage is applied and the electrophoretic mobility of an ion species is obtained by determining its drift velocity in the electric field. In principle, multinuclear studies (e.g. ¹H, ³Li, ¹⁹F) could yield a full characterization of an electrolyte system, but eNMR application is often hampered by artefacts.

With our eNMR setup we recently presented a systematic mobility study of the cations and anions in seven different IL in the range down to 10-10 m²/Vs [1]. The electrophoretic mobilities depend strongly on the cation and anion structure, i.e. they increase for the cation type with shorter alkyl chain length and with increasing delocalization of the positive charge. In different IL, either the cation or the anion provides the major contribution to the current, however, any ion species carries at least one-third of the current.

Furthermore, electrophoretic mobilities of Li⁺ ions in binary mixtures of Li salt and IL are determined for the first time. In both systems, LiBF₄/EmimBF₄ and LiTFSI/EmimTFSI, a negative mobility of the Li⁺ ions is found, proving its drift direction towards the anode, i.e. an opposite drift direction of Li⁺ as expected for a positively charged ion in the electric field. We discuss this surprising finding in terms of a correlated motion of Li⁺ and anions in negatively charged clusters, which is probably compensated by a diffusional flow of neutral Li clusters in the opposite direction.

Thus, electrophoretic NMR can identify transport mechanisms on a molecular level, and provides unique information; in particular, where correlated motion of different ion species is involved.

References
The ionic conductivity, or a measure of the conductance per cross-sectional area, is usually the default figure of merit used for comparing electrolytes and predicting battery performance at high cycling rates. Although these quantities are fine for predicting resistive losses during short current pulses, they do not describe longer term potential losses due to concentration polarization effects such as the depletion of reactive species near the electrode / electrolyte interface during fast and deep cycles. This talk will highlight this effect in lithium ion and other cells with high energy and power densities.

In the case of lithium ion batteries, it is often forgotten that a substantial concentration of lithium salt in the electrolyte is essential for the redox reaction, and that the salt concentration can be depleted when lithium ions are transported across the cell and into the depths of a composite or porous electrode. Thus, concentration polarization can shut down the discharge of a lithium-ion cell when a reactant is completely depleted at the electrolyte / electrode interface. This effect is shown in numerous detailed simulations e.g. [1], and our previous communication [2], in which diffusion of the salt, rather than lithium ions or electrons, was found to be the ultimate limiting factor during fast discharge of a LiFePO4 composite or porous electrode as shown in Figure 1.

![Figure 1. A simplified model of rate limitation due to slow salt diffusion during discharge of a composite or porous LiFePO4 electrode, from [2]](image)

For lithium metal cells, the most important effect of concentration polarization is dendrite formation, which can be alleviated by designing polymer electrolytes with exclusively cationic conductivity, although the effect of added plasticizers or inert conductive salts may complicate the issue. Current interest includes lithium-sulfur and lithium-air cells, where the electrolyte may contain several reactive species for which concentrations and diffusion coefficients need to be known.

References
Analysis of Ionic Transport in Polymer/Ionic-Liquid Systems

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Polymer electrolytes containing an ionic liquid (IL) as salt component have recently attracted much attention in basic research related to batteries, solar cells, and other electrochemical devices. In contrast to conventional polymer electrolytes with inorganic salts, well-chosen polymer-IL systems offer the possibility to vary the salt content from the IL-in-polymer to the polymer-in-IL domain. Most important for practical applications is the characterization of ion transport in these electrolyte systems. Experimentally, this is usually done by measuring the electrical conductivity as a function of temperature in a narrow range above and at room temperature. More information can be obtained by combining conductivity measurements with self-diffusion experiments of cations and anions using nuclear magnetic resonance (NMR) techniques. Comparisons of conductivity and diffusivity can be made based on the Nernst-Einstein equation, which allows for calculating either the charge diffusivity \( D_c \) from conductivity data or a hypothetical conductivity \( \sigma_{\text{eff}} \) from diffusion data. However, the theoretical evaluation of these experimental data is often rather simple and restricted to analyzing the relative difference between \( \sigma_{\text{eff}} \) and \( \sigma \) as a global measure of ion association.

The present contribution intends to show how substantially more information can be extracted from the same experimental data within a suitable theoretical framework [1]. This is demonstrated on PEO,EMIm electrolytes consisting of poly(ethylene oxide) complexed with 1-ethyl-3-methylimidazolium iodide for \( y = \text{EO/IL} \) ratios ranging from 0.6 to 60. Specifically, ionic conductivity measurements are compared to diffusivity data arising from \( ^1H \) pulsed-field-gradient NMR analysis for EMIm and \( ^{125}\text{I} \) radiotracer diffusion experiments for iodine over the temperature range from \( \sim 70 \) to \( \sim 120 \, ^\circ\text{C} \) [2]. The present approach allows for the determination of transference numbers as a function of composition. We also reveal the impact of ion pairing and provide data for the relative contributions of ion pairs to the diffusivity of cations and anions. Altogether, the results are relevant to dye-sensitized solar cells and show that a high ion density is crucial to enhance the iodine transport capacity.

![Figure 1](image.png)

**Figure 1.** Schematic drawing illustrating the transition from an IL-in-polymer to a polymer-in-IL electrolyte and *vice versa* for the system PEO-EMIm.

**References**
A local symmetry description of the Nafion exchange site environment vs. state-of-hydration

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Transmission FT-IR spectra of Nafion taken within a controlled humidity cell allowed for the correlation of Nafion FT-IR band intensities to the state-of-hydration. In fully hydrated Nafion, the sulfonate exchange-site ($C_{3v}$ local symmetry) yields bands at 1061 cm$^{-1}$ ($C_{3v, HF}$) and 969 cm$^{-1}$ ($C_{3v, LF}$). During dehydronation the exchange site associates to a sulfonic acid group which has no local symmetry ($C_{1}$). This yield bands at 1414 cm$^{-1}$ ($C_{1, HF}$) and 910 cm$^{-1}$ ($C_{1, LF}$). At intermediate states-of-hydration, both forms of the exchange site co-exist: the $C_{3v}$ and $C_{1}$ bands are observed in experimental FTIR spectra (see figure). A 37,000 atom assembly of Nafion and water molecules was constructed to model membrane water hydration. The model was sectioned into 320 sub-cubes and the number of water molecules to sulfonate exchange sites ($\lambda$) range from 1 to 50 per sub-cube with an average of 15. Density functional theory analysis of the exchange site environment versus $\lambda$ shows threshold $\lambda$ values separating regions of associated, dissociated (with protons in exchange site inner sphere) and dissociated (with protons in exchange site outer sphere).

![Figure 1. Nafion transmission spectra with overlaid DFT-calculated normal modes (drop lines). Spectra are plotted as normalized absorbance. Left: Hydrated Nafion-(H) (red). Middle: Partially dehydrated Nafion-H$_x$(H)$_{1-x}$ (purple). Right: Dehydrated Nafion-H (blue).](image)

References

Polymerized Ionic Liquid Block Copolymers for Alkaline Fuel Cells

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Alkaline fuel cells (AFCs) that employ solid-state anion exchange membranes (AEMs) as the electrolyte separator are of great interest as they produce high power densities at low operating temperatures (< 200 °C) and enable the use of non-platinum electrodes (e.g., nickel), significantly reducing cost relative to proton exchange membrane fuel cells. Several challenges limiting the wide scale use of membrane-based AFCs is the alkaline chemical stability and ion transport of polymers used as AEMs. Recently, polymerized ionic liquid (PIL) block copolymers with a range of chemically stable heterocyclic cations have become candidates to investigate for AFCs. PIL block copolymers constitute an emerging class of polymers and a distinct set of block copolymers that synergistically combine the advantageous properties of both PILs and block copolymers and are synthetically highly versatile with numerous cation and anion chemistries available. Specifically, the unique physiochemical properties of PILs, such as high solid-state ionic conductivity, high chemical, thermal and electrochemical stability, and widely tunable physical properties (e.g., via anion exchange), are incorporated in the block copolymer architecture, which allows for self-assembly into a range of nanostructures, where morphology type and domain size are tunable. In this talk, the synthesis, alkaline chemical stability, and ion transport of numerous PIL block copolymers developed in our research group will be discussed. More specifically, both the cation and backbone chemistry have a significant effect on alkaline chemical stability and various chemistries and chain architectures have a significant impact on ion conductivity. The AFC performance of PIL block copolymers as both the electrolyte and ionomer in the catalyst layer will also be discussed.
From neat ionic liquids to hybrid ionogels: challenges and progresses

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To address the global challenge of creating a sustainable energy economy, we must find alternatives to fossil based fuels but also implement sustainable and emission-free systems for power supply. The Fuel Cell is a device that converts chemical energy into clean electricity but, despite having many advantages for transport applications, it has not reached the broad international market. For the case of proton exchange membrane (PEM) fuel cells, this is partly due to the high cost associated to the catalyst (Pt) and the PEM (Nafion). In addition, Nafion has currently a performance strongly dependent on the presence of water and therefore also limited to below 80 °C due to dehydration.

For a technical breakthrough and a wider implementation of the fuel cell technology, it is desirable to develop new materials with a better performance at temperatures higher than 120 °C. In our laboratory we are trying to develop new hybrid materials based on silica (SiO₂) as the supporting matrix and a protic ionic liquid as the charge carrier [1,2], Figure 1. This research line requires designing appropriate silica pores in terms of size, geometry and surface chemistry, but also selecting the best ionic liquid with low viscosity, high mobility and possibly acidic protic sites [3,4].

In this contribution I will present some strategies that we have followed to obtain functional hybrid materials. Focus will be on the use of spectroscopic methods to understand how macroscopically observed properties, such as self-diffusion and conductivity, depend on the molecular level interactions. In particular, we make extensive use of ¹H NMR and vibrational spectroscopy (both Raman and infrared) to probe the strength of ion-ion interactions and of pulsed field gradient (PFG) NMR spectroscopy to measure the self-diffusion of neutral or charged molecules; but we also employ advanced 2D solid-state NMR experiments to investigate the local coordination at the ionic liquid/silica interface.

Figure 1. Illustration of the main experimental methods and of the materials investigated.

References
High Performance Electrolytes for Flow Batteries and Other Open Electrochemical Systems

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Various approaches can be taken to prepare ion-conducting polymers for a device. An optimal approach is based on the device requirements as well as the available polymer electrolyte. Recently, our work on redox flow batteries has led us to consider this problem at a general level, encompassing other applications including electrosynthesis. We emphasize that the defining characteristics of the electrolyte are the conductance of the membrane relative to its selectivity. In these open systems, rather different device properties become important.

The state of the art of our understanding of electrolyte functions in all-vanadium redox flow batteries will be presented and then used as a platform for discussion of the use of polymer-based electrolytes in other contexts. Descriptions of processes occurring at scales from molecular to macro-scale will be discussed. Of particular interest in the flow battery context, and of general interest for electrosynthesis, is a description of the complex interplay between component interactions with each other and with membranes. Some limits can be identified, as is the case with non-aqueous flow batteries. In each case, these aspects will be placed in context of device-level issues that are caused and prospects for possible or actual solutions to these issues will be discussed.
Faster Than Light: The Evolution Of Polymer Electrolytes For New Generation Solar Cells In The Last Five Years

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The stability of solar cells is a critical (but often disregarded) issue, since great focus is often devoted to the efficiency records (even if these values rapidly decrease upon time). However, today's research in the solar cells field must be connected to concepts such as long-term stability, safety and environmental impact.

One of the most studied device is the dye-sensitized solar cell (DSSC), that has recently exceeded 14% efficiency values and is day by day establishing itself as the leading photovoltaic technology in the fields of building-integrated and indoor light-harvesting [1]. In this device, the electrolyte plays a central role in determining both efficiency and durability. Since polymer electrolytes represent the main solution to the issue of poor stability of DSSC devices while maintaining almost intact the power conversion efficiency, the scientific community has recently made great efforts in this direction in recent years.

In this work, we present recent approaches in terms of novel polymeric architectures for DSSC polymer electrolytes [2], introduction of unconventional redox mediators [3], and photostability increase of solar cells components [4]. Reached the goals of high efficiency and good stability, we show how DSSCs can be used for the fabrication of smart windows in modern buildings [5]. Finally, a few preliminary results about one of the 2016 leading solar cells (i.e., aqueous solar cells) will be given [6].

References
Polymer Electrolyte Complexes/Composites: Organic-Inorganic Route for EMI Shielding

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For minimizing the ever increasing electromagnetic interference (EMI) noise, electromagnetic shielding of various electronic devices/setups is crucial. Electron conducting polymer composites have been studied for some time now as EMI shield materials. However, these composites show shielding effectiveness due to reflection. A more desirable shielding material should show shielding effectiveness due to absorption.

Since, the absorption mechanism of a material is directly proportional to the factor $\sigma/\mu$, organic-inorganic hybrids represent a novel approach for enhancement of shielding effectiveness due to the high ionic conductivity of the polymer composites as well as the simultaneous optimization of their dielectric properties. The charge transport properties of these hybrid electrolytes are critically dependent on the chemical nature of the organic and inorganic constituents, their size, morphology and the nature of the inter-phase interactions.

The shielding performance of a polymer composite comprising of Poly (vinylidenefluoride–co–hexafluoropropylene) PVdF–HFP, inorganic salt, organic salt, multi-walled carbon nanotubes (MWCNTs) and transition metal oxides' nano particles will be discussed. The high conductivity obtained has been attributed to the high ionic conductivity of the ionic liquids and the formation of a connecting network by the MWCNTs facilitating electron conduction. The electromagnetic interference (EMI) shielding effectiveness of the system under study has been found to be $> 44$dB in the $K_a$ band (12.4-18 GHz), which is almost twice the commercial requirement of 20dB.
Confined ionic liquids within Silica Based Host Networks: Systematic Study of the Effect of Pore Size.

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Ionogels represent a route to biphasic materials, for the use of ionic liquids (ILs) for all-solid devices. The confinement of ILs within host networks gives solids with striking behaviours. Confining ILs within host networks enhances their averaged dynamics, resulting in improved charge transport. Fragility, short relaxation times, low viscosity, and good ionic conductivity, all them seem to be related to the IL / host network interface. The presence of ILs at interface neighborhood leads to the breakdown of aggregated, structured regions that are found systematically in bulk ILs. This “destructures” aggregated pairs or domains in the ILs. Ionogels demonstrate this effect, coupled with percolation of their bicontinuous, solid/liquid, interface. This makes these materials very competitive solid electrolytes, since they could provide a route to lower the density and viscosity of ILs, as well as easier path for diffusion of charged species. The host networks studied range from fully inorganic to hybrid, polymeric, organic-inorganic matrices. This general approach can be applied to several all-solid devices, including lithium batteries (Fig 1, [1]) and supercapacitors (Fig. 2, [2]). Overall high performances were shown on these last two devices, along with the advantageous intrinsic, sometimes heightened, properties of the chosen ILs. Herein we will present a systematic study of the effect of pore size by using several mesoporous silicas prepared, for the sake of this study, beforehand [1(c)].

Figure 1. Lithium transport number shows an optimum for a given pore size. Figure 2. Solid SCap time response is as high as Scap with non confined ionic liquid.

References
Combining a Rigid-Rod Polyelectrolyte and an Ionic Liquid to form Thermally Stable Ion Gels with Tunable Modulus and Anisotropy

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Li metal as a battery anode material can enable a factor of 2 to 3 higher energy density compared to existing Li ion batteries. However, dendrite growth and limited columbic efficiency have prevented practical application. To potentially alleviate these problems, we present a new ion gel electrolyte[1] based on an interfacial ion exchange process between a rigid-rod sulfonated aramid (PBDT - poly(2,2- disulfonyl-4,4-benzidine terephthalamide)) and an ionic liquid. This ion gel provides an unprecedented combination of tunable properties: transport anisotropy up to 3.5X, ionic conductivity up to 8 mS cm−1, widely tunable modulus (0.03−3 GPa) and thermal stability up to 300°C. This material breaks the usual tradeoff between ionic conductivity and modulus, demonstrating its potential to resolve current limitations in Li metal batteries. Furthermore, we will describe the characterization of stable and dominant dimers of PBDT polyanions (potentially as a double helix) in solution and in gels, as well as progress to understand the electrostatic network that gives rise to stable gel formation. In addition to battery applications, this new class of gels promises to facilitate optimization of properties for a range of technologies such as “artificial muscle” electromechanical actuators, fuel cells, and other molecular separations applications.

Reference:
Zero-Solvent Electrolyte for Lithium Secondary Batteries

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Ionic liquids (ILs) composed of low-coordinating perfluoroanions such as bis(trifluoromethylsulfonyl)imide have been reported as a unique electrolyte for lithium secondary batteries for almost past two decades due to their unique properties such as less-flammability. Our group have been prepared various perfluoroimides and also perfluoroalkylperfluoroborate to improve performance of lithium secondary battery with using only ILs. During these studies, we found some tiny modification of such perfluoroanions lead to another interesting electrolyte such as organic ionic plastic crystals (OIPCs) and low temperature lithium molten salt, which are classified as “zero-solvent” as with ILs. In this talk, the possibility of our zero-solvent as a battery electrolyte will be introduced.
Lanthanide-doped red seaweeds-derived electrolytes for electrochemical devices

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Polymer electrolytes (PEs) are an important component of many electrochemical devices[1], due to some special features, in particular good electrode–electrolyte contact, ease of processing into thin films with a large surface area, the ability of accommodating a wide range of ionic salt concentrations, good mechanical properties and high ionic conductivity [2]. In recent years the community of PEs has turned its attention to the development of systems derived from renewable sources. Natural polymers are promising substitutes of synthetic polymers, due to their abundance in Nature, non-toxicity, biodegradability, interesting physical and chemical properties, low cost, and good performance. In this context the class of carrageenans (Cgs) is particularly attractive. These polysaccharides, which are located in the cell wall and intercellular matrix of the plant tissue of certain species of the class Rhodophyceae (red seaweeds), are used mostly as stabilizers and structure providers in the food and ice cream industries [3]. Cgs consist mainly of the potassium, sodium, magnesium, and calcium sulphate esters of D-galactose and 3.6 anhydro-galactose copolymers joined by α-1,3 and β-1,4-glycosidic linkages. There are three main types of Cgs: highly sulphated and easily soluble lambda-Cg (devoid of the 3.6-anhydro-D-galactose units); the less hydrophilic and less soluble kappa (k)-Cg, with a 3.6-anhydro-D-galactose residue as part of the repeat unit and fewer sulphate groups; and the very hydrophilic iota-Cg. Because of the presence of three types of cation coordinating oxygen sites per repeat unit (hydroxyl oxygen atoms, ether oxygen atoms and sulfate oxygen atoms) in its structure, k-Cg is a promising candidate as host matrix for the production of PEs [4,5,6]. In the present work PEs composed of k-Cg and variable concentrations of two different lanthanide salts and glycerol have been prepared by the solvent casting technique and their structure, morphology, thermal behavior, ionic conductivity and photoluminescence features have been studied.

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References
A Novel Polymer Electrolyte Containing Sulfonyl urea Moiety for PEMFC and Libattery

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Abstract
Ultrasound (UV) curable electrolytes have attracted much attention because they are useful as a gel and film states. Conventional UV curable electrolytes are mixture of LiFSI or LiPF₆, UV curable acrylated materials and oligomers. We developed a novel UV-curable monomer based on acryl functional group containing fluorosulfonyl urea. The prepared monomer was transferred to Li containing acryl electrolyte, and also directly prepared film with multi-acrylated monomers. This precursor was used for lithium ion batteries and proton exchange membranes. The resulting electrolytes can enhance the movement of Li⁺ ions inside the polymer matrix demonstrate mechanical integrity due to the cross-linked nature of the polymer network, and wide thermal stability. We will be studied by 1H NMR spectroscopy and properties will be measured by ion exchange capacity (IEC), water uptake (WU) and Fenton test and proton conductivity. And also electrochemical impedance spectroscopy (EIS) will be employed to characterize the electrolytes. The electrical analysis and conductivities of the electrolytes in solvent and film state are also studied.

![Figure 1. Synthesis of polymer electrolytes.](Image)

References
Oral Presentations
Polystyrene block copolymers bearing sulfonimide and PEG side chain for improved conductivity and mechanical performance

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The multiplication of the portable electronic market and also the development of environment-friendly transport motivate strongly the research in the field of the electric storage. Among different battery technologies, Lithium-Metal Battery is very well positioned thanks to the high energy density of lithium vs its weight and volume. However, the main problem using Li metal, as an anode associated with a liquid electrolyte is the risk of dendrite growth during charge/discharge cycles. This can lead to internal short circuits possibly followed by dramatic explosion and fire. To overcome these drawbacks, solid polymer electrolytes (SPE) combining both high conductivity and suitable mechanical properties to prevent the dendritic growth are perfect candidates. Recently, we shown the remarkable potential of single-ion triblock copolymer composing of polystyrene bearing sulfonimide group as external blocks and linear poly(ethylene oxide) as central block as SPE for Lithium-Metal batteries [1]. In order to constantly improve the SPE properties and to get the relationships among chemical composition, morphology, ionic conductivity and mechanical properties of block copolymers, we present in this work the preparation and the use of a series of SPE based on polystyrene block copolymers bearing sulfonamide group and poly(ethylene glycol) segments. The structure and architecture of these block copolymers are shown in Figure 1, their synthesis is performed using Nitroxide-Mediated Polymerization. The elaboration and macromolecular characterization of these materials will be described in detail and their thermodynamic behaviors, mechanical properties as well as electrochemical performances will be compared. Diblock copolymers with PEG methacrylate and PEG acrylate (Figure 1d) instead of PEG styrene are also studied for comparison.

![Figure 1. Structure and architecture of different polystyrene based block copolymers bearing sulfonamide group and PEG segments.](image)

References
Lithium battery with solid polymer electrolyte based on comb-like copolymers

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The liquid electrolytes in lithium batteries can pose potential safety problems, and they can cause damage to the environment and human health if they explode [1]. These safety issues are minimized by using batteries containing a solid polymer electrolyte (SPE). Since the first publication of Armand and co-workers [2], poly(ethylene oxide) (PEO) is the most-studied polymer electrolyte owing to its capacity to dissolve lithium salts and excellent ionic conductivity above 70°C. However, one problem still remains unsolved: inhibiting the growth of dendrites on the lithium anode. Monroe et al. reported that suppression of the formation of dendrites on lithium is possible if the Young modulus of the polymer is increased to a suitable level [3]. Also, poly(styrene-b-ethylene oxide) have been reported to be efficient in hindering the formation of dendrites [4].

We report on the synthesis of comb-like copolymers as SPE. The synthesis involves anionic polymerization of styrene and 4-vinylanisole, followed by grafting of poly(ethylene glycol) monomethyl ether methacrylate by ATRP. We observed by AFM and SEM that a nano and micro phase separation occurs which improves ionic conductivity which is proportional to the ratio of grafting on the polymer. The ionic conductivities were determined by AC Impedance, which showed that the SPEs have good conductivities (10⁻⁴ S.cm⁻¹) at room temperature owing to the very low values (<30 kJmol⁻¹) of the activation energies for conductivity. The batteries evaluated with these polymers exhibited good capacity (146 mAhg⁻¹) at C/24. However, poor cycle life was observed at C/6 and C/3, which is a consequence of several factors. We partially explain that behavior by arguing that whereas PEO lightly "solvates" Li' thus slowing Li-ion mobility, and PEGMA chains "solvate" Li ions too strongly, trapping and inhibiting their mobility [5].

![3D representation of membrane.](image)

**Figure 1.** 3D representation of membrane.

References

Multinuclear NMR Studies of Ion Solvation and Association in Glyme Solvents

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Low molecular mass polyethers, in particular glymes, serve as useful models for investigating ion/polymer and ion/ion interactions in higher molecular mass polyethers, i.e. PEO. Glymes have also garnered recent attention as attractive solvents for use in lithium metal and lithium sulfur batteries. [1-3] We have undertaken a comprehensive study of variable chain length glymes, ranging from DME to PEG 500 containing dissolved lithium salts or sodium salts, with salt anions including both LiTf and LiTFSI. Nuclear magnetic resonance (NMR) methods employed include (i) natural abundance ¹⁷O, in which small changes in charge on the methoxy, ether, and anion oxygens can be tracked as a function of chain length; (ii) pulsed field gradient diffusion of solvent (through ¹H), cation (¹Li or ²³Na), and anion (¹⁹F). In lithium salt glyme complexes, correlations between both solvent and anion ¹⁷O chemical shifts and chain length yield insight into solvation structures and ion pairing tendencies which are supported by the diffusion measurements. Roughly similar behavior is observed in the corresponding sodium solutions, with some differences attributed to the larger ionic radius of Na⁺.

References
Crystalline Organoboron Compound as Scaffold for Ion Conductive Path via Boron-Anion Interaction

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Organoboron electrolytes [1-4] are unique class of electrolyte materials which are useful for energy storage devices and anion sensing devices.

Cyclic crystalline organoboron compound [5] was prepared by dehydrocoupling of ethylene glycol and mesitylborane. The matrix of cyclic boron compounds/LiTFSI prepared by solid state grinding showed significant enhancement of ionic conductivity compared with samples prepared by conventional lithium salt insertion method (mixing in co-solvent followed by solvent evaporation under reduced pressure).

Under optimum ratio of cyclic boron compound and LiTFSI (at molar ratio of 1:1 or 1:2), the matrices prepared by grinding method showed marked decrease in the activation energy of ion transport, which resulted in significant enhancement of ionic conductivity. This will be explained by considering the presence of highly crystalline structure of cyclic boron compounds which rendered some regulation of ion conductive path through boron-anion interactions.

The lithium transference number was determined to be 0.28. The potential window of the sample measured by cyclic voltammetric analysis in a 3E configuration cell (using Pt-Pt electrode (wire) vs Ag/AgNO3) was found to be 5.3V. Further, reversible charge and discharge was observed in anodic half cells (Li/electrolyte/C) fabricated.

![Scheme 1 with images and graph]

Fig. 1 Comparison between ionic conductivities of samples prepared by solid state grinding and conventional method (by dissolving in solvent) at various lithium salt concentrations at 51 °C.

Some other updates on organoboron electrolytes will also be presented if time permits.

References
Solid Polymer Electrolyte Based on Poly(2,2-dimethoxytrimethylene carbonate)

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Poly(ethylene oxide) (PEO) has been widely studied as electrolyte material for all solid secondary lithium polymer batteries. However, PEO-based polymer electrolytes do not show high ionic conductivity to meet a basic requirement for lithium battery application though large research efforts have been made to improve it. On the other hand, although poly(vinylene carbonate)- and its derivatives-based electrolytes do not show high ionic conductivity, temperature dependence of ionic conductivity is relatively small because of ion hopping mechanism, decoupled with the segmental motion [1]. Previously, we investigated alternating copolymers of vinylene carbonate with vinyl ethers having various ethylene oxide (EO) chain length as polymer electrolytes with combination of ion transport coupled with the segmental motion and of one decoupled with the segmental motion [2]. Recently, polycarbonate-based polymer electrolytes such as poly(trimethylene carbonate) and poly(methylene carbonate) have been actively investigated [3,4]. In connection with alternating copolymer-based electrolytes, in this work, we prepared poly(2,2-dimethoxypropylene carbonate) (poly-1) with both carbonate and ether groups, and its hydrolyzed polymer (poly-2) with both carbonate and carbonyl groups to explore the possibility of decoupled-type polymer electrolytes, and investigated electrochemical and thermal properties of their polymer electrolytes with lithium ion.

Poly-1 was prepared by ring-opening polymerization of 2,2-dimethoxypropylene carbonate (1) with DBU. Hydrolysis of poly-1 with CF₃COOH afforded poly-2. The solid polymer electrolytes were prepared by casting from solutions of poly-1 or poly-2 and lithium salt (LiTFSI and LiFSI) in CH₃CN.

Glass transition temperatures (T_g) of poly-1/LiTFSI electrolytes decreased with an increase in lithium salt concentration, but at high lithium salt concentrations such as [Li]/[repeat unit] ratios of 1/1, 1.5/1, and 2/1 T_g increased. Ionic conductivities of poly-1/LiTFSI electrolytes constantly increased with an increase in lithium ion concentration (Fig.1). This result indicates that poly-1/LiTFSI electrolytes are typical decoupled-type electrolytes. On the other hand, for poly-1/LiFSI electrolytes, decrease of T_g and increase of ionic conductivity were observed with an increase in lithium salt concentration, suggestive of the contribution of decoupled-type ion transport. From the ionic conductivities at the [Li]/[repeat unit (RU)] ratio of 1/1, poly-2-based electrolytes showed lower ionic conductivity than poly-1-based electrolytes (Fig.2).

References
Lignocellulosic Materials for the Next-Generation of Eco-Friendly Polymeric Energy Storage Devices

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In the last 20 years, the Li-ion battery (LiB) market has rapidly grown thanks to the extensive diffusion of mobile electronics devices. In order to lower the cost and reduce the environmental impact of LiBs, efforts must be devoted to reduce the amount of inactive components in the cell, to substitute synthetic polymer binders / separators and organic solvents with low-cost and biosourced materials and to develop new eco-friendly processes for the manufacture of cell components [1]. Natural nanoscale-microfibrillated cellulose (NMFC) fibers are readily available; they show stiffness, impressive mechanical robustness, low weight and, furthermore, their preparation process is easy and does not involve chemical reactions. They can significantly reinforce polymer electrolytes already at low filler loadings and also replace the commonly used PVdF as binder for self-standing and flexible electrodes, thus serving as a promising candidate for bio-composite production [2,3].

Here we review the use of paper-making technique for manufacturing low cost bio-inspired all-paper Li-ion polymer cells, constituted by NMFC-binded paper-electrodes, and NMFC reinforced polymer electrolytes. The use of NMFC as filler/binder leads to produce high performing, safe and extremely flexible electrolytes for LiBs. No organic solvents or synthetic polymer binders are used during the entire electrode/electrolyte/cell preparation process. Materials and procedures are also extended to other “beyond-LiB” technologies, such as Na-ion and Li-S, thus demonstrating the possibility of obtaining “truly green” energy storage devices in the near future. Noteworthy, the all-paper-cell can be easily re-dispersed in water by simple mechanical stirring, as well as common paper handsheets and battery materials can be recovered using well-known water-based recycling process.

References
Polymer electrolytes comprising oligomeric lithium borate salts and poly(ethylene oxide).

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Polymer electrolytes intended for application in Li-ion rechargeable batteries should exhibit not only high ionic conductivity, but also high lithium transference numbers. In traditional approach to electrolyte synthesis, the lithium salts are dissolved in polymer matrix, which usually contains oxyethylene units convenient for dissociation and coordination of lithium ions. These systems provide high ionic conductivity, but the lithium transference numbers are usually much below 0.5, which strongly limits their performance in a battery.

Our research represents an alternative approach, in which the structure of the anion is extended using short fragments of polymer chains - oligomers. The oligomers are expected to participate in the cation transport by providing coordination sites. This is in contrast to traditional electrolytes, in which the anion only releases lithium ion, and its further interactions with cations are limited by the polymer matrix. Extended structure of the anion is also aimed at lowering its mobility, and thus increasing lithium transference number. The mechanical properties of oligomeric systems, which are often obtained in form of viscous liquids, can be improved by mixing oligomeric salts with polymer of high molecular weight, such as poly(ethylene oxide).

The subject of our studies were oligomeric borate salts, with branched structure of the anion (Fig. 1) which contained three oligomeric oxyethylene segments of various length n. Such a structure was obtained in two-step synthesis process [1]. Dried and purified salts were subsequently mixed with poly(ethylene oxide) PEO, Mₘₜₜ=5×10⁶, in an acetonitrile solution. The weight proportions of polymer and oligomeric salts were chosen so that they represented certain molar proportions of EO units (coming both from anion and from polymer) to lithium: 50:1, 32:1, 16:1 and 10:1. After removal of solvent under vacuum, polymer electrolytes in the form of free-standing films or waxes were obtained. Samples of these electrolytes were investigated by differential scanning calorimetry DSC. Studies of electrical properties were performed by impedance spectroscopy in a series of heating and cooling runs covering a wide range of temperature. For each of the electrolytes, the temperature dependence of ionic conductivity was fitted with VTF function, and characteristic parameters of the fit, such as ideal glass transition Tₛ have been calculated. This temperature was compared with the glass transition temperature Tₘ estimated from DSC.

![Figure 1. Structure of oligomeric lithium borate salts.](image)

Our presentation will discuss dependence of values of ionic conductivity and glass transition temperature on the electrolyte composition: length of oligomeric units n, weight proportion of PEO to oligomeric salts, and molar proportion EO:Li. This detailed study revealed some general trends which were difficult to determine in previous preliminary research on this system [1], and which can be used to set directions for further development of electrolytes based on oligomeric salts as well as description of ion transport in such systems.

References
Solid polymer electrolyte based on Comb-like SPEEK-g-PEG for lithium ion batteries

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As one of the critical components, the electrolyte is very important for preparing safety and high performance lithium ion batteries[1]. In most of the commercial batteries, liquid electrolytes based on lithium salts containing organic solvents and separators have been optimized to high performance with respect to conductivity. However, the performance decay and safety concerns of liquid electrolytes, which include inflammable solvents, fire, and explosion hinder the commercialization of lithium ion batteries on a large scale[2].

Solid polymer electrolyte (SPE) provides an important alternative to conventional liquid electrolytes to address the issues on battery safety and efficiency[3]. Unfortunately, the inability of achieving both high ionic conductivity and strong mechanical strength, coupled with the problem of concentration potential, impeded its chance to replace the liquid electrolytes.

Here, we report a modification method to prepare sulfonated poly(ether ether ketone) grafted poly(ethylene glycol) (SPEEK-g-PEG) (Figure 1). Firstly, SPEEK were prepared by the sulfonation of PEEK using concentrated sulfuric acid. Then the partially hydroxyl-functionalized SPEEK was obtained by the reduction of some benzophenone moieties of SPEEK into the corresponding benzhydrol moieties, using NaBH₄ as reducing agent. Lastly, hydroxyl-functionalized SPEEK was further reacted with m-PEG epoxide. The effects of alkoxy chains, grafting rate, and O/Li⁺ on the ionic conductivity of SPEEK-g-PEG have been investigated by EIS in this work. The ionic conductivities increase with increasing the alkoxy chains, grafting rate, and O/Li⁺.

Figure 1. Schematic representations of the Li ion transport in SPEEK-g-PEG.

Acknowledgments
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References
Ionomer Design, Synthesis and Characterization for
Ion-Conducting Energy Materials

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For ionic actuators and battery separators, it is vital to utilize single-ion conducting ionomers that avoid the detrimental polarization of other ions. *Ab initio* quantum chemistry (DFT) calculations are used to characterize ion interactions and ion solvation by various functional groups, allowing identification of constituents with weak interactions to be incorporated in ionomers for facile ion transport. Single-ion conducting ionomers are synthesized based on these calculations, with low glass transition temperatures (facile dynamics) to prepare ion-conducting membranes for battery separators that conduct Li⁺ or Na⁺. Characterization by X-ray scattering, dielectric spectroscopy, FTIR, NMR and linear viscoelasticity collectively develop a coherent picture of ionic aggregation and both counterion and polymer dynamics. The *ab initio* calculations can also be used to quantify the dipole moment of contact ion pairs, separated ion pairs and the energy change in forming quadrupoles from these ion pairs to understand experimental observations of dielectric constant, glass transition temperature and conductivity of these ionomers, with and without non-volatile polar plasticizers. Representative ionomer structures are shown in Figure 1, including PEO-based alternating copolymers and random copolymer ionomers with either PEO or cyclic carbonate side chains.

Figure 1. Representative structures of single-ion conducting ionomers that we have designed and synthesized.
SINGLE-ION CONDUCTING BLOCK COPOLYMER ELECTROLYTES FOR SOLID STATE LITHIUM BATTERIES

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Polymer electrolytes have been proposed as a replacement for conventional liquid electrolytes in lithium-ion batteries (LIBs) due to their intrinsic enhanced safety. Nevertheless, the power delivery of these materials is limited by the concentration gradient of the lithium salt. Single-ion conducting polyelectrolytes represent the ideal solution since their nature prevents polarization phenomena. Herein, the preparation of a new family of single-ion conducting block copolymer polyelectrolytes via reversible addition–fragmentation chain transfer (RAFT) polymerization technique is reported.

In this presentation, we will introduce a novel approach for the creation of solid-state batteries by using the new family of single-ion conducting block copolymers as both the solid separator and the binder for electrode material. The new anionic monomer namely lithium 1-[3-(methacyrloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonylimide (LiMTFSI) was designed, prepared and further used for the synthesis of well-defined anionic di- and tri-block copolymers via RAFT polymerization technique [1]. The prepared ionic block copolymers comprise poly(LiMTFSI) and poly(ethylene glycol) (PEG) blocks. The effect of the macromolecular architecture and molecular weight on thermal and ion conducting properties will be discussed. These single-ion conducting polymer electrolytes showed low $T_g$ (up to $-61 \, ^{\circ}C$), high $\sigma$ ($\sim 10^{-5} \, S \, cm^{-1}$ at 55 $^{\circ}C$), a lithium transference number approaching unity, and high electrochemical stability (up to 4.5 V vs. Li$^+$/Li$^-$). Owing to the combination of all mentioned properties, the prepared polymeric materials were used as solid electrolytes as well as binders in the elaboration of LiFePO$4$/lithium-metal cell prototypes delivering large capacities (up to 130 mAh g$^{-1}$), with an impressive charge/discharge efficiency and the capability to reversibly operate at high rates.

References

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Effect of polymer network structure on physical and chemical properties of resulting gel polymer electrolyte materials

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Gel polymer electrolytes (GPE) based on 2-ethoxyethyl methacrylate with various amounts of fluorine-containing co-monomer, 2-(perfluoroocetyl) ethyl methacrylate (F17EMA), were prepared, with 1M LiClO₄ in propylene carbonate as solvent and crosslinked with n-ethylene glycol dimethacrylate monomers where n is in the range from one to four. It was shown that ionic conductivity and mechanical properties were greatly dependent on both the amount of solvent and salt used, but also on the combined impact from the content of fluorinated monomer and the type of used cross-linker. The best results within our experimental series were achieved with the GPE containing the longest cross-linker (tetraethylene glycol dimethacrylate) and 10 wt% of the fluorinated co-monomer. [1]

In the current study we put forward a working hypothesis to explain these results by thoroughly examining the network structure of the UV-polymerised gels and assessing the impact of the used component concentrations on the cross-link density (concentration of elastically active network chains) [2] which is determined from equilibrium swelling and equilibrium modulus of elasticity of the swollen samples in the linear viscoelasticity region of the networks. Also the flexibility of the system as a function of dilution at network preparation is established. The final properties such as temperature region of glass transition (Tg range), modulus and equilibrium swelling is also investigated as functions of salt addition and concentration of the fluorinated co-monomer and concentration of solvent. Finally, the resulting chain composition and sequencing of the co-monomers as a function of component concentration is determined.

References
Sorption calorimetry: measuring the thermodynamics of interactions between charged polymers and water

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For polyelectrolytes and ionomers, their interaction with water is of significant interest and there are many methods used to investigate how water influences the properties of such polymers. We here discuss how the sorption thermodynamics of such interactions can be assessed. The main thermodynamic parameters are Gibbs energy (ΔG), enthalpy (ΔH) and entropy (ΔS), and these parameters are functions of the moisture state of a material, expressed either as moisture content (u) or water activity (aw). The function u(aw) is commonly called the sorption isotherm.

Of the three thermodynamic parameters, ΔH is the one most easily measured, as it is the heat produced during the polymer-water interaction. Classically, wetting/solution-calorimetry has been used to measure the “integral ΔH" when polymers are saturated in liquid water (heat per mass/amount of material). However, it is of more interest to measure “differential ΔH” when water vapor interacts with the polymer at a certain moisture state (heat per mass/amount of water). We use special isothermal sorption calorimeters to directly measure ΔH when water vapor is absorbed by polymers and other materials [1]. These instrument continuously measures u, aw and ΔH as a sample absorbs water vapor from dry conditions up to typically aw=0.9. Figure 1 gives an example of results from such a measurement on a common polyelectrolyte. Note that even for this chemically simple homopolymer, the variation of the differential ΔH with the moisture content features several quite distinct regions. More examples of sorption calorimetric results are found in references [1, 2].

Figure 1. Example of result from sorption calorimetric measurement on poly(acrylic acid) with 25 repeat units (protonated). Indices ‘w’ and ‘ig’ are ‘water’ and ‘ionizable group’, respectively.

Results such as the ones in Fig. 1 makes it possible to monitor and understand the sorption process in detail: How much water that is absorbed at different water activities, how this relates to the number of ionic/ionizable groups, and what the driving forces are.

References

Crosslinked Anion Exchange Membranes with Complex Structures

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New membranes for alkaline fuel cells and other anion transport applications continue to generate a lot of interest in the electrochemical community. Over the last 10 years there has been great progress in determining the key attributes of anion exchange membranes that lead to high performance in fuel cells [1] and other electrochemical devices such as water electrolyzers [2], redox flow batteries [3] and reverse electrodialysis cells [4].

Our group has demonstrated a number of new polymer structures based on commercially-available polymers and inexpensive modification reagents. We have focused on poly(phenylene oxide) as a backbone platform and employed ammonium cations that have relatively good stability in light of their low cost and reasonable performance. In previous work, we employed alkyl chains to cause phase separation in random copolymers [5]. This phase separation increased the conductivity and decreased the water uptake of the materials. We have since continued to investigate crosslinking [6,7] and interpenetrating networks as further methods to optimize the properties of anion exchange membranes, Figure 1 [8]. Many of these polymers have shown reasonable performance in anion exchange membrane devices, but more work is required to extend the lifetimes of the cells beyond 1000 hours.

This talk will highlight our recent work on new anion exchange polymer structures and demonstrate how stability and conductivity can be increased by iterating on the quaternary ammonium poly(phenylene oxide) material motif.

Figure 1. Semi-interpenetrating network demonstrating AEMs with high toughness.

References
Alternative polymer electrolyte membranes consisting with supramolecular charge-transfer complex structure for high temperature operation
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Stable high temperature PEFC (HT-PEFC) has many advantages such as high CO tolerance etc. In order to realize stable HT-PEFC, polymer electrolyte membranes (PEMs) have to be considered several important functions for high temperature operation. Especially, the enough proton conductivity at high temperature is very important because high temperature condition becomes lower relative humidity condition than standard condition. Therefore, we have to introduce new concept of the molecular design of PEMs to work at the harsh condition. Currently, we have developed charge-transfer (CT) complex hybrid films which have CT complex in the films$^{[1,2]}$. The CT films consist from the electron-accepting polymer and the electron-withdrawing additives. We can modify various properties of the CT films by changing the type and the amounts of the electron-donating additives.

In this study, we designed a proton conductive additive (2,6-dipropyl naphthalene disulfuric acid, SDPN). SDPN has two sulfuric acids (proton conductor) with alkyl linkers (hydrophobic unit) connected to naphthalene unit (CT formation unit). Sulfuric acid would be placed sulfonic acid of the electron-accepting polymer (sulfonated polyimide, SPI). Therefore, the CT complex hybrid films consisting of SDPN and SPI would have packed-acid region and physical cross-linked region by CT complex in the film (Figure 1). The packed-acid region would contribute proton conductivity at lower humid condition and CT complex region would work as physical stabilizer. On the basis of this concept, we evaluated proton conductivity of the CT complex hybrid films consisting of SDPN at high-temp condition ($<120$ °C).

The color of the obtained films was brown indicating CT complex formation. The obtained CT complex hybrid films were used for proton conductivity measurement to the through-plane direction of the films. At high temperature condition (100-120 °C), the CT complex hybrid films showed about 100 mS/cm at 100 RH%, which were higher than that of Nafion 212. We also evaluated humidity effect to the CT complex hybrid films at high temperature. The proton conductivity of the CT films decreased with the decrease of humidity at 120 °C. However, the proton conductivity of the CT films was higher than Nafion 212 at all humidity.

![Figure 1. CT complex hybrid films consisting of SPI and SDPN. Proton conductivity (100 RH%) of SPI/SDPN CT complex hybrid films (red and blue are SDPN/SPI (mol) = 0.5, 0.25, respectively), low IEC SPI/DHN CT complex hybrid films (green) and Nafion 212 (black).](image)

References
Prototype solar panels with polymer electrolyte based dye sensitized solar cells

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Dye-sensitized solar cells (DSSCs) have aroused considerable research interest due to their low production cost, environmental friendliness and easy fabrication. DSSCs consist of three main components namely photo-electrode containing a dye-sensitized mesoporous titanium di oxide (TiO2) layer coated on a conducting glass, an electrolyte containing an iodide/triiodide redox couple and a platinum counter electrode. The DSSC operates by separating the light generated charges in the dye through interfacial kinetics. Most of the reported DSSCs utilize liquid based organic electrolytes and their lifetimes are limited due to leakage and corrosiveness of the liquids. Many solvents used in the electrolytes are volatile and flammable as well. Use of suitable solid polymer electrolytes can solve some of the problems but they have low ionic conductivity and make poor contact with electrodes. These problems can be solved to a larger extent when gel polymer electrolytes (GPEs) are used as they are flexible and can have almost liquid like ionic conductivity. We have been carrying out research on dye sensitized solar cells for the past ten years concentrating on finding a suitable gel polymer electrolyte that can replace the usually used liquid electrolytes. We have successfully developed a gel electrolyte based on polyacrylonitrile polymer that can produce high power conversion efficiency (PCE) in DSSCs greater than 7 % with ruthenium based N3 dye. In this paper, we report a small prototype solar panel made with these high efficiency solar cells. The panel consists of a number of DSSCs connected in series and parallel to produce power suitable for operating small devices. The panel consisting of eight single cells in series connected in parallel with another set of eight cells in series produces an average PCE of around 4 % with a voltage of 5.4 V. The objective of this work is to make a long lasting small solar panel with highest possible efficiency. This can be achieved by sealing the panel using different materials and sealing techniques
Nanostructured Liquid-Crystalline Single-Ion Conductors for Lithium Battery Electrolytes

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While lithium-based batteries are already the energy storage technology of choice for small- and medium-scale devices, their widespread implementation in large-scale applications like, for instance, electric vehicles remains hampered in particular by safety concerns. These concerns are, in fact, basically related to the commonly employed liquid organic electrolyte, comprising toxic, corrosive, and unstable LiPF6 as conducting salt [1]. Thus, one of the major targets of actual research activities is the replacement of such electrolytes by intrinsically safer alternatives, including *inter alia* solid inorganic and polymer-based systems, both providing intrinsic advantages and challenges [2,3]. While inorganic systems frequently provide high single-ion conductivity following a hopping mechanism [4], they commonly suffer interfacial issues related to their inflexibility and improvable electrochemical stability in contact with lithium. Polymer-based systems, in contrast, allow the realization of completely flexible or three-dimensional batteries and suitable electrode/electrolyte interfaces, but suffer relatively lower lithium ion conductivity due to the dependence of the cationic transport on the segmental motion of the polymer chains [5–7].

In an attempt to combine the advantages of these two different systems, i.e., macromolecular organic (flexibility, suitable interfaces/phases) and inorganic electrolytes (single-ion conductivity by hopping), we have developed thermally stable, thus, intrinsically safer ion macromolecules with covalently bonded anionic functions, showing liquid-crystalline behavior at elevated temperatures.

A combination of optical, electrochemical, and large scale facility characterization methods confirmed the Arrhenius-type lithium transport mechanism along self-assembling, lamellarly ordered ionic nanochannels. Very recent results showed moreover that the cation mobility can be enhanced by several orders of magnitude by enhancing the ion dissociation and optimizing the molecular design. Herein, we will introduce this new class of lithium-ion electrolytes and present our most recent results, targeting an in-depth understanding of the structure-to-transport interplay and further optimization regarding their application as lithium battery electrolytes.

References


Ion-Conducting Membranes with Vanadium Barrier Motif for Redox Flow Battery Applications

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Redox flow batteries are electrochemical energy storage devices aimed at grid-level application, in particular in the context of energy scenarios with a high share of fluctuating renewables (solar, wind). The electrolyte membrane is a key cost driver in the all-vanadium redox flow battery (VRB) system and accounts for about half of the stack cost. An ideal membrane for a redox flow battery should have low ohmic resistance, low permeability for redox-active species and water, and high chemical stability in the respective electrolyte solution. The currently widely used perfluorinated materials such as Nafion® have neither been designed for this application, nor are they cost-effective.

We present a membrane design concept for the use in all-vanadium redox flow batteries based on a bifunctional (amphoteric) polyelectrolyte component grafted onto a fluoropolymer [1]. The membrane contains protogenic sulfonic acid groups and amidoxime units acting as vanadium barrier (Figure 1a). Such membranes with suitable graft level and composition of grafts show an ohmic resistance similar to that of Nafion® 212 in the flow cell with a vanadium crossover that is much lower (factor of 6) than that of Nafion® 117 (Figure 1b). The vanadium barrier functionality is a unique feature related to the presence of the amidoxime. The mechanism by which it operates will be discussed in detail. In the cycling test (Figure 1c), the single cell with the grafted membrane showed stable discharge capacity over 122 charge/discharge cycles, whereas the cells with Nafion® membrane showed a gradual fading of the capacity [2]. This is related to the gradual build-up of electrolyte imbalance, indicated by the difference in electrolyte volume of 30 % at the end of test (35 cycles). In case of the grafted membrane, the imbalance is much lower (11 %) after 122 cycles.

Figure 1. a, Chemical structure of the grafted bifunctional membrane. b, Key membrane properties relevant to the application in the VRB. c, Charge/discharge cycling test at a current density of 120 mA/cm² in a single cell (25 cm² active area, SIGRACELL® GFD4.6 EA carbon felt electrodes, flow rate: 30 mL/min), using 1 M vanadium in 2 M H₂SO₄ as electrolyte (100 mL on either side).

References
Polymer Electrolytes based on Ionic Liquids and their combination with Multifunctional Electrodes in Electric Double Layer Capacitors

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Conventional EDLC mostly utilize carbon electrodes with high specific surface area in combination with liquid electrolytes such as aqueous, organic, or more recently ionic liquids (ILs). Hence, the use of heavy encapsulation materials to prevent liquid leakage is inevitable and make these EDLC unsuitable to be integrated into textiles, microelectronics or structural and lightweight energy storage systems. Replacement of liquid electrolytes by solid or quasi-solid polymer electrolytes might alleviate this strict sealing and housing requirements. The development of iongels, which contain electrochemical stable and non-volatile ionic liquids in the polymer matrix, have attracted ever-increasing interest due to the unique characteristics of ILs such as high thermal and electrochemical stability, high ionic conductivity, non-volatile and non-flammable nature.

Here we report the recent advances of our group in the development of polymer electrolytes based on ionic liquids and their application to develop solid EDLC [1]. In the first part, we will report the effect of polymer electrolyte composition, in particular the type of ionic liquid within the polymer matrix, in the physicochemical properties of polymer electrolytes. Four different polymer electrolytes prepared by blending a polymeric ionic liquid (poly(diallyldimethylammonium TFSI), with four different ionic liquids (PYR14TFSI, PYR14FSI, HEMimTFSI and PYR14DCA), were synthesized, characterized and used in combination with electrodes based on activated carbon to assemble solid EDLC. When iongels contained electrochemical stable ionic liquids such as PYR14TFSI and PYR14FSI, the corresponding EDLC could operate at voltages as high as 3.5 V with capacitance values of about 100-150 F/g and energy densities of about 30-35 Wh/kg, being similar to figure of merits for EDLC operating with pure IL. In the second part of the talk, multifunctional carbon nanotube fibers (CNT Fiber) will be investigated in combination with polymer electrolytes to develop solid EDLC with optimal compromise between mechanical and electrochemical properties [2]. This combination of materials paves the way towards development of tough, flexible and/or structural supercapacitors that can be stretched, bent, woven, and withstand large strains/stresses.

Figure 1. a) Chemical structure of polymer electrolytes and photographs, b) specific capacitance against toughness for different carbon-based materials

References
Novel Bio-Based Polyurethane Polycation for Solid-State Electrochemical Devices Application

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The growing awareness on developing sustainable tetraalkylammonium (R₄N⁺) salts has increase the demand for cheap, low-cost and renewable ammonium salts. The utilization of bio-based polyurethane (PU) from vegetable oils based polyols as alternative starting material for energy materials in electrochemical devices has been investigated. The novel bio-based polyurethane polycation was synthesized by using alkylation reaction. The presence of alkyl group in the PU backbone after alkylation reaction is observed by significant shift of wavenumber at N-H stretching, N-H bending and C=O stretching, respectively. This finding is supported by the presence of a new alkyl group attached to nitrogen atom on PU backbone provided by nuclear magnetic resonance (NMR) spectrum. The observation were supported by the increased of pH values from pH 4 to pH 6 and stable over a period of time for all ratios. This indicates that the presence of alkyl groups having electron-releasing inductive effect attached to nitrogen atom increases the overall electron density on the molecule and able to donate electrons, making it becomes more basic, less polar and causing the pH to increase. The reaction that occurs between the PU and alkyl halide also cause the increment of $M_n$ (~1000 g mol⁻¹ to ~2000 g mol⁻¹) and $M_w$ (~4000 g mol⁻¹ to ~14000 g mol⁻¹). Glass transition temperature of PU polycations reduced with increasing ratio of alkyl halide with thermal stability up to 180 °C. The ionic conductivity value of PU increased from ~10⁻⁹ S cm⁻¹ to ~10⁻⁵ S cm⁻¹ as the ratio of alkyl halide increased. The increment in ionic conductivity reflects an increase of free ion after the alkylation reaction to produce PU polycations. This preliminary study proves that the alkylation reaction was successful conducted with promising ionic conductivity values of novel bio-based PU polycations. These promising results could be a first step toward a new generation of low-cost energy materials for electrochemical devices.
Young Investigator Presentations
Ion Transport in Polycarbonate-Ester Based Solid Polymer Electrolytes

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Alternative host materials derived from poly(trimethylene carbonate) (PTMC) and its co-polymers with ε-caprolactone (CL), i.e., P(TMC/CL) (Fig.1), have demonstrated promising functionality in all-solid Li polymer batteries from ambient to elevated temperatures [1]. While polyether-based SPEs have been thoroughly investigated, but yet have displayed only limited progression in performance for battery applications, the more favorable lithium ion transport features in polycarbonate-based SPEs have not yet been properly understood. With the goal to explore the lithium ion transport behavior further, both computational and experimental approaches were here integrated.

Notably high Li$^+$ transference numbers for polycarbonate-based SPEs, as compared to conventional polyether-based SPEs, were determined from diffusion NMR data and by electrochemical polarization methods [1,2]. A more favorable dissociation of ion-pairs and/or aggregates into “free” ions, as detected by FTIR spectroscopy (Fig.1), might explain the enhanced ion diffusion upon incorporating flexible CL units in the P(TMC/CL) co-polymers. Locally oriented polymer domains of a few hundred nanometers in size were inferred from the NMR spin relaxation and diffusion data, which might lead to a potential hindrance of ion transport pathways in both SPEs. Coupled Li$^+$–polymer motions were observed, with a preferential local coordination between Li$^+$ and ester carbonyl oxygen atoms in P(TMC$_{20}$CL$_{30}$) SPEs being distinguished. The overall enhanced cationic transport in P(TMC/CL) SPEs is likely due to a delicate balance between the promotion of “free” charge carriers and the Li$^+$–polymer complexation. This very first fundamental insight on polycarbonate–ester SPEs provides great possibilities for SPE development beyond the polyether paradigm.

Figure 1. Chemical structures of the PTMC polymer and the P(TMC/CL) co-polymer (left) and the FTIR spectra of P(TMC$_{20}$CL$_{30}$)$_{1.4}$LiTFSI and PTMC$_8$LiTFSI SPEs in the 752–730 cm$^{-1}$ region (right).

References
Hybrid solid electrolyte for high safety solid-state lithium ion batteries

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Since lithium ion batteries use an organic liquid electrolyte, there is a risk of explosion and environmental pollution, which restricts any development of the large size Li-batteries. Solid-state lithium ion batteries have the potential to achieve higher energy density with better safety than conventional liquid-based lithium batteries. Usually, two-types of solid electrolytes are explored for solid-state lithium batteries: the ceramic solid electrolyte, and the solid polymer electrolyte [1,2]. Ceramic solid electrolytes such as Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_3$ (LTAPo) have a high ionic conductivity, a high lithium transference number (t$_{li}$=1), and are non-flammable. However, the ceramic electrolyte displays drawbacks such as brittleness and high interface resistance to electrodes [3]. On the other hand, the solid polymer electrolyte has high flexibility and is lightweight but shows low ionic conductivity with a low lithium transference number (t$_{li}$=0.3–0.6) and poor electrochemical stability at high voltages [4]. To overcome the disadvantages of ceramic and polymer solid electrolytes, a hybrid solid electrolyte using polymer and ceramic is introduced in this study.

![Photo and SEM images of the hybrid solid electrolyte.](image)

**Figure 1.** Photo and SEM images of the hybrid solid electrolyte.

References


Properties of High Na-Ion Content Solid-State N-Propyl-N-Methylpyrrolidinium Bis(Fluorosulfonyl)Imide Ionic Liquid Gel Electrolytes


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Sodium-based batteries have emerged as promising alternatives to Li-based batteries for the development of safe, low-cost and high energy density energy storage. One of the main challenges is the lack of safe and conductive solid-state Na-ion electrolytes. The preparation and properties of high sodium content gel sodium electrolytes as potential highly conductive solid-state electrolytes have been investigated. The gel electrolytes have been prepared by dispersion of nano sized fume silica into methylpropylpyrrolidinium bis(fluorosulfonyl)imide (C₃mpyrFSI) + NaFSI mixture electrolytes. We report here the effect of high concentration of NaFSI salt into our gelled electrolytes (up to 4.0 mol/kg) as well as the influence of low molecular weight plasticizer of ethylene carbonate (EC) on the ionic conductivity, electrochemical stability and Na⁺ transference number. The stabile plasticized gel electrolytes was observed even at 30 wt. % EC and the ionic conductivity increased up to 4 times (6.4 x 10⁻³ S.cm⁻¹) in the case of the 1.0 mol/kg NaFSI in C₃mpyrFSI mixture. The temperature dependence conductivity is well described by the Vogel-Tamman-Fulcher (VTF) equation. The chemical interaction was also studied using ATR-FTIR and the thermal stability was studied via thermogravimetric analysis. In applications where high ionic conductivity in solid-state materials is desirable, the prepared gel electrolytes are potential candidates for electrochemical devices.
Can only proton cations pass selectively through a non-ionomeric membrane?  
From polymer design to a fuel cell

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The self-assembling strategy applied for polymers showed benefit for investigation of ion conducive materials and seems to be an alternative to the commonly used systems based on ionomeric structure. Percec and co-workers, as one of the first researchers, merged this approach with knowledge about liquid crystals to design and synthesise series of liquid crystalline macromolecules and polymers, which self-assembled into columnar structure mimicking the nature [1,2].

We report on a new generation of biomimetic materials arisen from a fusion between materials science, life science and nanotechnology. The process of self-organization was achieved, using disc-like dendritic group side linked to a polymeric chain; because of tapered shape and big dimensions, the dendrons will preferably form the outer part of a column as a result of exo-recognition. The combination of liquid crystalline dendronised polyamines (Figure 1a) resulted in self-assembled columnar structures, forming ionic paths able to transport cations [3].

The columns formation and their homeotropical-like orientation was proved by XRD (Figure 1b). Moreover, the Scanning Electron-microscopic (SEM) studies of the membranes morphology revealed formation of columnar aggregates (Figure 1c and d). Electrochemical studies were employed to investigate the ionic transport across the membranes. The results proved the cationic transport through the membranes; moreover, the results disclosed cation-permselective behaviour for all tested materials.

![Figure 1. An example of LC polyamine structure (a) with XRD diffractograms (b) proving columns formation and SEM micrographs (c and d) presenting polymeric wires [3].](image)

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Poster Presentations
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Poster Session 1
Monday 15th
Na-Ion Polymer Batteries: Cheap and Easily Processable Electrolytes for Large-scale Energy Storage

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The life style of modern civilization is strongly dependent on the use of portable devices, which necessarily require safe and very efficient storage and conversion energy systems. Nowadays, lithium-ion batteries (LiBs) represent the most widely used technology in this respect. One of the arduous challenges in this field is the substitution of conventional liquid electrolytes based on organic solvents, which are volatile and hazardous. Solid polymer electrolytes (SPEs) exhibit appealing properties to replace liquid electrolytes. Moreover, research efforts are directed towards alternative systems to LiBs, because lithium is expensive and its resources are geographically constrained. Sodium exhibits suitable electrochemical properties, close to those of lithium, and it is very abundant. These features make Na-based batteries proficient candidates to replace LiBs, particularly when large-scale energy storage is envisaged.

Here, we offer an overview of our recent developments on polymer electrolytes for Na-ion batteries (Fig. 1). Polymer electrolytes were prepared through different techniques, exploiting both UV-curing [1] and simple casting [2]. All samples were thoroughly characterized in the physico-chemical and electrochemical viewpoint. They exhibited excellent ionic conductivity and wide electrochemical stability window, which ensure safe operation at ambient conditions. Electrochemical performances in lab-scale devices are presented, evaluated by means of cycling voltammetry and galvanostatic charge/discharge cycling exploiting different electrode materials (prepared by water-based procedures with green carboxymethylcellulose as binder).

Work on Na-ion polymer batteries for moderate temperature application is at an early stage, only lab-scale cells were demonstrated so far. Nevertheless, with the appropriate choice and optimisation of electrode/electrolyte materials (and successful combination thereof), the intriguing characteristics of the newly developed SPEs here presented postulates the possibility of their effective implementation in safe, durable and high energy density secondary Na-based polymer devices conceived for green-grid storage and operating at ambient and/or sub-ambient temperatures.

![Figure 1. Scheme of a Na-ion polymer battery.](image)

References

Influence of the architecture of cationic poly(ionic liquid)s on the ion dynamics in polymer gel electrolytes

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Polyelectrolytes are promising components for ternary polymer gel electrolyte systems or ion gels, consisting of an ionic liquid, a polymer and a lithium salt [1]. Recently, poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl) imide (PDADMATFSI) was introduced as a charged polymeric component in gel electrolyte systems. This cationic poly(ionic liquid) (PIL) interacts with the salt’s anion and is able to break lithium-TFSI clusters, thus it promotes salt dissociation and facilitates the lithium ion movement [2-4].

Here, we compare the influence of the polycation’s architecture (Figure 1) on the ion dynamics in gel electrolyte system consisting of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (P14TFSI) ionic liquid and LiTFSI. Three main factors were investigated: the position of the cation in PIL (in the main polymer chain or on the flexible spacer, PIL1 and PIL2, PIL3); the rigidity of the polymer chain (PIL2 and PIL3) and the nature of the flexible spacer (alkyl spacer in PIL3 and oligo-oxoethylene in PIL4).

In order to analyse the influence of the polymeric structure on the ion dynamics, temperature-dependent pulsed field gradient NMR (PFG-NMR) and impedance spectroscopy measurements were performed. Furthermore, the local lithium ion mobility was analyzed by temperature dependent spin-lattice relaxation measurements (T1).

From the spin-relaxation experiments it is possible to conclude that the local lithium mobility and the local lithium environment is influenced by the polymer. It is possible to fit the data using the BPP model. The following trend was observed by multinuclear diffusion and conductivity measurements: PIL1 > PIL3 ≥ PIL4 > PIL2. To identify the PIL with an optimal effect on the lithium mobility, the ratio $D_{Li}/D_{e}$ was calculated. The highest ratios were obtained for PIL1 and PIL3. Lower ratios for PIL4 can be explained by the interaction of the Li cation with ethylene oxide spacer, while for PIL2 by the rigid backbone. The results show that PIL1 has a more beneficial effect on the lithium ion dynamics in comparison to the other polymers.

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References
Efficient dye sensitized solar cells using a phthaloylchitosan based gel polymer electrolyte incorporated with ionic liquid

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Of the phatholylchitosan (PhCh)-polyethylene oxide (PEO) based blended gel polymer electrolyte (GPE) system investigated as electrolytes for dye sensitized solar cells (DSSCs), the composition of 5.04 wt.% PhCh-1.26 wt.% PEO-31.51 wt.% DMF-37.81 wt.% EC-24.38 wt.% TPAI(+/I₂) has been found to exhibit the highest conductivity. To this composition, X wt.% of tert-butyl pyridine (TBP) [X=2, 4, 6, 8, 10, 12] has been added as an additive in order to improve the performance of the GPE in DSSCs and the conductivity of the GPEs obtained using impedance spectroscopy. The GPE with 10 wt. % TBP exhibits the highest room temperature ionic conductivity of 9 mS/cm. On adding an ionic liquid, 1-butyl-3-methylimidazolium iodide (BMI), the conductivity is enhanced and the electrolyte added with 8 wt. % of BMI exhibits the highest conductivity of 13.52 mS/cm. DSSCs have been fabricated with these GPEs using ruthenium based (N3 dye) as the sensitizer and the performance studied under white light illumination of 1000 W/m². The area of the cell illuminated was 0.20 cm². The GPE electrolyte containing 10 wt. % TBP and 8 wt. % BMI exhibits the highest solar cell efficiency of 9.33 % with Jsc = 19.55 mA/cm², Voc = 0.70 V and FF = 0.68. The incident photon to current conversion efficiency (IPCE) measurement on the DSSC showed the highest IPCE value of 78.3 % at 530 nm.
Ion Dynamics in a Dual-cation Ionomer Electrolyte

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The poly(N1222),Li\textsubscript{1-x}[AMPS] ionomer system with dual cations has previously shown decoupled Li ion dynamics from polymer segmental motions, characterized by the glass transition temperature, which can result in a conductive electrolyte material whilst retaining an appropriate modulus (i.e. stiffness) so that it can suppress dendrite formation, thereby improving safety when used in lithium metal batteries. To understand this transport behavior, molecular dynamics techniques have been used in this work to simulate structure and dynamics in these materials. These simulations confirm that the Li ion transport is decoupled from the polymer particularly at intermediate N\textsubscript{1222}\textsuperscript{+} concentrations. At 50 mol\% N\textsubscript{1222}\textsuperscript{+} concentration the polymer backbone is more rigid than for higher N\textsubscript{1222}\textsuperscript{+} concentrations, but with increasing temperature Li ion transport is more significant than polymer or quaternary ammonium cation motions. Here we suggest an ion hopping mechanism for Li\textsuperscript{+}, arising from structural rearrangement of ionic clusters that could explain its decoupled behavior. Higher temperatures favor an aggregated ionic structure as well as enhancing these hopping motions. The simulations discussed here provide an atomic-level understanding of ion dynamics that could contribute to designing an improved ionomer with fast ion transport and mechanical robustness.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{chemical_structure.png}
\caption{Chemical structure of poly(N1222),Li\textsubscript{1-x}[AMPS]}
\end{figure}
Molecular Dynamics Modeling the Polymer Electrolyte/Li-Metal Interface

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Replacing the common graphite anode with a metallic Li foil in rechargeable lithium batteries would significantly improve their energy density. One of the main challenges for the Li metal anode is the growth of dendrites during the charge/discharge cycles, which typically occurs with usage of conventional liquid electrolytes. Solid polymer electrolytes (SPE), formed by doping a polymer with a lithium salt, do not display this disadvantage if their modulus is high enough. Moreover, they also display several other advantages, such as improved safety, low toxicity, less decomposition at the interfaces of the electrodes and no need for separators. The major disadvantage of SPEs is, however, their low inherent ion conductivity, but can be overcome by a higher operational temperature where also SPEs conduct reasonably well.

Molecular Dynamics (MD) simulation studies of SPEs can provide information about ionic motion and the influence of the polymer structure on the transport processes in these materials, and has frequently been used in studies of bulk polymer electrolytes [1, 2]. Comparatively less scientific work has been performed with MD on surfaces and interfaces involving SPEs. In this work, we therefore perform MD simulations on polyethylene oxide (PEO) based polymers doped with LiTFSI salt at the lithium metal anode surface (shown in Figure 1), to study how polymer structure and dynamics influence ionic transport and display fundamental differences in their properties as compared to the bulk of the SPE material.

Figure 1. PEO and LiTFSI at the electrolyte/Li metal interface.

References
The performance of poly(vinyl alcohol) polymer electrolyte for battery applications

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Poly(vinyl alcohol) (PVA) as an alternative to poly(ethylene oxide) (PEO) based polymer electrolytes has previously been studied for uses in electrochemical applications in the 1990s, and was found to be highly ionically conducting at temperature below the glass transition temperature of the polymer in presence of dimethyl sulfoxide residues[1-3]. The ionic conductivity dropped significantly when fabricated by solvent free hotpressing instead. In fact, as a proof of concept, a PVA:LiClO₄ electrolyte has been applied in an earlier study as electrolyte medium for supercapacitors [4]. In this study emphasis is placed on the compatibility of PVA-based polymer and gel polymer electrolytes, respectively, in lithium-ion batteries

Various lithium salts and solvents have been used to produce solid polymer electrolyte films, and the effect of residual solvent and plasticizing effects on the glass transition temperature has been studied along with the nature of hydrogen bonding of the polymers’ functional groups. For the first time, PVA:LiTFSI polymer electrolytes have been evaluated at different salt concentrations. The materials show superior ionic conductivity compared to previous lithium salts investigated and yet remain very mechanically stable even at elevated temperature, which qualifies these electrolytes for use in Li-battery applications. Lastly, galvanostatic cycling data of lithium metal | PVA-LiTFSI (DMSO) | LFP batteries at elevated temperatures and different cycling rates is presented (figure 1).

![Figure 1: Discharge profile of lithium metal | PVA-LiTFSI (DMSO) | LFP cell conducted at a rate of C/25 at 60°C](image)

References
Fabrication of CoIr$_x$/γ-Al$_2$O$_3$ modified glassy carbon electrode and electrochemical oxidation of hydrazine

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The aim of present work was optimal loading of CoIr$_x$ over γ-Al$_2$O$_3$ for hydrazine electrolysis. Electrocatalytic oxidation of hydrazine was investigated on glassy carbon electrode (GCE) modified with CoIr$_x$/γ-Al$_2$O$_3$ using cyclic voltammetry (CV). The prepared catalyst materials, CoIr$_x$/γ-Al$_2$O$_3$, were characterized by using AAS, XRD, N$_2$ physisorption, TPR, TPO, and SEM equipped with EDX which showed the formation of Co-Ir nanoparticles well dispersed onto γ-Al$_2$O$_3$ support. All powders showed activity for catalytic oxidation of hydrazine owing to synergistic effect of Co-Ir nanoparticles. However, the optimum composition of CoIr$_{0.081}$/γ-Al$_2$O$_3$ exhibited an excellent electrocatalytic activity towards hydrazine oxidation with anodic peak current of 47.2 μA at 0.86 V potential. This is first time report on CoIr$_x$/γ-Al$_2$O$_3$ modified GCE successfully developed and applied for electrooxidation of hydrazine.
Modelling of Super-Concentrated Electrolytes for Lithium-Ion Batteries

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During 2013 there was a very surprising development in the area of lithium battery electrolytes applied in real cells; several groups reported on excellent cell performance by using “super-concentrated” electrolytes [1-2]. These seem to allow for fast-charging as well as stabilizing Li metal anodes. The electrolytes were based on solvents like acetonitrile (AN), salts like LiPF$_6$ or LiTFSI, and salt concentrations typically above 2.5 M and up to ca. 7(!) M [2].

The large surprise arises from the “common knowledge” in the lithium battery electrolyte field being that the ionic conductivity and the lithium-ion transfer properties are to be optimized by keeping the viscosity low. Traditionally, this has almost always resulted in a predominance of ∼1 M salt solutions using low viscosity solvents with large dipole moments.

While the new concept is a truly disruptive happening in the field, the relation between local structure and transport properties of super-concentrated electrolytes is very poorly understood. Here we have approached this by computational investigations, at PM6 and HF levels, of various clusters of LiPF$_6$ and AN to address the concentration dependence.

The predominant 4-fold tetrahedral coordination of Li$^+$ is found to be progressively disordered and the AN ligands to be replaced by the PF$_6^-$ anions, possibly affecting the de-complexation process at the electrodes. The HOMO energies are not affected, in contrast to the experiments, pointing to more of a kinetic control or a specific role of the anode surface.

![Graph](image)

**Figure 1.** The changes in coordination number of Li$^+$ as a function of salt concentration.

**References**


Effect of alkaline cations as a counter-ion for iodide ion conducting gel polymer electrolytes intended for dye sensitized solar cells

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Iodide ion conducting electrolytes are intensively studied as effectual electrolytes for dye-sensitized solar cells (DSSCs). However, the nature and concentration of the counter-ion (cation) in the electrolyte exert a profound influence on the performance of the thin film meso-porous TiO$_2$ based dye-sensitized solar cells (DSSCs). A series of gel electrolytes containing the alkaline iodides LiI, NaI, KI, RbI and CsI and polyacrylonitrile (PAN) were fabricated together with the non-volatile plasticizers ethylene carbonate (EC) and propylene carbonate (PC). The ionic conductivity of the electrolytes was studied in order to investigate the dependence of conductivity in the electrolyte on the nature of the alkaline cation. The results showed that the conductivities were higher in electrolytes with the larger cations, namely K$^+$, Rb$^+$ and Cs$^+$. The temperature dependence of conductivity in this series appears to follow the Vogel-Tammann-Fulcher equation. Quasi-solid state DSSCs were assembled using the above mentioned series of gel electrolytes and TiO$_2$ photo-anodes prepared with a meso-porous TiO$_2$ layer overlaid on a compact spin coated layer of the same oxide. A clear trend of an open circuit voltage enhancement with increasing cation size is observed for the single salt containing electrolyte series. The shift of the flat band potentials with adsorbed ions were investigated using Mott-Schottky plots.

![Graph](image)

**Figure 1.** Variations of the open circuit voltage ($V_{oc}$), the short circuit current density ($J_{sc}$) and the fill factor (FF) and the efficiency of dye-sensitized solar cells series

The short circuit current density ($J_{sc}$) also increases with increasing size of the counter-ion in the electrolyte up to Rb$^+$. However, the opposite trend has been observed with liquid electrolytes [1]. Therefore, the trend exhibited in this work, shows a clear difference compared to the effects for liquid electrolytes regarding the performance of solar cells. The highest $J_{sc}$ of 9.4 mA cm$^{-2}$ was shown for the RbI and CsI containing cells. The efficiency 3.48%, was shown by the cell containing CsI. Subsequently, the cell performance was further enhanced by incorporating different additives to the electrolyte series.

References

Synthesis and Characterization Of Novel Phosphonium Based Ionic Liquid Electrolyte for Li-ion battery

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Ionic liquids were prepared as solvent in future polymer electrolyte system for Li-ion battery. Ionic liquids based on phosphonium were synthesized and various concentrations of different lithium salts added. Conductivity, thermal stability and coordination situation were investigated together with electrochemical stability window. Cycling tests with different types of additives to meet requirements for stable SEI were conducted as well as post mortem analysis.

Figure 1. DSC analysis of prepared IL and effect of added Li salt on crystallinity phase

Figure 2. a) TGA analysis of prepared IL, b) conductivity measurements of IL with different Li salts
New Insights Towards Aging Resistant Li-ion Polymer Batteries For Wide Temperature Applications

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A wide interest is mounting towards polymer electrolytes, due to their application in energy efficient rechargeable batteries, photo-electrochemical cells, electrochromics, and supercapacitors. Polymer electrolytes exhibit unique advantages such as mechanical integrity, wide variety of fabrication methods in desirable size and shape, possibility to fabricate an intimate electrode/electrolyte interface and adapt to a lightweight, leak-proof construction, and economic packaging structure. In this communication, we offer a summary of our recent results regarding the synthesis, physico-chemical and electrochemical characterization of solid polymer electrolytes (SPEs) based on different monomers/oligomers (methacrylic and/or ethylene oxide based) with specific amounts of lithium salt, plasticizers and/or fillers. Profoundly ion conducting (\(\sigma > 10^4 \text{ S cm}^{-1}\) at 20 °C), electrochemically stable (> 5 V vs. Li), self-standing, robust and tack-free SPEs are successfully prepared via a rapid and easily up-scalable process including a light and/or thermally induced polymerization step. The resulting crosslinking allows the incorporation of high amounts of plasticisers (e.g., RTILs) and lithium salt (based on TFSI anion), leading to a material with remarkable morphological characteristics in terms of homogeneity and mechanical abusability under highly stressful conditions.

![Figure 1](Figure 1, Sketched picture of the preparation along with the different components and aspect of the SPE.)

Lab-scale Li-polymer cells assembled show stable charge/discharge characteristics without any capacity fading at C/5 current regime (> 130 mAh g\(^{-1}\) in LiFePO\(_4\)/Li configuration and > 150 mAh g\(^{-1}\) in TiO\(_2\)/Li configuration even @ 20 °C). The overall performance of the SPEs postulates the possibility of effective implementation in the next generation of safe, durable and high energy density secondary all-solid Li-ion polymer batteries working at ambient and/or sub-ambient temperatures.

References

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Synthesis and Properties of New Tetraalkoxyborate Lithium Salts

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Nowadays many studies focus on the improvement of the ionic conductivity and the lithium transference numbers of polymer electrolytes. The most commonly used industrial salt LiPF₆ has low thermal and hydrolytic resistance. HF evolves from its decomposition, which acts destructively on the chemical cell components [1,2]. For this reason new lithium salts, which could replace those currently utilized in lithium-ion batteries, are being developed. Our previous proposal was lithium alkyltriaalkoxyborates, containing oxyethylene groups [3]. Further research led to the development of analogous lithium tetraalkoxyborates, anions of which have molar masses specific to oligomers and contain oligooxyethylene groups.

The presented synthesis method allows obtaining salts with both asymmetrical and symmetrical anions. Their properties depend on their molecular weight - the salt comprising only the CH₃OCH₂CH₂ (n = 1) groups is a crystalline solid under normal conditions, while salts with longer substituents exhibit room temperature ionic liquid properties. Their advantage due to the application in polymer electrolytes is the presence of oligooxyethylene groups, which provide good compatibility of these salts with poly(oxyethylene) (PEO) matrix. The presented compounds were obtained in a simple reaction of trialkoxyborate with lithium alkoxide, which are derived from the corresponding poly(ethylene glycol) methyl ethers.

\[
6 \text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OH} + \text{B}_2\text{O}_3 \rightarrow 2 \text{B}[(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3]_3 + 3 \text{H}_2\text{O}
\]
\[
\text{CH}_3(\text{OCH}_2\text{CH}_2)_m\text{OH} + \text{C}_4\text{H}_9\text{Li} \rightarrow \text{CH}_3(\text{OCH}_2\text{CH}_2)_m\text{OLi} + \text{C}_4\text{H}_{10} \uparrow
\]
\[
\text{B}[(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3]_3 + \text{CH}_3(\text{OCH}_2\text{CH}_2)_m\text{OLi} \rightarrow \begin{align*}
\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2)_n\text{OCH}_3 \\
\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2)_m\text{OLi}
\end{align*}
\]

where: \( n, m = 1, 2, 3, 7 \)

**Figure 1.** Synthesis of lithium tetraalkoxyborates in the reactions of trialkoxyborate with lithium alkoxide, derived from poly(ethylene glycol) methyl ethers.

We present our results regarding the ionic conductivity, thermal stability and the lithium cation transference numbers for obtained salts as well as for polymer electrolytes based on PEO containing new lithium tetraalkoxyborates.

References
Multi-scale modeling of lithium-ion batteries

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ABSTRACT

In this study, we present a three-dimensional (3-D), multi-scale, multi-physics lithium-ion battery (LIB) model wherein a mesoscale spherical particle model is applied to an electrode particle domain and a comprehensive 3-D continuum model to a single cell domain consisting of current collectors, porous electrodes, and separator. The model is first validated against the experimental voltage evolution data measured at various charge and discharge current densities. In general, the model predictions compare well with the experimental data and further highlight key electrochemical and transport phenomena occurring in LIBs. Besides solid electrode/electrolyte potential profiles, multidimensional contours of species concentration, temperature, and current density are analyzed under several different cell configurations in order to provide valuable insight into charge and discharge characteristics of LIBs. The present multiscale LIB model can be applied to a realistic LIB geometry to search for the optimal design and operating conditions.

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A novel electrochemical sensor for selective determination of Bisphenol-A based on imprinted sol-gel polymer and multi-walled carbon nanotubes modified carbon paste electrode

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Molecularly imprinted polymers (MIPs) are becoming an important analytical tool. The possibility of tailor-made, highly selective artificial receptors at low cost, with good mechanical, thermal and chemical properties makes these synthetic materials appear ideal chemoreceptors. There are great hopes for development of a new generation of electrochemical sensors using these novel synthetic materials as recognition elements [1]. The majority of the sensor systems explored to date have used radically initiated polymerization with acrylic or vinylic polymers as recognition elements, but other phases (electro-generated polymers, monolayers, sol-gel systems) have also been tested. Sol-gel imprinting is an emerging field, due to its straightforward synthesis path. Sol-gel materials are extremely rigid because of the high degrees of cross-linking in their network. This property is very important and influential in designing and synthesizing the imprinted materials since both the size and shape of the cavities created by the template molecule should be retained after the template removal. High thermal stability of sol-gel derived materials and possibility of using high temperatures assists the removal process. In addition, sol-gel glasses are structurally porous and can be engineered to have extremely high surface area. These properties make sol-gel matrix as an appropriate imprinting host. In practice, the sol-gel process is rather simple. In one step and at room temperature, it transforms a molecule into a material ready for shaping.

In this study, a new Bisphenol-A imprinted sol-gel polymer (BPA-MIP) was synthesized using functional monomer and cross-linker. The morphology and structure of BPA-MIP were characterized by FT-IR, BET analysis and scanning electron microscopy. Carbon paste electrode was fabricated by mixing BPA-MIP with multi-walled carbon nanotubes, graphite powder and paraffin oil. The electrochemical characterization of the sensor electrode was achieved with cyclic and differential pulse voltammetric techniques. The results revealed that the newly developed sensor displayed high sensitivity and selectivity, more excellent electrochemical performance and fast response to BPA, allowing it to be used for the detection of BPA in real samples.

References
Fire-retarding Nanoporous Polymer Electrolyte based on Hyperbranched Polyphosphoester by SCROP

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High performance polymer electrolyte requires high ionic conductivity, suitable mechanical strength, flexibility, inflammability, chemical and electrochemical stability [1]. The well-known PEO polymer electrolytes can be obtained with good mechanical properties; however the low ionic conductivity as well as the poor compatibility with electrodes restricted their commercialization. One efficient method to solve those is to make hybrid polymer crosslinking networks with ionic conductors [2], meanwhile which inflammability can be controlled by grafting EO side chains onto inorganic cores [3].

The phosphoester compounds are well-known fire-retardant which may improve the thermal resistance for safety and high electrochemical stability for lithium battery [4]. In this study hyperbranched ionic conductors and crosslinkers were prepared by introducing oligomeric EO chain arms onto phosphate backbones. Firstly, serials of hyperbranched polyphosphoesters were synthesized by SCROP (self condensing ring-open polymerization), and then novel fire-retarding intrinsic polymer electrolyte membranes were prepared by in-situ polymerization from a precursor solution containing phosphate crosslinker, polyphosphoester ion conductor, lithium salt and thermal initiator. Free-standing films were obtained with good mechanical stability. The nanoporous network structures of the hybrid polymer membranes were showed in scheme 1.

The ionic conductivity was achieved with great enhancement with above 10⁻⁴S/cm, which maybe due to the hybrid network structure can prevent crystallization thus enhance the ionic conductivity even at low temperature. In particular, the methacrylate functional group attached in the crosslinker established 3D network structure whereas the EO chains attached improved the compatibility with the polyphosphoester. Moreover, this nanoporous electrolyte membrane can be used directly between the cathode and anode without separator, which significantly eliminate the cost for lithium batteries’ fabrication.

Further studies of electrochemical properties such as ionic conductivity, cyclic voltammetry and chronopotentiotetry were investigated to figure out the contribution of ionic conductors to the improvements of electrochemical properties of this NPE system. All above is to prove this promising electrolyte system for the application for lithium battery.

Figure 1. Morphology of nanoporous network structure for the hybrid polymer membrane.

References
Structural Features and Proton Transport of Polymer Electrolyte Membranes for High-Temperature Fuel Cells

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High-temperature polymer electrolyte fuel cells (HT-PEFC) are promising electrochemical energy converter for automotive, stationary and portable equipment due to their environmentally friendly operation. The main part of the HT-PEFC is the membrane electrode assembly (MEA), which consists of two catalytic layers separated by a polymer electrolyte membrane acting as a proton conductor. Since the elevated operation temperatures (160°C) require polymers with excellent thermal and chemical stability, commercially available polybenzimidazole (PBI)-based polymer membranes attract particular interest. Owing to the basic nature of PBI polymer it can be impregnated with a high amount of phosphoric acid (PA), providing high protonic conductivity of the impregnated membrane. The catalytic layer composed of nanoporous carbon, poly(tetrafluoroethylene) (PTFE) and platinum (Pt) nanoparticles is in direct contact with the membrane doped with PA and as consequence contains some amount of the acid. Knowledge about the structural features of the polyelectrolyte membrane and catalytic layer as well as understanding the distribution of the PA between structural elements of the catalyst would help to design more efficient electrodes for fuel cells. Structural properties of MEA have been investigated on length scales ranging from sub-nm up to some μm by means of X-ray diffraction (XRD), neutron diffraction with polarization analysis, small angle neutron- and X-ray scattering (SANS and SAXS respectively), polarized light- and transmission electron microscopy (TEM) [1, 2]. Impact of the temperature changes as well as aging effects will be discussed. Obtained results are linked to the proton diffusion, measured over a wide time scale by means of pulsed-field-gradient nuclear magnetic resonance PFG NMR spectroscopy and quasielastic neutron scattering [3].

Figure 1. Scheme of a proton conducting fuel cell. Membrane electrode assembly is zoomed in.

References
Synthesis and Characterization of Poly(isatin biphenylene) with Sulfonyl Imide via Super Acid Catalyzed Polymerization for PEMFC Applications

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Abstract
In the past decades, many researchers made an effort to develop hydrocarbon membranes which have better properties than Nafion. Our research group were also made a lot of effort to improve properties by making structural change, sulfonation adjustment, and functional group induction. In this research, we synthesized carbon-carbon bonding polymer using super acid catalyst. Sulfonyl imide monomer was prepared by chlorosulfuric acid and fluorosulfonilsocyanate. Poly(isatin biphenylene)s were prepared by super acid catalyzed polyhydroxalkylation reaction with isatin, 2,2'-biphenyl, 2,2'-dihydroxybiphenyl. In these polymers sulfonyl imide groups were used instead of sulfonic acid groups. Because sulfonyl imide group have higher acidity than sulfonic acid group. Therefore, these membranes expect to improve performance of proton conductivity, water uptake, and dimensional stability. The structure of the synthesized polymer was investigated by \textsuperscript{1}H NMR spectroscopy. These membranes will be studied by proton conductivity, water uptake, dimensional stability, and ion exchange capacity (IEC). Surface morphologies will also be assessed by atomic force microscope (AFM).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{synthesis_diagram.png}
\caption{Synthesis of sulfonyl imide polymer membranes.}
\end{figure}

References
Polymer-ceramic particle composite gel polymer electrolyte for 4 V-class cathode

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Although the dry and composite types of polymer electrolytes are highly desirable in view of their mechanical strength and safety, they possess relatively low ionic conductivity (typically <10^{-6} S/cm) at room temperature, which limits their practical applications. The gel polymer electrolytes (GPEs) show higher ionic conductivity (~10^{-3} S/cm at 25 °C), but are less advantageous with regard to mechanical strength and leakage [1-3]. In this study, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP)-based gel polymer electrolyte incorporating nano-size Al2O3 ceramic particle was prepared by electrospinning. The incorporation of ceramic particle to form the composite GPE can enhance the handling strength and ionic conductivity, and lead to better compatibility with lithium metal electrode. The GPE incorporated with Al2O3 ceramic particle showed higher ionic conductivity of 9.5x10^{-2} S/cm than general GPE without ceramic particle. Moreover, the GPE with Al2O3 exhibited high oxidation electrochemical stability to >5 V. Therefore, electrochemical tests of the Li [Ni_{1/3}Mn_{1/3}Co_{1/3}]O2 (NMC) cell was performed and showed high discharge capacity and stable cycle performance.

![Figure 5. Comparison of ionic conductivity with electrospun gel polymer electrolytes.](image)

References
Ion Exchange Membrane with Low Cost and High Selectivity for Vanadium Redox Flow Battery

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Nafion membrane has been conventionally used for the ionic exchange membrane of VRFB. However, it has high production cost and high vanadium permeation during the operation of VRFB system. To address these issues for the long-term operation of VRFB, new candidate for the polymer electrolyte membrane in VRFB is introduced in this study. Specifically, sulfonated poly(phenylene oxide) (sPPO) are prepared for vanadium redox flow batteries (VRFBs). The key idea of this work is to combine high proton conducting property and low vanadium permeability of sPPO. The membranes are characterized by water uptake, dimensional change, proton conductivity, vanadium ion permeability, and cross-sectional morphology. Proton conductivity of sPPO membrane significantly increased with the increase of ion exchange capacity, while vanadium permeability changed only a little, resulting in higher proton selectivity against vanadium ion transport. The VRFBs employing the sPPO membranes exhibit significant improvements in discharge capacity and energy efficiency (EE) in comparison with those based on the Nafion 211 membrane. Therefore, the sPPO membrane can be useful for VRFB applications and evaluated the feasibility of commercial production using a pilot casting machine in the lab.

![Graph](image)

**Figure 1.** Performance of VRFB system with Nafion and sPPO membranes.

**References**


**Acknowledgement**

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Characteristics of H⁺ Ion Conducting Biopolymer Electrolytes Based on Methyl Cellulose for Electrochemical Device Application

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Studies on biopolymer electrolytes (BPEs) have been improving actively due to their potential application in solid state electrochemical cells, high energy density batteries, fuel cells and electrochromic devices [1]. Methyl cellulose (MC) is the naturally occurring polysaccharide and the most abundant organic substance on earth [1, 2]. Due to abundance, low cost and easier processability, cellulose based electrolytes are expected to bring better future green nations than non biodegradable, toxic and harmful materials used in the commercial electrochemical devices [2, 3]. In the present work, biopolymer electrolyte films based on MC doped with ammonium bromide (NH₄Br) salt and plasticized with glycerol were prepared by solution casting method. Fourier transform infrared (FTIR) spectroscopy analysis confirms the interaction between MC and NH₄Br. X-ray diffraction (XRD) explains that the enhancement of conductivity is affected by the degree of crystallinity. This result is verified by field emission scanning electron microscopy (FESEM) and differential scanning calorimetry (DSC). For plasticizer free system, sample containing 25 wt.% NH₄Br possesses the highest ionic conductivity of 1.89 × 10⁻⁵ S cm⁻¹. The addition of 30 wt.% glycerol increases the conductivity value up to 1.67 × 10⁻³ S cm⁻¹. The conductivity at different temperatures for both systems obey Arrhenius rule. Dielectric studies show that the electrolytes obey non-Debye behavior. From transference number of ion (tᵢ⁺) measurement, proton ion is found as the dominant conducting species. The linear sweep voltammetry (LSV) result confirms the suitability of the highest conducting electrolyte to be employed in the fabrication of an electrochemical device.

![Figure 1. Room temperature conductivity for plasticized electrolyte](image_url)

References
Effect of Solvation Structure on Electrochemical Performance of Carbonate-based Solid Polymer Electrolytes

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We have focused on poly(alkylene carbonate)s generated by copolymerization of CO₂ and epoxides as polymer hosts of Li ion conductive solid polymer electrolyte (SPE) [1-3]. We previously found unusual properties of SPEs based on poly(ethylene carbonate) (PEC), one of the CO₂/epoxide copolymers. They show decrease in glass transition temperature (T_g) and increase in ionic conductivity with increasing salt concentration (Fig. 1a), and high lithium transference number (t_+) [3]. We have also demonstrated operations of Li/LiFePO₄ cells utilizing reinforced PEC-based electrolytes [4,5].

Elucidation of salt solvation state is necessary to better understand the origin of the above particular properties, and to further the development of CO₂/epoxide copolymer-based electrolytes. In the present study, we adopted spectroscopic studies including FT-IR, Raman spectroscopy, and solid-state ⁷Li magic angle spinning (MAS) NMR to investigate the solvation structure of PEC-based electrolytes containing lithium bis(fluorosulfonyl)imide (LiFSI) with varying concentration [6]. The FT-IR and Raman analyses suggested that Li ions constantly contact with both FSI ions and C=O groups. The Raman spectra also indicated that all FSI ions exist as aggregate state at a concentration of 50 mol%, as shown in Fig. 1b. The ⁷Li MAS NMR spectra in Fig. 1c for 10 and 50 mol% electrolytes show a large up-field shift with increasing concentration, which demonstrates the ionic aggregation and weakened electron donor ability (Lewis basicity) felt by Li ions induced by both FSI ions and PEC chains. We concluded that this loose coordination structure, in which C=O groups allow the large amount of ions to remain amorphous and to migrate, enable the reasonable conductivity and high t_+ (e.g. 0.6 for 90 mol% sample) simultaneously. We believe that this finding will provide a new insight into developing SPEs showing both high conductivity and high t_. In the presentation, the implications of the highly aggregated ionic structure for battery electrolyte performances will also be discussed.

![Figure 1](image-url)

Figure 1. (a) Salt concentration dependence of ionic conductivity and glass transition temperature (T_g), (b) Raman spectra (ν(S-N-S)), and (c) ⁷Li MAS NMR spectra of PEC/LiFSI electrolytes.

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References:
Graphene-Selenium Hybrid Microballs as a Cathode Material for High-performance Lithium-Selenium Secondary Battery Applications

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We report the one-step preparation of graphene-selenium hybrid microballs (G-SeHMs) via the aerosol microdroplet drying method using a commercial spray dryer, which is a simple and scalable continuous process, and their suitability for use as a cathode material in lithium-selenium secondary battery applications. These morphologically unique graphene microballs filled with Se particles exhibited good electrochemical properties, including high initial specific capacity (642 mA h g⁻¹ at 0.1C; corresponded to a Se electrochemical utilization as high as 95.1 %), good cycling stability (544 mA h g⁻¹ after 100 cycles at 0.1C; 84.5% retention), and high rate capability (specific capacity of 301 mA h g⁻¹ at 5C) in an organic electrolyte prepared by dissolving 1 M LITFSI in a mixture of tetraethylene glycol dimethyl ether and 1,3-dioxolane mixed in a 1:1 volumetric ratio. These were attributable to the fact that the structure of the G-SeHMs acted as a confinement matrix for suppressing the dissolution of polyselenides in the organic electrolyte, as well as an electrical conduction path for increasing the electron-transport rate for electrochemical reactions. Importantly, the electrochemical performances obtained by the weight of hybrid materials are considerably higher than those of previous reported Se-based cathode materials due to high Se loading content (80 wt. %) in hybrid materials.¹⁻⁵

References
Bicontinuous designed anion-conducting/-repelling polymeric phase to transport ion selectively through channel for rechargeable zinc-air battery separator membranes

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The artificially-engineered, bicontinuous anion-conducting/-repelling polymeric phase were designed to selectively transport ions through channel for improved rechargeable Zn-air batteries performance. This new membrane exhibits unique structure that effectively suppress Zn(OH)₂⁻ crossover (by continuous phase of Nafion) with slightly impairing the OH⁻ conductivity (through PVA/PAA nanofiber mat). Activity of ion selective transport phenomena attributed to improving the cycling stability far beyond that achievable with conventional separator membrane.

Figure 1. Design of membrane and ion selective activity within membrane.

References
A Novel Polymer Electrolyte Containing Sulfonyle urea Moiety for PEMFC and Libattery

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Abstract
Ultraviolet (UV) curable electrolytes have attracted much attention because they are useful as a gel and film states. Conventional UV curable electrolytes are mixture of LiFSI or LiPF₆, UV curable acrylated materials and oligomers. We developed a novel UV-curable monomer based on acryl functional group containing fluorosulfonyle urea. The prepared monomer was transferred to Li containing acryl electrolyte, and also directly prepared film with multi-acrylated monomers. This precursor was used for lithium ion batteries and proton exchange membranes. The resulting electrolytes can enhance the movement of Li⁺ ions inside the polymer matrix demonstrate mechanical integrity due to the cross-linked nature of the polymer network, and wide thermal stability. We will be studied by ¹H NMR spectroscopy and properties will be measured by ion exchange capacity (IEC), water uptake (WU) and Fenton test and proton conductivity. And also electrochemical impedance spectroscopy (EIS) will be employed to characterize the electrolytes. The electrical analysis and conductivities of the electrolytes in solvent and film state are also studied.

References
Comparative study of PBI Cross Linked Utilizing Agents of Varying Steric Configurations

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The high thermal and chemical stability of poly[2,2’-(m-phenylene)-5,5’ bibenimidazole] (PBI) accounts for its wise spread use in high temperature polymer electrolyte membrane fuel cells (HT-PEMFC). By doping the membrane with phosphoric acid (PA) ionic conductivity is obtained. Thus conductivity is dependent on the amount of PA present within the membrane. However mechanical properties are reduced are significantly reduced due to the plasticizing effect shown by PA [1]. This effect is due to PBI chain displacement. This effect can be lessened by use of cross linking [2-4]. This can be obtained using ionic or covalent cross linking. When considering such, little attention is devoted to explore the effect of the sterical configuration of the cross linking agent. In this contribution three different cross linking agents are utilized to evaluate how these affects final membrane properties.

![Chemical structures](image)

**Figure 1.** Different cross linkers utilized in this work.

References

Ion-Conductive Behavior of a Gel Polymer Electrolyte with Mg(TFSI)$_2$

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Introduction
Rechargeable magnesium (Mg) battery has been expected as a promising candidate for next-generation system because of the high volumetric energy density, low reduction potential of Mg and the abundant Mg resources [1]. The Mg deposition/dissolution was gained by Grignard ethereal solutions and Mg(TFSI)$_2$ in glyme solutions have been recently reported [2-3]. However, liquid electrolytes in battery systems are often associated with safety problems due to their leakage. A use of GPE can be provided to the ideal batteries to conduct Mg ions effectively without any safety problems. In this paper, we prepared novel GPEs based on crosslinked poly(tetrahydrofuran) (PTHF) with triethylene glycol dimethyl ether (G3)/Mg(TFSI)$_2$ and investigated their electrochemical properties.

Experimental
A crosslinked PTHF membrane was prepared by casting from THF solution of imidazole-terminated trifunctional PTHF with $a,a'$-dichloro-p-xylene as crosslinking agent at 90 °C for 22 h. The PTHF membrane was soaked in G3/Mg(TFSI)$_2$ solution until its weight became constant. Ionic conductivity of the membrane was measured by electrochemical impedance spectroscopy for symmetric cells with two stainless steel electrodes. Cyclic voltammetry was carried out for the same cells with two AZ31 magnesium alloy electrodes at 80 °C and a scan rate of 0.01 V s$^{-1}$.

Results and Discussion
Crosslinked PTHF including G3/Mg(TFSI)$_2$ solution provided a flexible and mechanical strength GPE. A GPE membrane containing G3/Mg(TFSI)$_2$ showed that the swelling ratio was more than 150%, and the solution in the membrane was difficult to squeeze out. The values of conductivity were scarcely different among GPEs with different Mg(TFSI)$_2$ concentrations. The GPE including 0.3 M G3/Mg(TFSI)$_2$ showed the highest values ranging from 0.7 × 10$^{-4}$ S cm$^{-1}$ at 30 °C to 1.4 × 10$^{-4}$ S cm$^{-1}$ at 80 °C. Those values are much smaller than those of the corresponding liquid electrolyte ( > 1.0 × 10$^{-3}$ S cm$^{-1}$). The cyclic voltammograms in 1st–4th cycles showed the reduction and oxidation with peak top values at -2.5 V and +2.5 V, respectively (Figure 1). The values of current density of peaks increased in each cycle, indicating that Mg ions are mobile in the PTHF membrane. Although those values are small, the Mg may be capable to deposit from and dissolve into PTHF membrane.

Conclusion
We prepared novel GPEs based on PTHF with G3/Mg(TFSI)$_2$ solution and investigated their electrochemical properties. Flexible GPEs exhibited the desirable mechanical properties and allowed Mg dissolution and deposition. These results indicate that the PTHF-based GPE might have a potential as electrolyte membrane for rechargeable Mg batteries.

Acknowledgment
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References
Synthesis and characterization of block copolymer electrolytes for lithium metal polymer batteries

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Electrochemical energy storage is one of the major societal challenges of this century. Performances of classical lithium–ion technology have made great strides in the past two decades [1]. However, one major issue towards large-scale application (electric vehicles or stationary applications) concerns their safety, due to the use of large amount of liquid, volatile, flammable, electrolytes. The use of a solid polymer electrolyte (SPE) which is commonly a lithium salt associated with polyethylene oxide (PEO), could solve most of the safety issues encountered with liquid electrolytes. However, these SPE have some cons. In effect, PEO is a semi crystalline polymer, in order to have good conductivities it has to be used above its Tm, but at these temperatures the mechanical properties are not good enough to prevent dendritic growth [2].

In order to combine, in a same material, the two antagonistic properties (mechanical and conductivity), block copolymer electrolytes (BCE) have recently been proposed as SPE [3-7]. Interesting properties of these functional materials is a consequence of their self-assembly properties, which give rise to ordered structures and permits an addition of properties instead of average ones.

In this work we have designed a new polymer electrolyte with both good conductivity and good mechanical properties. To reach that goal, we synthesized a block copolymer with a central block composed of a linear modified PEO (which presents a lower Tm) and two lateral blocks of polystyrene.

The impact of the ratio between the PS and the modified POE on the mechanical strength, conductivity, and performances in lithium metal battery are largely discussed in this work.

How to prepare ionomer inks for well-performing porous electrodes for anion-exchange membrane fuel cells?

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Anion-exchange membrane fuel cells (AEMFC) use hydroxide ion conducting polymer electrolytes that are potentially more environmentally friendly than the fluorinated polymer electrolyte, such as Nafion®, used in proton exchange membrane fuel cells (PEMFC). The alkaline environment enables use of more readily available and lower cost catalysts, but the AEMFCs still need further development with regard to stability, conductivity and water management [1, 2].

One of the important fuel cell properties that largely influences the cell performance is the structure of the composite porous electrodes. This is determined by ionomer content in the electrode, retaining a stable framework in the porous structure [3, 4] and the ionomer wetting of the catalyst particles ensuring ion conduction to the catalytic sites. More studies are needed to understand ink properties for electrode preparation, i.e. the interaction between polymer and solvent in the ink. In this study we have varied the solvent (isopropanol and water) composition in the electrode ink and the ionomer content separately, using commercially available membranes and ionomer solution from Tokuyama. The performance study at fuel cell conditions shows that an H2O:propanol ratio of 0.4 (Fig 1a) results in an even distribution of ionomer in the electrode structure as the colloidal suspension of the polymer in the ink is optimized. Further, an ionomer:Pt/C ratio of around 0.6 (Fig 1b) gives rise to improved mass transport and catalyst utilization as the wetting is improved at the same time as pore clogging is avoided. Both results point out that there are more polymer properties to consider than the conductivity to prepare well-performing AEMFC electrodes [5].

**Figure 1.** a) Influence of solvent composition, b) Influence of ionomer content on fuel cell performance using ion exchanged Tokuyama membranes at 50 °C, R.H. 95%, 1 mV/s scan rate and 7.4 l h⁻¹ O₂/H₂ flow rates.

**References**


Solid Polymer Electrolytes (SPEs) have attracted much attention as electrolyte materials for next generation lithium-ion batteries, because they show promising advantages such as flexibility, shape diversity, light-weight, safety and so on. Furthermore, these properties will be the trend of the next generation batteries development. However, ionic conductivities of SPEs are lower than most of liquid electrolytes, that have not been widely used in commercial lithium-ion batteries. To overcome those problems, there are tremendous works have been done about polyether-based electrolytes in the recent years. Previously, we are focusing on a carbonate structures in the polymer. The poly(ethylene carbonate) (PEC)-based electrolytes shows different ion-conductive behaviors from typical polyether-based electrolytes. In this electrolyte, the ionic conductivity can increase with increasing in Li salt concentration [1]. In addition, we have been reported that the addition of non-calcined silica nanofibers (SNFs) to poly ethylene-based electrolyte was able to improve more ionic conductivity and mechanical properties [2], because they have high aspect ratios and many functional groups on the surface. Here, we prepared PEC-based SPEs filled with SNFs to improving electrochemical properties and mechanical strength. Meanwhile, we filled with SNFs with different sizes of diameter (300, 700, and 1000 nm) in SPEs and tried to explore the diameter effects on the ionic conductivity properties.

From the result of scanning electron Microscopy (SEM), we confirmed that SNFs have well dispersibility in the PEC/LiTFSI electrolytes. The temperature dependence of ionic conductivity for the PEC/LiTFSI 100 mol% electrolyte and filled with SNFs composite electrolytes are shown in Figure 1. The ionic conductivity of PEC/LiTFSI 100 mol% original electrolyte shows the order 10^{-6} S cm^{-1} and the Li transference number (t_{Li^+}) was 0.71 at 60°C. Compared to the original electrolyte without SNFs, an appreciable enhancement of conductivity could be detected only filled with 5 wt% of SNFs. Furthermore, the ionic conductivity increase with filled with thinner SNFs. The composite electrolyte containing 300 nm SNFs displays the highest conductivity of the order of 10^{-4} S cm^{-1} and the t_{Li^+} as high as 0.77 at 60°C. Meanwhile, the mechanical strength is quite improved throughout all fiber diameter sizes. Which filled the thinner SNF, shows the stronger mechanical strength, and up to 7 times more strength than that of fiber free electrolyte.

Acknowledgements
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References
The role of hydrogen bonds in the melting points of sulfonate-based protic organic salts

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There are three main types of interactions inside organic salts – electrostatic interaction, hydrogen bonding and van der Waals force \cite{1-4}. While van der Waals force is relatively weak, it is hydrogen bonding and particularly electrostatic interaction that determine the lattice energies of ionic systems and other physicochemical properties like melting points \cite{5}. The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment \(X-H\) in which \(X\) is more electronegative than \(H\), and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation \cite{6}. Hydrogen bonds in the solid state fall into the classification of strong, moderate, and weak hydrogen bonds \cite{7}. In molecular systems like \(H_2O\) \textit{(vs.} \(H_2S)\) or \(NH_3\) \textit{(vs.} \(PH_3)\), strong hydrogen bonds lead to higher melting points. However, in organic salts, the situation may be different \cite{8,9}.

In this presentation, we will present our important discovery on the influence of hydrogen bonding on the melting points of sulfonate-based protic organic salts \cite{9}. We found five pairs, among which we will discuss in detail results of two highly similar protic organic salts – \(1,2,4\)-triazolium methanesulfonate and imidazolium methanesulfonate. Both of them are solid-state proton conductors. The electrostatic interaction energy was calculated based on the single crystal X-ray and neutron diffraction data, showing that \(1,2,4\)-triazolium methanesulfonate has higher electrostatic interaction energy at various temperatures. Moreover, variable-temperature infrared spectra, deuterium isotope effects, and single crystal data indicate much stronger hydrogen bonding inside \(1,2,4\)-triazolium methanesulfonate. Therefore, \(1,2,4\)-triazolium methanesulfonate is expected to have a higher melting point than imidazolium methanesulfonate. However, surprisingly, \(1,2,4\)-triazolium methanesulfonate exhibits a much lower melting point (134 °C) than imidazolium methanesulfonate (188 °C). Therefore, it is concluded that stronger hydrogen bonding inside \(1,2,4\)-triazolium methanesulfonate results in a much lower melting point than imidazolium methanesulfonate.

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Polymer Electrolytes Based on Polymer Blends, Plasticized Polymers, or Polymer Gels

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Lithium ion batteries are important as power sources for many portable electrical devices (e.g. laptops and mobile phones) and the use of Li-ion batteries is predicted to grow substantially in the near future, whilst branching out into new application areas. Despite this rising demand, we presently lack safe, easy to process and thus low-cost, ideally mechanically flexible batteries.

One way to achieve safe and flexible batteries is to use solvent-free polymeric electrolytes. However, a key challenge is to resolve how to decouple the ionic transport from the segmental relaxation and thus achieve good transport properties combined with mechanical rigidity. Recent work has indicated the possibility of tuning the monomer structure in co-polymers to control the local packing properties, dynamics and ionic decoupling [1]. Another route could be the use of polymer blends [2]. Moreover, a decoupling between ionic transport and segmental polymer dynamics can also be achieved by addition of solvent either as a plasticizer or to form a polymer gel [3]. We will here present work that aims at a better understanding and control of the decoupling between ionic transport and polymer segmental dynamics. We will present results on polymer electrolyte systems including polymer blends, plasticised polymers and polymer gels and discuss results from experimental studies including calorimetry, broadband dielectric spectroscopy, rheology, scattering and microscopy techniques.

References

Synthesis by Polycondensation of New Aliphatic Polycarbonates for Polymer Electrolytes

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Among the different polymers investigated as solid matrix in Solid Polymer Electrolytes (SPEs), aliphatic polycarbonates have recently shown interesting properties. In comparison with the commonly investigated poly(ethylene oxide), aliphatic polycarbonates based SPEs have shown superior ionic conductivity values at room temperature and excellent electrochemical stability window [1]. In these works, two synthetic strategies have been used to design aliphatic polycarbonates, namely ring-opening (co)polymerization (ROP) of cyclic carbonates [2] and co-polymerization between CO₂ and epoxides [3].

In this poster, we present the synthesis of a series of aliphatic polycarbonates by polycondensation. The synthetic reaction involves the melt condensation of dimethylcarbonate with a diol at high temperatures and high vacuum conditions in the presence of a catalyst [4]. This route is valid for designing a great variety of aliphatic polycarbonates using different diols. The influence of reaction conditions such as temperature, time and type of organocatalyst in the properties such as molecular weight and crystallinity of aliphatic polycarbonates based on different diols will be presented.

Figure 1. Synthetic route to aliphatic polycarbonates by polycondensation

References
Investigating the Electrochemical Stability of Electrolytes for Light-Emitting Electrochemical Cells

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The electrochemical stability of the electrolyte is a well-known limitation for the performance of light-emitting electrochemical cells (LEC). [1] This can be true both on the anodic side [2] and on the cathodic side. [3] While the anodic stability is in practice typically sufficient, the cathodic stability of current electrolytes is insufficient in comparison with typical light-emitting polymers, [4] leading to electrochemical degradation of the electrolyte instead of the preferred $n$-type doping of the light-emitting polymer at the cathode–electrolyte interface. [3]

Several authors – including us – have suggested that the cathodic instability of these electrolytes can be attributed to limited stability of the anion towards reduction. [5-7] In this context, the observed premature failure of LECs using LiTFSI rather than LiCF$_3$SO$_3$ salt could thus be explained by the larger number of strongly electron-withdrawing groups in the anion of the former salt, thereby increasing its susceptibility to reduction, leading to detrimental electrochemical side reactions. [5, 6]

Here, we show that the aforementioned effect is minor on the cathodic side and that the electrochemical insufficiency of polymeric LEC electrolytes instead is related to the cathodic instability of the ion transporter–cation complex towards reduction. We also address the origin of previous misconceptions and discuss the implications for the interpretations of results obtained in conjunction with these earlier investigations as well as for the future development of LEC electrolytes and devices with improved electrochemical stability.

![Graph](image)

**Figure 1.** Comparison of the cathodic stability of LEC electrolytes based on salts with different an- and cations.

References

INVESTIGATION OF COUNTER ELECTRODE MATERIALS FOR GEL POLYMER ELECTROLYTE BASED QUANTUM DOT SENSITIZED SOLAR CELLS

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In this article, we report CdS based QDSSCs with polysulfide-methylcellulose gel polymer electrolytes (GPEs) with Pt or PbS or Cu₂S counter electrodes. The ionic conductivity of the GPE is 0.18 S/cm with the composition of 30.66 wt% methylcellulose, 67.44 wt% Na₂S, and 1.90 wt% sulfur. The QDSSCs fabricated with Pt as counter electrode exhibits a power conversion efficiency (PCE) of 1.42 % with a short-circuit current density (Jₘ) of 7.30 mA/cm², open circuit voltage (Vₘ) of 0.51 V and fill factor (ff) of 0.34. When Pt was replaced with PbS, the PCE of the QDSSC enhanced to 2.90 % with Jₘ of 9.61 mA/cm², Vₘ of 0.60 V and ff of 0.50. With PbS as the counter electrode material, the overall performance of the QDSSC was enhanced by 104 %. The configuration of the cells is FTO/blockingTiO₂, mesoporous TiO₂/perovskite/hole conductor/counter electrode.
Performance of Solid-state Dye-Sensitized Solar Cells Based Carboxymethyl Chitosan-Ammonium Nitrate

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The awareness on environmental issues and the leakage problem of electrolyte motivate towards the development of solid polymer electrolyte (SPE) based on carboxymethyl chitosan. SPE based on carboxymethyl chitosan-ammonium nitrate (NH₄NO₃) has been prepared by solution casting technique using 1% acetic acid solution. The highest ionic conductivity achieved at room temperature is 1.18 x 10⁻³ S cm⁻¹ by 30 wt. % of NH₄NO₃ salt and the film is electrochemically stable up to 2.89 V. The potential of SPE based carboxymethyl chitosan and the influenced of NH₄NO₃ on the performance of solid-state Dye-sensitized Solar Cells (DSSC) was further studied. In order for electrolyte based carboxymethyl chitosan to be applied in DSSC, 1% acetic acid solution had been exchanged with iodolyte solution for 1 h. The liquid DSSC based iodolyte exhibited short-circuit current (Jsc) of 8.3 mA/cm² and an open-circuit voltage (Voc) of 759 mV with fill factor (%) of 30.70 % and efficiency of 1.9 %. The decrease of Jsc value of 0.2 mA/cm² and Voc of 757 mV with fill factor (%) of 35.21 % and efficiency of 0.1 % has been observed for a solid-state DSSC based carboxymethyl chitosan. The decrease of the device performance was due to poor infiltration of the polymer in to highly-structured metal oxides. However, the presence of NH₄NO₃ in carboxymethyl chitosan exhibited an increase of Jsc value of 2.0 mA/cm² and Voc of 827 mV with fill factor (%) of 48.95 % and efficiency of 0.8 % for solid-state DSSC. Modifying surface of a TiO₂ photoelectrodes through a dip-coating process using NH₄NO₃ solution revealed that NH₄NO₃-modified TiO₂ have extends the absorption edge of the visible light range and make the red shift more distinct. The increase in both Jsc and Voc showed that the presence of NH₄NO₃ improve the interface between SPE and TiO₂ in solid-state DSSC.

Keywords: ammonium nitrate (NH₄NO₃), carboxymethyl chitosan, DSSC
PTMC: A polycarbonate candidate for polymer electrolytes in sodium batteries?

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Energy storage on a large scale is emerging as a separate market for batteries. This new market shifts focus from energy per gram to price per kilowatt hour. Sodium-based batteries can be combined with polymer electrolytes in order to reduce the cost of batteries through the use of cheap materials. The use of sodium instead of lithium means that aluminium can be used as current collectors at the anode-side and use of polymer electrolytes removes the need for separators and organic liquids in the battery. The implementation of polymer electrolytes can also improve safety and durability as the polymers used are often non-flammable and the resistance to dendritic penetration through the electrolyte is generally better. The presentation will demonstrate an early effort to show the potential and challenges of sodium-polymer batteries.

The poly(trimethylene carbonate)–sodium bis(fluorosulfonyl)imide system has been investigated as polymer electrolytes for sodium batteries. The properties of poly(trimethylene carbonate) with salt concentrations ranging from 8.7 wt% to 67 wt% have been measured by DSC, FTIR, and EIS. Half-cells based on both high-salt and low-salt electrolytes have been tested in order to determine their performance in a realistic environment. The tests reveal two distinct regions in salt concentration and the best-performing electrolytes show a conductivity of 50 μS/cm at 25 °C and 1 mS/cm at 100 °C. The presentation contains cell data from sodium–prussian blue half-cells with only 10% capacity fade after 80 cycles at 60 °C and additional tests of high-salt cells capable of cycling at reduced temperature with good rate capability.

![Figure 1](image_url): Performance data for a half-cell using PTMC;NaFSI at 60 °C cycled at C/5. Voltage profiles (left), discharge capacity and coulombic efficiency (right).
Polymers containing N-spirocyclic quaternary ammonium moieties as electrolyte materials

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Anion-exchange membrane fuel cells (AEMFCs) have quite recently been proposed as viable alternatives to proton exchange membrane fuel cells [1]. For example, operating under alkaline conditions, AEMFCs may utilize non-platinum catalysts and show faster cathode reaction kinetics. One of the main obstacles towards the development of these devices is the current lack of anion-exchange membrane materials that combine high hydroxide ion conductivity with sufficient alkaline stability [2]. Here, the alkaline stability of the cationic ion-exchange group is especially critical. Recently, Marino and Kreuer reported on the remarkable stability of N-spirocyclic quaternary ammonium model compounds, even at temperatures up to 160 °C in concentrated aqueous alkaline solutions [3].

Our research group is presently preparing and studying polymers and membranes which incorporate N-spirocyclic quaternary ammonium moieties (see example in Figure 1) [4]. We have found that despite their bulkiness, these cationic moieties efficiently form clusters in the membranes which facilitate high hydroxide ion conductivities. In the present contribution we will further discuss synthetic strategies and the characteristics of this new class of polymer electrolytes.

![Figure 1. Polysulfone incorporating bis-N-spirocyclic quaternary ammonium moieties.](image)

References
Jeffamine®-based polymer electrolytes

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Solid polymer electrolytes (SPE) have been intensively studied for nearly 40 years. The most widely used polymer host is poly(ethylene oxide) (PEO) and is advantageous for safety, processing, simplicity and cost. Recently, solid polymer electrolytes (SPEs) were successfully implemented in the “Bluecar” EV battery commercialized by Bolloré [1]. This already shows the great potential of polymers in Li² based batteries. This work describes a synthesis route towards a new type of polymer material based on Jeffamine® compounds grafted to Poly(ethylene-alt-maleic anhydride) backbone by imide ring formation, as followed by NMR. Jeffamine compounds are composed of propylene oxide/ethylene oxide units (PO/EO) providing excellent elastomeric properties to the polymer host and ended by a NH₂ group allowing attachment. Amorphous polymer electrolytes with Tg temperature ~ -40°C exhibit high ionic conductivity (10⁻³ Scm⁻¹ at 70°C with 1:20 LiTFSI:EO) and sufficient electrochemical stability to apply those materials in Li based batteries. Salt-matrix interaction was followed by infrared spectroscopy. Different modifications have been investigated to improve mechanical strength of polymer membranes. As first use, considering their elastomeric properties, such polymer electrolyte has been successfully implemented as a polymer binder in a cathode composite imparting superior electrochemical performance of the cells. Cathodes based on LFP and elemental sulphur were tested with Li² as an anode (figure 1).

Figure 1. Voltage profiles and capacity of the cells with LFP active material (upper graph) and elemental sulphur (bottom graph).

References

Superlithiation of Dilithium Benzenedicarboxylate: Stability and Reversibility with Liquid or Solid Electrolytes

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Organic electrode materials (OEMs) for lithium-ion batteries (LIBs) constitute a very promising alternative to standard electrodes materials that are prepared from finite and non-renewable minerals resources, since they instead are being potentially environmental friendly, cheap, and abundant if derived from biomass via ecofriendly processes. However, their commercial use is currently held back, primarily due to their poor energy density. High specific capacity OEMs are therefore of utmost interest. During the last 3 years, OEMs with the ability of an unexpected reversible reduction of carbon-carbon double bonds have sporadically been reported \cite{1}. As a consequence of this redox process – coined ‘superlithiation’ – specific energies several times higher than commercial standards (graphite) and Li/C ratios of 1/1 have been reported.

We recently reported the ‘superlithiation’ of dilithium benzenedicarboxylate \cite{2}. When cycled in liquid electrolytes, this material can reversibly reduce its unsaturated carbon-carbon bonds in addition to the expected reduction of its carboxyls, leading to a Li/C ratio of 1/1 and specific capacity as high as 1363 mAh g\textsuperscript{-1}: the highest ever reported for a lithium carboxylate. However, this corresponds to an insertion of 11.5 lithium ions while a maximum of 18 lithium ions is theoretically expected. Better capacity and stability can be achieved when industrial quality polymer electrolytes are used instead of liquid electrolytes, which we demonstrate in this presentation.

![Graphical representation of superlithiation](image)

Fig. 1 a) ‘Superlithiation’ mechanism. b) Proposed lithium insertion mechanism in dilithium benzenedicarboxylate.

\begin{itemize}
\end{itemize}
Towards Robust Membranes Based On Poly-Electrolytes

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Sulfonated poly(phenylene sulfone)s (sPSO2s) are typical polyelectrolytes. Robust membranes based on this class of material could enable bringing their unique transport and stability properties – that are distinctly different from those of PFSAs – into the field of fuel cell applications.

Their properties are extreme with regard to ion density and backbone polarity. Advantages emerging from their unique molecular architecture are high ion conductivity, high (thermal, hydrolytic) stability, low water transport, and low gas permeability. At the same time, the highly ionic character of the architecture causes salt-like brittleness in the dry state and high water uptake at elevated relative humidities. These critical mechanical properties need to be compensated in order to realize applicable ion exchange membranes based on sPSO2s.

Our approaches revolve around combining the pure materials’ advantageous properties with stability at both, low and high relative humidities and high temperatures.

The first approach is polymer blending using stabilizing basic-functionalized blend components: in order to overcome the severe challenges that blending with extremely polar polymers of a high IEC such as sPSO2s presents, we try to utilize acid-base interaction between the blend components to achieve compatibility. We present first results on mixing behaviours with different blend components.

The second approach is reinforcement by impregnating thin, porous fiber mats with solutions of sPSO2s: these composite membranes could significantly improve processability and control the swelling at high RH. Interaction between the reinforcing matrix and the conductive phase is induced by graft-polymerization of basic functionalities onto the matrix. We present first results on impregnation control and grafting degree.
Sodium Polymer Electrolytes Based on Sulfonated Polysulfone (SPSU-Na) towards Post Li-Ion Batteries

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Li-ion batteries are currently the alternative of choice in several technological fields, including portable electronics, electrical transportation and smart grids [1]. Nevertheless, the growing demand of lithium-based batteries has provoked not only a considerable rise in lithium production but also in raw material prices. This has put back on stage the current and unsolved debate of lithium resources: they are scarce in nature and not homogeneously distributed. Hence, to meet growing demands in terms of green and sustainable electric power storage, alternative electrochemical technologies towards Post Li-Ion Batteries (PLIB) are necessary.

In this work, we present the development of blended membranes based on sulfonated polysulfone and molecular and macromolecular polymers (polyethylene oxide-PEO and propylene carbonate-PC) to produce ionic conductive polymeric films with enhanced mechanical, electrochemical and thermal properties towards the attainment of reliable PLIB. The use of polymer materials provides several advantages to the electrolyte material, including no leakage, volumetric stability, solvent-free conditions, easy handling and wide electrochemical stability. Moreover, in agreement to its mechanical, thermal and chemical/electrochemical stability as well as its excellent film-forming capability, the polysulfone contributes to enhance the mechanical performance of the polymer electrolytes [2,3].

The polysulfone was sulfonated using trimethyl silyl chlorosulfonate (TMSCS) as described previously [4] and films were prepared through a green approach, based on lyophilization followed by hot-pressing, using water as solvent [5]. To improve ionic exchange in the polymer films, they were also immersed, under argon atmosphere, in PC during controlled periods of time. The high dielectric constant of PC contributes to reduce the attraction forces among ions, promoting ion dissociation and, therefore, ion mobility. The films performance was evaluated through a characterization process, which included electrical (complex impedance spectroscopy), mechanical (dynamic mechanical thermal analysis), thermal (differential scanning calorimetry, thermogravimetric analysis) and structural/morphology (scanning electron microscopy, X-Ray diffraction) studies. Results demonstrate an improved behavior of those membranes in contact with PC (SPSU-Na+PC) in terms of conductivity when compared with membranes free of PC. Improvements in conductivity ranging up to 2.5 times were observed at high temperatures. However, most relevant results were observed at room temperature, where conductivity increased from 4 to 5 orders of magnitude. Further work is still undergoing to improve ionic mobility as well as mechanical performance by the introduction of Poly(ethylene glycol) methacrylate (PEGMA) to the polymer complex.

References

EFFECTS OFIODIDE/TRIIODIDE (I⁻/I₃⁻) RATIOS ON PALM BASED POLYURETHANE POLYMER ELECTROLYTE FOR SOLID-STATE DYE-SENSITIZED SOLAR CELL

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In this investigation, the optimization of iodide/triiodide (I⁻/I₃⁻) ratios on palm-based polyurethane (PU) polymer electrolyte’s composition for solid-state dye sensitized solar cell (DSSC) application is explored. Polyurethane polymer electrolyte is synthesized under nitrogen gas atmosphere by pre-polymerization reactions between palm kernel oil monoester-OH (PKO-p) and methylene diphenyl diisocyanate (MDI) at different LiI/Li2 molar ratios. The effects of I⁻/I₃⁻ molar ratios optimization on photovoltaic characteristics, photo-response behavior and internal charge transport properties of solid-state DSSC is examined by light-current-voltage (LIV), incident photon-to-current efficiency (IPCE) and electrochemical impedances spectroscopy (EIS) measurements. Transferance number (TN), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) was tested on solid polyurethane polymer electrolyte membrane to study number of mobiles ion, electrochemical stability and its electrochemical behavior. The current-voltage characteristics of FTO/TiO₂-dye/PU-LiI-Li₂/Pt at LiI/Li₂ 1:0.125 molar ratio demonstrated a photovoltaic response with a power conversion efficiency of 1.8 % under a standard AM 1.5G illumination with 42% of internal quantum efficiency. The short circuit current density (Jsc) and open circuit voltage (Voc) is measured at 8.7 mA cm⁻² and 0.68 V, respectively. These promising results could be a first step toward a new generation of low-cost and effective solid-state DSSC.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Ratio LiI/Li₂</th>
<th>Jsc (mAcm⁻²)</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>I (%)</th>
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</tr>
<tr>
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</tr>
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</table>

Figure 1. Photovoltaic characteristic of different PU electrolyte compositions, under light intensity of 100 W m⁻²

Keywords: Bio-based Polyurethane, iodide/triiodide, dye sensitized solar cell, Polymer electrolytes
Ion Conduction Mechanisms in Nanocomposite Polymer Electrolytes With and Without Ionic Liquid

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This study consists of two parts. In the first part we investigated how the addition of δ-Al₂O₃ nano-fillers affected the dc-conductivity, dielectric relaxations and calorimetric glass transition temperature of the polymer electrolyte (PEO):LiClO₄. The results show that the introduction of 4 wt% δ-Al₂O₃ enhanced the dc-conductivity by approximately two orders of magnitude to a value of 1.5·10⁻⁵ S/cm at 298 K [1]. This conductivity increase is associated with a decrease in the calorimetric glass transition temperature and speeding up of the segmental polymer dynamics [1,2]. In fact, we are able to conclude that the dc-conductivity is directly coupled to the segmental polymer dynamics, as in the ordinary polymer electrolyte without nano-fillers (at least in the case of δ-Al₂O₃ nano-fillers at concentrations up to 4 wt%) [1,2]. This filler induced speeding up of the segmental polymer dynamics is probably caused by an enhanced ‘free volume’ and mobility of polymer segments in the vicinity of the non-attractive filler surfaces [1,2].

In the second part we have replaced the lithium salt LiClO₄ for lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (with PEO:Li ratios of 16:1 and 8:1) in order to make the anion of the lithium salt the same as that of the added ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMITFSI). We have performed a similar study of this nanocomposite polymer electrolyte with the added ionic liquid in order to determine whether the ionic liquid is able to dissociate the Li-ions from the ether oxygens and thereby decouple the ionic conductivity from the segmental polymer dynamics. The results show that the ionic liquid also speeds up the segmental polymer dynamics, and thereby decreases the glass transition temperature Tₛ as shown in the left panel of figure 1, but only to concentrations of about 20 wt%, despite that the ionic conductivity increases further (to above 10⁻⁴ S/cm at 300 K) at higher concentrations of the ionic liquid, as shown in the right panel of figure 1. Thus, it is evident that the motion of the Li ions decouples from the segmental polymer dynamics at higher concentrations of the ionic liquid and instead becomes more dependent on the viscosity of the ionic liquid.

Figure 1. Left panel: DSC scans of PEO-LiTFSI (16:1) with 4 wt% Al₂O₃ and 0-40 wt% BMITFSI, showing the decrease in Tₛ for concentrations up to 20 wt% ionic liquid. Right panel: Temperature dependence of the dc-conductivity for the same samples.

References
Enhanced Ion Conduction in Polymer Electrolyte Films having Nanophase Separation and Nanoimprinting

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Polymer electrolytes with enhanced properties, especially high ionic conductivities, are critical for technological applications in systems such as batteries and fuel cells. An interesting area of work has involved nanofiller materials and nanoscale interpenetrating networks where one component of the network is the ion conducting phase while the other component is a non-conducting phase. This work involves the use of nanophase separation in PEO electrolyte to make nanoscale structures (nanoparticles and interpenetrating networks) in the polymer electrolyte. The effect of ion conduction with the addition of this phase will be discussed. In addition, the non-conducting phase can be removed from the polymer electrolyte by choosing a solvent that will dissolve this material but not affect the polymer electrolyte. Removal of the non-conducting phase resulted in nanoimprinted films containing nanochannels or nanofoam-like structures. The ion conduction of these systems has also been studied. A series of PEO-LiTf electrolyte films have been prepared using three non-polar aromatic hydrocarbons (anthracene, biphenyl, and naphthalene), as the non-conducting phase were made. In other samples, the non-conducting phase was extracted by using hexanes in order to create a higher degree of surface porosity and cavity formation in the inner film. The resulting conductivity of both types of electrolyte films was measured using ac impedance and a comparison between “filled” and “empty” structures lends information concerning interfacial conduction. Thermal analysis, X-ray diffraction, SEM, AFM and FTIR were also used to characterize bulk and interfacial properties of these systems. An enhancement in conductivity was observed in nanophase separated films and nanoimprinted films.

Figure 1. AFM phase image of surface of nanophase separated polymer electrolyte. Light “spots” are the phase separated material having diameters 20 – 30 nm. Exposure to solvent will remove this material leaving nanochannels or nanofoam-like structures.
Effect of temperature on mixing enthalpy during low-humidity vapor sorption in Nafion

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The formation of a nanophase separated water network is essential for the transport properties of many proton exchange membranes (PEMs), making the understanding of water-membrane interactions of great interest for the development of new ionomers. One approach to study this is by sorption calorimetry, a method in which the water activity is continuously increased over an initially dry ionomer, while monitoring the moisture flow and the thermal power of the sorption process. The mixing enthalpy, $\Delta_{\text{mix}}H$, thus determined is the difference between the sorption enthalpy in the sample and the condensation enthalpy of water.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Mixing enthalpy of Nafion N115 (left), vacuum-dried at 120°C and measured at 25°C (grey) or 50°C (black) and the corresponding sorption isotherms (right).}
\end{figure}

Monitoring $\Delta_{\text{mix}}H$ as a function of water uptake $\lambda$ (mol water/mol acid) reveals details of the sorption process not seen in the sorption isotherm. For the PEMs Nafion \textsuperscript{2} and Aquivion (unpublished), vacuum drying at temperatures of 80 °C and above yield one or more steps in $\Delta_{\text{mix}}H$ measured at 25 °C. These steps, shown to the left in Figure 1, are sloping and vary between measurements when measured at 25 °C. However, if the temperature is increased to 50 °C, the repeatability improves and the step in the curve becomes sharp. The integrated hydration enthalpies of all the above samples are similar, about 50 kJ/mol acid. This indicates that the same process is taking place at the two temperatures, albeit at different $\Delta_{\text{mix}}H$ and $\lambda$. One possible explanation is that the different shapes in $\Delta_{\text{mix}}H$ are related to the mobility in the membrane, which would be higher at 50 °C, and that the “extra steps” in the enthalpy are due to moisture-induced relaxations.

References
Thermal and electrochemical properties of zwitterion based ionic liquids as substitute for H$_3$PO$_4$ in fuel cell applications

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Polymer electrolyte membrane fuel cells (PEM) are well established electrochemical converters with a bright future to replace classical mechanical electricity generators in future. In order to operate for long times and with high efficiency, strict requirements for the fuel gases, like low carbon monoxide or sulfur contents, have to be fulfilled currently. Since current successful PEM devices mainly operate below 100°C, a possible solution is to use higher temperatures where contaminants have less effect. This should be an advantage for the high temperature polymer electrolyte fuel cell (HT-PEFC) but its performance did not scale with temperature as expected until now. One of the reasons for this major stebback is found in the electrode processes, where the currently well-established electrolyte H$_3$PO$_4$ causes conversion limits due to partial blocking of the catalytic sites of the platinum [1]. Attempts to replace the platinum with other catalytic materials showed often only little or short-term improvement [2, 3]. An alternative way is the substitution of the electrolyte H$_3$PO$_4$ with one that has comparable proton conduction but less blocking properties.

We present a possible candidate from the class of highly acidic proton conducting ionic liquids, as suggested and shown by Nakamoto et al. [4]. In our case the cation is a zwitterion based on the natural occurring aminoalkylsulfonic acid, also known as taurine, combined with the superacid trifluoromethanesulfonic acid (TFOH) acting as anion. The PILs formed from these compounds are highly hygroscopic and show hardly any crystallization. The thermal properties including electrical data are presented along with the first results on the oxygen reduction capabilities.

![Drying of (2-SEA)(TFO)](image)

Figure 1. Heat capacity of a zwitterionic IL in successive drying runs n with image of a crystallized IL.

References
Synthesis and Characterization of Oligomeric Ethylene Oxide Functionalized Dicarboxide Oxanorbornene Polymers and Block Copolymers as Potential Solid Polymer Electrolytes

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Novel polymers based on dicarboximide oxanorbornene monomers have been synthesized to better understand ionic conductivity mechanisms in polymers and the design of solid polymer electrolytes for lithium ion batteries. Polymerizations have been conducted using ring opening metathesis conditions with a Grubbs third generation catalyst. These polymers have a fairly rigid and bulky backbone and are used to study the decoupling of ionic motion from polymer segmental motion. Homopolymers have been synthesized with varying lengths of ethylene oxide (EO) side chains (2, 3, 4, 8 and 12 units). Additionally, diblock copolymers have been synthesized with varying ratios of phenyl and ethylene oxide monomers (2, 3, and 8 units). The phenyl block has a substantially higher glass transition temperature, which may aid in the reduction of dendritic growth and allows for the use of nano-structured morphologies. The molecular weights of the polymers ranged approximately from 24 kDa to 100 kDa with polydispersities typically less than 1.1. The ionic conductivity of the homopolymers and relevant segmental dynamics with varying levels of added lithium salt were characterized with dielectric spectroscopy and quasi-elastic neutron scattering (BASIS) has also been used to characterized the segmental dynamics for the homopolymer with two ethylene oxide units as a function of salt concentration. The dielectric spectroscopy results demonstrate significant decoupling of ionic conductivity from polymer segmental motion compared with typical values at the glass transition temperature. Surface morphologies of solvent annealed thin film diblock copolymer samples have been studied by AFM as well as optical birefringence measurements of bulk samples demonstrating a variety of morphologies. Added salt increases ordering in addition to solvent annealing.

Figure 1. a) General chemical structure of the polymers studied, and b) an example of a solvent annealed thin film of a diblock copolymer with n=2, 60 wt% EO, and a Mw of 43 kDa.
Designing of high performance organic ionic plastic crystal/polymer composites for all solid electrolyte lithium metal batteries

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The developments of electronic devices and electric vehicles require advanced rechargeable batteries with high safety and high energy density. Combining the high capacity lithium metal and no-leaking, non-flammable electrolyte, all solid state lithium metal batteries have been received considerable attention for their applications in advanced energy storage systems. Organic ionic plastic crystals (OIPCs), which are homologues of ionic liquids but solid form at room temperature, possess the features of solid, low flammability and negligible volatility, have shown to be one of promising candidates as solid electrolyte\(^1\) and been demonstrated on several energy storage devices\(^2\). However, OIPCs normally show relatively slow ionic dynamics especially in low temperature crystal phase, which greatly influences the ionic conductivity and limits their applications in high performance batteries. It has been proven that the grain boundary, defects region or disordered phase in OIPC play a critical role in ion conduction process of OIPCs\(^3\), and this assumption was further verified in recent developed OIPC/polymer fiber composite system \(^4\). Herein, based on previous studies, we proposed one strategy which can greatly improve ionic dynamics of OIPC by incorporation of polymer nano materials (nano fibers and nano particles). The effects of interfacial interactions on the ion dynamics, ionic conductivity in the composite system will be investigated by solid state NMR, DSC and impedance spectroscopy techniques, and the lithium batteries performance will be also discussed in this report.

References

Ionic Liquid Electrolytes in Mg-Air Batteries

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Metal air batteries have attracted increasing interest in recent decades, mainly because of their high theoretical energy densities which meets the requirements of the growing high energy applications such as electric vehicles and grid energy scale devices. Magnesium is considered as a promising anode material in batteries. Compared to lithium, it’s much cheaper, more abundant, more environmental friendly, easier and safer to handle. Utilised with an air cathode, a magnesium-air battery has the potential to exhibit excellent cell performance for high energy density applications. Ionic liquids (ILs) are molten salts with a melting point below 100°C. Due to a combination of unique properties such as high conductivity, non-volatility, high chemical and thermal stabilities, ionic liquids have been studied as a promising electrolyte alternative in batteries.

This research focuses on the trihexyl(tetradecyl)phosphonium chloride ([P6,6,6,14][Cl]) IL which was shown to be able to support a high current density 1 mA·cm⁻² of Mg discharge with the help of 8 wt% water. This work started with the investigation on roles of water in enhancing the Mg discharge behaviours and concluded that an ideal additive in the [P6,6,6,14][Cl] IL for primary Mg-air battery should have active protons, be polar enough to lead to high conductivity of the electrolyte and have the complexation ability to form an Mg interfacial film with less resistivity. Ethylene glycol was shown to be an alternative to water regarding the Mg discharge behaviour. Using 72 mol% ethylene glycol diluted IL electrolyte, the primary Mg-air battery can supply a discharge operation at 0.2 mA·cm⁻² for around 24 h at an average potential around 1.15 V without any air catalyst. Properties and compositions of the Mg interphase formed in this electrolyte were also investigated. A highly crosslinked structure was proposed and considered responsible for the limited ionic conductivity of the interphase which leads to the final discharge failure. This battery system can be further optimized by the application of air catalysts and optimization of the battery configuration for further development.

![Figure 1. Discharge behaviour of Mg-air full cells using 72 mol% EG/IL electrolyte at 0.0075, 0.01, 0.025, 0.125 and 0.2 mA·cm⁻²](image-url)
High performance ionic liquid-based polymer electrolytes using polymeric ionic liquid-functionalized mesoporous silica nanoplates

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The structural design of ion-conducting channels within polymer electrolytes (PEs) is of prime importance if we wish to optimise transport properties, especially in high performance electrochemical devices. Although much effort has been directed towards enhancing the transport properties of PEs through nanoscopic modification, few studies have successfully used nanofillers to show enhanced target ion conduction in composite polymer electrolytes (CPEs). In this work, we show that the transport properties of polymeric ionic liquid (PIL)-based PEs can be optimized by the introduction of 2D silica nanofillers and that desirable transport properties result from the inclusion of abundant, shorter, continuous and interconnected ion transfer pathways created by a combination of grafted PIL and mesoporous structures in 2D silica nanofillers. The presence of PIL-functionalized mesoporous silica nanoplates (PIL-FMSiNP) increases the ionic conductivity of PIL/IL PEs by 1130 % at room temperature (30 °C) while significantly decreasing the ion transport activation barrier (ca. 10 KJ mol⁻¹). Such nanofillers simultaneously confer both high ionic conductivity [(~1 × 10⁻³ S cm⁻¹ at 130 °C) with only a small amount of IL loading (15 wt.%)], and excellent IL immersion and retention properties to the PIL/IL PE. The CPE’s favorable transport properties make it well-suited for the fabrication of electrochemical devices including Li batteries, fuel cells, dye-sensitized cells, and supercapacitors. Preliminary Li battery tests have demonstrated that Li/LiFePO₄ cells with PIL/IL/PIL-FMSiNP CPE are capable of delivering 101.2 mA h g⁻¹ capacity at 40 °C during 30 charge/discharge cycles, suggesting that their capacity and capacity retention are superior to cells using unmodified PIL/IL PE (38.9 mA h g⁻¹).

![Figure 1](image-url)

**Figure 1.** SEM images of (a) PIL-FSiNP and (b) PIL-FMSiNP; TEM images of (c) PIL-FSiNP and (d) PIL-FMSiNP.
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Tuesday 16th
New organic-inorganic hybrid for nano-composite solid polymer electrolyte based PVDF-HFP/PG49-LiBF₄-(ZrO₂-TiO₂)-BmimBF₄ ionic liquid: A comprehensive study

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ABSTRACT

A new organic-inorganic hybrid for nano-composite solid polymer electrolyte (NCPE) which comprises the blend of two semi-crystalline co-polymers with hybrid fillers and ionic liquid has been prepared for application in lithium ion battery (LIB) [1]. The poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) was blended together with 49 %-poly (methyl methacrylate) grafted natural rubber (MG49) at weight ratio of 70:30 and lithium tetrafluoroborate (LiBF₄) was used as charge carriers. Different mixture ratios of nano-sized ZrO₂-TiO₂ were synthesis via in-situ sol-gel technique and the various ionic liquid BmimBF₄ loadings were added into the polymer electrolyte [2]. The NCPE films were obtained through solution casting method. A comprehensive study was done on structural properties, chemical interactions and electrochemistry properties. The analyses done are FESEM, ATR-FTIR, XRD, EIS, LSV and LTN. The charge-discharge half-cell performances for optimized NCPE samples for application in LIB were evaluated. Nano hybrid fillers of ZrO₂-TiO₂ particles were successfully synthesis and have size range of 7-16 nm. With addition of ionic liquid, the nano-particles were clearly well-dispersed and significant decrease in agglomerations is observed [3]. The introductions of nano-fillers and ionic liquid have helped in reduction of crystallinity in semi-crystalline polymers [4]. Analysis of impedance showed higher ionic conductivity result at higher percentage of zirconia ratio in hybrid fillers [5]. The highest ionic conductivity of 1.1×10⁻² S cm⁻¹ was obtained at 60 wt. % of BmimBF₄ at ratio ZrO₂:TiO₂ = 5:1. For the same sample, the highest LTN value achieved at T_LTN = 0.501 with high electrochemical windows at 6.9 V. The preliminary charge-discharge evaluations show that the NCPEs have potential to be applied in LIB with maximum capacity achieved at 244.7 mAh g⁻¹ at 0.1C rate with addition of ionic liquid.

References:

Quinone based Conducting Redox Polymers for Renewable Energy Storage

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To meet future energy needs and to minimize CO₂-emissions, a higher share of produced electricity must come from renewable resources [1]. Unfortunately, the output of renewable energy sources varies and does not always correlate with the temporal demand for electricity. For this reason, high capacity electrical energy storage (EES) is needed to fully utilize renewable energy sources [2]. Today’s battery technologies primarily rely on metals extracted at large economic and environmental costs [3], and the benefits of converting to carbon based materials are several, e.g. lower weight, flexible materials, and better recycling possibilities. In addition, the total energy consumption in the production chain may be reduced if the high temperatures required for extracting and processing metals can be avoided. Conducting redox polymers (CRPs), i.e. conducting polymers with redox active side groups, are currently investigated as possible organic electrode materials [4]. In this work we focus on finding stable side groups with high charge storage capacity. Quinones, which occur in natural energy conversion systems, i.e. during photosynthesis and respiration, are an attractive side group for CRPs due to their high gravimetric capacity. Importantly, for a functioning battery application the redox group and the polymer backbone must be active in the same potential window and this can be tuned effectively over a wide potential range by substitution on the quinone ring; hence various quinone derivatives could match different polymer backbones. A high potential- and high charge capacity quinone derivative has been synthesized and electrochemically characterized with the aim of producing a novel CRP to function as an organic high charge capacity material, targeting renewable organic batteries for a future of sustainable EES.

References
Morphology of single-step processed CH$_3$NH$_3$PbI$_3$ perovskite


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Abstract

In this study, perovskites of lead has been prepared by dissolving equimolar ratio of methylammonium iodide (MAI) lead iodide in dimethylformamide (DMF). The products obtained have been verified by x-ray diffraction (XRD) and energy dispersive analysis of x-rays (EDX). The reflection planes (110), (220) and (310) can be observed at 20 angles of 14.2°, 28.4° and 31.9° indicating a tetragonal structure for α-CH$_3$NH$_3$PbI$_3$. EDX shows a Pb:I ratio of 1:3. From UV-Vis studies, the optical band gap for lead perovskite is 1.56 eV and calculations using CASTEP reveals the electronic band gap as 1.84 eV. FESEM studies indicate that the CH$_3$NH$_3$PbI$_3$ perovskite exhibits needle and flowery-like structures. On zooming the flowery-like structures to 40K magnification, nanosized (80 to 120 nm) bead-like structures were observed. Solar cells will be fabricated with the perovskite.
Thermally-Responsive Novel Gel type Polymer Electrolytes for Lithium-Sulfur Batteries

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Electrochemical energy storage has been receiving increasing attention in recent years, particularly with regard to the dissemination of electromobility and the integration of renewable energy. Currently, commercially available lithium-ion battery systems to a large extent make use of lithium transition-metal oxide cathodes, e.g., LiCoO2, and graphite anodes. However, these materials provide only limited energy density for application in electric vehicles [1-3].

Apart from the high theoretical specific capacity and the high theoretical energy density (2500 Wh kg-1), the use of sulfur for the development of next-generation lithium batteries is highly desirable. Because the sulfur is abundant, low cost and environmentally friendly material. However, the practical application of the Li/S battery is still hindered by capacity fading upon cycling, which can be mostly ascribed to the highly soluble intermediate polysulfide species in conventional liquid organic electrolyte solutions. Comparing with liquid type electrolytes, gel type polymer electrolytes (GPE) have advantages of a wide variety of shape, size and dimensions and blocking ability of the polysulfide migration.

Gel polymer electrolytes generally composed of polymer matrix and liquid electrolyte have excellent ionic conductivity, low rates of safety failure and mechanical stability. Unfortunately, these materials do not completely mitigate the thermal hazards associated with LIBs. Therefore, thermally-responsive polymers are needed to exhibit a significant change the ionic conductivity and device performance when the temperature of the system passes a defined threshold.

In this work, novel gel polymer electrolytes with temperature-dependent properties are examined as possible candidate to develop Li/S batteries where key thermal mechanism can be used to alter device operation with temperature. Furthermore, addition of functionalized natural and synthetic clay nanoparticles as ceramic filler allows overcoming the main problem of GPE – the loss of their mechanical strength when they are plasticized. A Li/S polymer cell containing a composite GPE has exhibited a good cycling performance with improved coulombic efficiency. In addition, thermal stability, mechanical properties, electrolyte uptake, polysulfide migration, impedance, cyclability of thermally-responsive electrolytes are investigated.

References

Acknowledgements
This research was supported by the research grants 5156/GF4 “High energy density polymer lithium-sulfur battery for renewable energy, electric transport and electronics” from the Ministry of Education and Science of the Republic of Kazakhstan for 2015-2017.
Morphology of Deuterated BAB Type Block Copolymers Studied by Small Angle Neutron Scattering

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Block-copolymer structures have the possibility to phase separate, and an ordering of segments could promote both ionic conductivity and mechanical stability. Previous simulation studies have proposed that if the ion dissolving functionality is grafted to the polymer backbone, it is possible to lower Tg of the conductive phase, and hence decouple the ionic segmental motion from the main chain (Figure 1) [1]. This will, in turn, result in better power performance of the resulting battery device. Our group has in an earlier publication investigated the effect of using random copolymers based on different ratios of PMMA, POEGMA and LiTFSI with a fixed ratio of 20:1 (EO:Li). The effect of compositional variation on conductivity, lithium ion affinity and battery performance was investigated. The battery cycling showed that the Coulombic efficiency during cycling was fairly high (90%) and stable at 60 °C, vs LiFePO4 [2]. The increase of MMA and the associated improvements of the mechanical properties however decreased the conductivity, which lead us to investigate block copolymers of the same system.

We have here investigated a series of BAB block copolymer of PMMA-POEGMA-PMMA with different PMMA block lengths, and how the conductivity and morphology is affected by temperature in the temperature range 25-95 °C. Understanding the phase behavior at different temperatures and salt concentrations, could broaden the understanding of how morphology affects the conductivity profiles and battery cycling, and hence have an impact on the development of solid polymer electrolytes. The phase separation, or its absence, is governed by the composition of the block copolymer, temperature and type and amount of salt. By tuning these parameters, it is possible to obtain self-assembled block copolymers. The study of bulk properties is typically done with techniques like small angle neutron scattering (SANS) and small angle x-ray scattering (SAXS). For the SANS measurements a deuterated PMMA block was used in order to create a contrast variation between the PMMA and POEGMA blocks.

The PMMA-POEGMA-PMMA system is interesting since the phases are partly mixable without salt. SANS experiments show that the B-block length is crucial for the micro-phase separation, and that the temperature affects the domain sizes and the order to disorder temperature (ODT). One example is the sample with 57wt% deuterated PMMA (Figure 2), which shows a clear phase separation with no ODT below 100 °C.

![Figure 1: Simulation of solid polymer electrolyte with bipolar properties.](image1.png)

![Figure 2: SANS data for the 57wt% deuterated sample. Increased temperature promotes bigger and more pronounced domains of deuterated PMMA.](image2.png)

References
Polymer Electrolytes for Stabilization of High-Voltage Li-Ion Battery Cathodes

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Lithium titanate (Li₂TiO₃) is an electrode material with several advantages compared to other electrode materials for Li-ion batteries. Titanium is an abundant element in the earth’s crust [1], making it possible to produce in large amounts. The price is low, it is environmentally compatible, and it allows aluminum to be used as current collector [2].Titanate electrodes also exhibit long calendar life [3] and it is good to use in heavy duty applications since the electrode can deliver high power [2][3]. However, it operates at 1.55 V vs. lithium, but this is advantageous since no SEI formation should occur at these potentials [3]. Unfortunately, this also makes the energy density of the electrode poor [2]. In order to have as high energy density as possible, the cathode should operate at a much higher potential, which motivates the use of the high power cathode Nickel Manganese Cobalt Oxide (NMC). NMC is used in several commercial applications, especially in vehicles. During long-term cycling it shows, however, some ageing problems, e.g. dissolution of transition metals [4] which migrates through the electrolyte poisoning the anode. Its high operation potential might cause degradation of the electrolyte, resulting in oxidation products on the cathode surface and in the pores of the electrode. Manganese dissolution has previously been reported to be caused by presence of HF in the electrolyte [4], formed by reactions between trace amounts of water and LiPF₆ [4] electrolyte salt. In order to solve these problems, LiTFSI can be used instead of LiPF₆. A stable electrolyte is required in addition to a non-degrading salt also a stable electrolyte is required, which is why we here investigate a polymer electrolyte. The solid polymer electrolyte used in this study consists of a poly(ε-caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC) copolymer, P(TMC₂₀CL₈₀)₃₄,6 LiTFSI, which have been shown to perform stable cycling at high cycling rates also at room temperature [5]. Here, we will investigate the degradation mechanisms of the polymer at the surface of the electrodes and how the use of the polymer electrolyte will influence the cycling stability of the LTO-LMO cell chemistry.

Figure 1. Stable cycling of LTO polymer-electrolyte half-cells at room temperature at different c-rates.

Physical Properties of Siloxane/Polyether Hybrid Polymer Electrolytes for Li Metal Batteries

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This study describes the physical properties of networked, polysiloxane/polyether-based, hybrid polymer electrolytes for application in lithium metal batteries. The electrolytes were obtained by a simple synthetic process, consisting of a sol-gel reaction followed by polymerization of cross-linkable moieties. The thermal, mechanical, and transport properties, were studied by differential scanning calorimetry, rheological analysis and by impedance spectroscopy, respectively. The lithium transference numbers were determined by a potentiostatic polarization method, using a formalism independent on the initial current of the potentiostatic polarization step. The materials are characterized by high thermo-mechanical stability, thanks to the presence of the chemical cross-links network, and by conductivity, higher than $10^{-4}$ S cm\textsuperscript{-1} at room temperature. The high values of ionic conductivities were achieved thanks to the high structural disorder, induced by the presence of siloxane clusters, and by the enhanced polyether chains segmental mobility, which can be modulated by controlling the density of cross-links and the length of the polyether chains. Finally, the effect of introducing TiO$_2$ nano-particles was also examined.
Influence of the anion on the ion dynamics in polymer gel electrolytes

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Ternary polymer gel electrolytes consisting of an ionic liquid (IL), a polar neutral polymer and a lithium salt were considered as promising materials for a compromise between sufficient conductivity and mechanical stability in lithium ion conducting battery electrolytes. Recently a new class of polyelectrolytes, namely poly(ionic liquid)s (PILs), such as for example poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl) imide (PDADMATFSI) has gained considerable attention and was introduced as the polymeric component [1-3].

To explore the influence of anion structure on the physical properties of complex electrolyte systems (PIL/IL/Li salt), in particular the mobility of ions, a series of poly(diallyldimethylammonium) based PILs with five different anions was prepared (Fig. 1). To isolate the effect of anion from physical properties of PILs, a common chloride precursor was used to maintain constant the average degree of polymerization (DPn) and chain polydispersity. After anion exchange, ternary electrolytes were formed and the multinuclear long range ion dynamics was studied by using pulsed field gradient NMR measurements (PFG-NMR), while the local ion dynamics by using spin-lattice NMR relaxation measurements (T1). These results were compared with conductivity data obtained by impedance spectroscopy measurements. Furthermore the gel electrolyte systems were characterized using differential scanning calorimetry (DSC) and electrochemical stability measurements.

Five different anions, including the novel asymmetric 2,2,2-trifluoromethylsulfonyl-N-cyanoamide anion (TFSAM) [4] were compared both in binary (IL/Li salt) and in ternary electrolyte systems. The following trend was obtained in the diffusion coefficient measurements: D_{TFSI}>D_{DCA}>D_{TFSAM}>D_{TFSI}>D_{TIO}. This order is in agreement with that of the conductivity values. Furthermore, the apparent transference numbers were calculated from the diffusion measurements and they rank as follows: D_{TFSI}>D_{TFSAM}>D_{TIO}. The electrochemical stability determined at 70 °C for the gel electrolytes increases from 3.8 to 5.6 vs Li+/Li and can be ranked in the following order: DCA<TFSI<TFSAM<TIO<TFSI. To conclude, the TFSI represents the best anion of choice for the compromise of the relevant parameters.

![Figure 1. Components of the gel electrolyte systems.](image)

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References
Quaternary piperidinium-functionalized poly(phenylene oxide) as anion-exchange membranes

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Anion exchange membrane fuel cells (AEMFCs) have been drawing great attention recently as they offer the potential use of non-precious metal catalysts and alternative fuels under alkaline conditions. One of the major challenges in the development of AEMFCs is the synthesis of anion exchange membranes (AEMs) with high hydroxide conductivity and long-term alkaline stability. [1]

In the current work we have attached mono- and bis-piperidinium (QPi) groups to poly(phenylene oxide) (PPO) via flexible heptyl spacers. In the first step, bromoalkylated PPOs were prepared by reacting lithiated PPO with 1,6-dibromohexane [2,3]. The polymers were then quaternized using Menshutkin reactions involving 1-methylpiperidine and 4,4′-trimethylethenebis(1-methylpiperidine) to prepare the mono- and bis-QPi derivatives, respectively. The QPi-functional polymers have excellent solubility in, e.g., methanol, dimethylsulfoxide and N-methyl-2-pyrrolidone at room temperature, and solvent cast AEMs are tough and transparent.

Especially the AEMs with bis-QPi side chains efficiently form ionic clusters and reach very high hydroxide ion conductivities, up to 69 and 186 mS cm⁻¹ at 20 and 80 °C, respectively. In order to further tune the AEM properties, a reactive membrane casting process was developed which allows the controlled formation of bis-QPi crosslinks through an efficient reaction between bromoalkylated PPO and 4,4′-trimethylethenebis(1-methylpiperidine). In conclusion, our results suggest that AEMs with excellent alkaline stability and hydroxide conductivity can be produced by incorporating QPi groups via aliphatic spacer units.

Figure 1. PPOs functionalized with mono- and bis-piperidinium groups, respectively, via heptyl spacers. The photograph shows an AEM based on the former derivative.

References
N-Functionalised Polyketone Ion Exchange Membranes for AEMFCs

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Anion exchange membrane fuel cells (AEMFCs) provide significant advantages over their proton exchange membrane counterparts. In the alkaline environment, the oxygen reduction reaction (ORR) is more facile, there is diminished fuel crossover, and a greater flexibility regarding fuel and catalyst choice. The membrane at the heart of AEMFCs not only facilitates the ion exchange but also separates the fuel feedstocks and acts as a support for the membrane electrode assembly (MEA). However, to date there are still no membrane materials that satisfy all the needs (long term stability in alkaline environment, high ionic conductivity, low swelling and good structural integrity) for use in AEMFCs and this remains one of the larger obstacles for further AEMFC development.

The amination and subsequent quaternisation of polyketone leads to a new family of ionomer containing N-substituted pyrrole moieties. The degree of amination can be controlled by manipulating reaction conditions, allowing the composition and resulting structural properties of the polymer to be tuned. Membrane fabrication results in thermally stable ($T_D > 250 \degree C$), structurally robust polymer electrolytes that exhibit ionic conductivity. These new solid state ion conducting materials have the potential to be used in a variety of applications including anion exchange membrane fuel cells (AEMFCs).

Here we present an in depth study focusing on the structure-property relationships of this new polypyrrole/polyketone polymer. A variety of analytical techniques are used to probe the thermal and structural properties of the polymers, these include high-resolution thermogravimetric analysis, modulated differential scanning calorimetry, dynamic mechanical analysis, vibrational, NMR and UV-Vis spectroscopies. In addition, broadband electrical spectroscopy is used to gauge the interplay between the structural properties and electrical response.

\[ \text{Figure 1. Conversion of 1,4-polyketone} \]
Iongels for Zinc batteries based on PolyDADMA-TFSI and 1-Ethyl-3-methylimidazolium dicyanamide mixtures

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Iongels, which are composed of a polymer and ionic liquid, have emerged as a promising electrolyte alternative to overcome some of the liquid electrolyte limitations, such as evaporation and leaking of the electrolyte [1]. Furthermore, ionicgels also present good mechanical properties, and chemical and electrochemical stability as well as easy handling. In this work, we report a series of ionicgels based on polydiadamyltrimethylammonium chloride- trifluoromethanesulfonimide (PolyDADMAC-TFSI) and 1-Ethyl-3-methylimidazolium dicyanamide (emimdca) (e.g. weight ratios between 90:10 to 75:25 Polymer:IL, %wt), and membrane preparation of these materials. The effect of Zn(dca)2 as well as water in the ionicgels mixtures has also been studied.

In general, the obtained membranes showed good mechanical properties and good conductivities, up to 3.5 \( \times 10^{-3} \) S cm\(^{-1} \) at 50 °C for the composition 65.35 %wt. The conductivity of these ionicgels has been determined between 0°C and 100°C. Finally, alumina nanoparticles have been included in the optimal electrolyte mixture leading to improvement in both conductivity and mechanical properties. The electrochemical stability of the membranes has been studied based on cyclic voltammetry experiments. Finally a zinc/zinc symmetric battery and a PEDOT/Zinc battery has been developed showing promising performance at an applied current density of \( \pm 0.01 \) mA/cm\(^2\). Further experiments are currently underway.

![Conductivity](image)

**Figure 1.** (Left) Conductivities of the different ionicgels at different temperatures using different ratios of PolyDADMATFSI/emimdca (%wt) +10 mol% Zn(dca)2 + 0.23 wt% H\(_2\)O. (Right) Structure of the PolyDADMAC-TFSI and emimdca.

**References**
Synthesis and Properties of New Carboxyborate Lithium Salts

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Solid polymer electrolytes (SPEs) have many advantages, but their ionic conductivity and lithium cation transference numbers are still insufficient for application in large, high power and high voltage lithium-ion batteries. From studies carried out until now it appears that poly(ethylene oxide) (PEO) is characterized by the best properties as a solid solvent for lithium salts. A majority of works are concerned with the modification of electrolytes based on PEO, in order to increase the ionic conductivity while maintaining suitable mechanical properties and achieving such operating conditions in which completely or partly the anionic current is eliminated [1]. Methods for improving these parameters are for example the use of new lithium salts with a bulky anion and the addition of plasticizers or compounds which hinder the crystallization of the polymer matrix. Our research combines these two trends. We previously obtained and described new trifluoroalkoxyborate lithium salts, which have improved ionic conductivity of SPEs based on PEO [2].

![Figure 1. Synthesis of carboxyborate lithium salts in the reaction of poly(ethylene glycol) bis(carboxymethyl) ether with butyllithium and BF₃.](image)

In this research study we present the results of synthesis and characterization of new carboxyborate lithium salts, anions of which have molar masses specific to oligomers and contain oligooxyethylene groups. Depending on the molecular weight of the anion it is possible to obtain salts of various forms. A salt with a molecular weight of 400 g/mol is a crystalline solid, whereas with a molecular weight of 750 g/mol has the properties of an ionic liquid. Moreover, the presence of oligooxyethylene groups provides good compatibility of these salts with PEO matrix.

These new salts are obtained in a two-step synthesis. The first step involves the reaction of poly(ethylene glycol) bis(carboxymethyl) ether with butyllithium. After purification, the obtained carboxylate lithium salt undergoes reaction with BF₃ leading to the intended product. We report ionic conductivity, stability and the lithium cation transference numbers of polymer electrolytes based on PEO with new carboxyborate lithium salts.

References
From Salt-in-Polymer to Polymer-in-Salt in Polyesters

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Solid-state batteries are the object of revived interest as the safety shortcomings of liquid electrolytes still remain. Besides a solid electrolyte may allow the use of metallic lithium (Li$^+$) with an appreciable increase in the specific energy density.

Most of the polymer electrolytes from the beginning of the field in the 70’s has contained variations of poly(oxyethylene) moieties, the workhorse being high $M_w$ PEO. However, if the conductivity reaches practical values in the 60-80°C range, the transport number is low (t. $\approx$ 0.2) and the oxidation limit is 4V only. Recently, Uppsala University reported new poly(esters) with appealing conductivities (4×$10^{-5}$ S.cm$^{-1}$ at RT). The best results were obtained from copolymerization of trimethylene carbonate (TMC) and ε-caprolactone (CL) laden with LiTFSI at a ratio of solvating carbonyl C=O to Li$^+$ of $\approx$ 4:1. [1]. As a good surprise, these polymer electrolytes have t. $> 0.6$.

Angell has on the other hand reported that “polymers-in-salt”, i.e. very high concentration of salts compared with the available solvating centers, the macromolecule mainly providing only the mechanical properties may have high conductivities and transport numbers. [2] At its time, however, the concept was mostly conjectural. In this vein, recently, polypropylene carbonate with 2:1 salt to repeat unity was shown to have good conductivity ($\approx 5 \times 10^{-4}$ S.cm$^{-1}$) at 60°C. [3]

In this work, we have used the same polymer as reported, copoly(TMC)$_{0.2}$ (CL)$_{0.8}$ and scanned the salt content form 5:1 to 0.5:1, from salt-in-polymer to polymer-in-salt with both LiTFSI and LiFSI. Especially with the latter, high conductivities ($10^{-4}$ - $10^{-3}$ S.cm$^{-1}$) have been found. Conductivity, CV and transport number will be presented.

References
Fluorescent Ion-Imprinted Polyelectrolyte Hydrogel for Selective Sensing of Uranyl Ion

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The gel is a semi-rigid mass of a lyophilic sol in which all the dispersion medium has penetrated into the sol particles. A particular class of gels, hydrogels, are hydrophilic polymer networks, which can take up large volumes of water and swell while retaining their shape. Responding to external conditions, gel networks swell by absorbing solvent until thermodynamic swelling equilibrium is reached. Charged, or polyelectrolyte hydrogels are composed of polymer chains containing charged groups. Unlike the uncharged hydrogels, the dominant driving force for swelling in these systems is the inherent electrostatic repulsion between gel charges. As a result, swelling of polyelectrolyte hydrogels can be induced through such stimuli as changes in pH and salinity [1]. Molecular imprinting is a method for synthesizing host molecules to recognize targeted guest species. Upon removal of the template species, cavities that recognize the spatial features and binding preferences of the template are produced. Ion-imprinted polymers could be designed as recognition receptors for in situ measurements of the concentration of metal ions in solutions. Fluorescent indicators that are sensitive to metal ions and exhibit changes in fluorescence intensity depending on the metal-ion concentration can be used as molecular recognition materials in common optical sensors [2]. Immobilization of the indicators in the supports has significant effects on the performance of the optical sensors in terms of selectivity, sensitivity, and stability.

In this study, fluorescent ion-imprinted polyelectrolyte hydrogel was synthesized and characterized. Imprinted polyelectrolyte hydrogel, which was prepared in the presence of uranyl ion, contains negatively charged monomer units to interact with positively charged uranyl ion. Upon interaction with uranyl ion, fluorescent polyelectrolyte gel exhibits change in fluorescence intensity. As uranyl ion concentration increases in solution, the quenching of fluorescence of imprinted polymer increases. When compared with non-imprinted polyelectrolyte hydrogel which was prepared in the absence of uranyl ion, the amplified fluorescence quenching was observed in the case of imprinted polyelectrolyte hydrogel, showing that certain cavity was created for selective binding of uranyl ion. In addition, swelling behavior polyelectrolyte hydrogel was investigated in solvent mixture and collapsing behavior of the hydrogels was evaluated depending on temperature.

References
Characterization of Starch-Methyl Cellulose Blend Based Proton Conductor and Application in Energy Device

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Solid polymer electrolytes (SPEs) have attracted the attention of researchers due to its high potential to be used as an electrolyte in energy device systems [1]. Starch is a natural polymer consists of repeating 1,4-d-glucopyranosyl units: amylose and amyllopectin [2]. Several negative aspects possessed by starch based films such as retrodegradation, gel syneresis and breakdown in high shear can be eliminated by blending starch with methyl cellulose (MC) [3]. MC is one type of cellulose derivative which is obtained from methylation of alkali cellulose. MC is able to form transparent film, soluble in water and has good electrical and mechanical properties [4]. The ionic transference number and mobility can be enhanced by blending starch and methyl cellulose, indirectly increase the ionic conductivity [5]. In this work, salted and plasticized systems of starch-methyl cellulose blend-based electrolytes doped with ammonium nitrate (NH₄NO₃) are prepared via solution cast method. The interaction between the components of the electrolyte is confirmed by Fourier transform infrared (FTIR) analysis. The doping of 30 wt% NH₄NO₃ has optimized the room temperature conductivity of the electrolyte up to ~ 10⁻⁵ S cm⁻¹. The addition of glycerol further enhanced the ionic conductivity. The enhancement of conductivity can be attributed to the decrease in degree of crystallinity as proven by X-ray diffraction (XRD) analysis. Arrhenius behavior is obtained for temperature dependence conductivity of all electrolytes. Higher conducting electrolyte is found to possess lower activation energy (Eₐ). From transference number measurement, the highest conducting electrolyte obtains the highest value of ionic transference number (tᵢₒ). Linear sweep voltammetry shows that the highest conducting electrolyte is suitable to be used in energy device application.

References
Green Fluorine-Free Salts for Aqueous Lithium-ion and Sodium-ion Battery Electrolytes

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Today Li-ion batteries are the primary energy storage medium in portable devices such as cellphones, laptops and cameras, however transforming to large scale storage such as electric automotive applications is a challenging feat. One major obstacle for large scale implementation is to overcome the problems with stability and toxicity of the electrolyte, which is not only costly and toxic because of their fluorinated anions [1], but also contains flammable solvent. Here we present the synthesis and characterization of the first generation of fluorine-free electrolytes based on a pseudo-delocalized concept [2, 3]. The synthesis is carried out via a green and scalable synthetic method from readily available starting materials leading to high yield and purity of desired electrolytes [4]. We envision that this class of electrolyte can be applicable in future low voltages aqueous electrolytes for Li and Na-ion batteries to resolve their current challenges in safety and cost.

Figure 1. a) The concept of pseudo-delocalized “Mickey Mouse™” anions and b) (di-methyl-ammonio) bis(butane-1-sulfonate), MM4411.

References
Solid Polymer Electrolytes via Reaction Induced Phase-Separation for Structural Batteries: High Storage Modulus and High Ionic Conductivity

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A series of phase separated thermoset films with varying degree of crosslink-density and liquid electrolyte concentration has been produced. By utilizing Hansen solubility parameters, a system where the monomers and liquid electrolyte are miscible prior to curing was found. During the UV-light initiated polymerization the miscibility of the system decreases and the liquid electrolyte phase-separates from the growing polymer, creating a two-phase thermoset film. The crosslinked polymer provides the film with stiffness, while the liquid electrolyte is responsible for transporting ions through the solid polymer electrolyte (SPE). At ambient temperature the ionic conductivity can reach $1.6 \times 10^{-4}$ S cm$^{-1}$ with a corresponding storage modulus of 750 MPa, see Figure 1.

![Figure 1](image_url)  

**Figure 1.** Ionic conductivity ($\sigma$) plotted vs. storage modulus ($E'$) at ambient temperature, for two different amounts of liquid electrolyte and three different monomer compositions.
SEI-forming Electrolyte Additives for Lithium-ion Batteries: 
Prediction of Properties by DFT Calculations

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Lithium-ion batteries (LIBs) have been used in a wide range of application since 1990s, but further improvement is still needed for safety, lifetime, and energy density. Research and development currently focuses on improvement of electrode materials and the compatibility with electrolytes where stable solid electrolyte interphases (SEIs) are key components. The SEI is most often a self-forming passivation layer on the anode, significantly affecting the LIB performance.

One way to improve the process of the SEI formation is to use special electrolyte additives. These act to create an SEI prior to solvent decomposition and thus need to have higher reduction potentials and enable the formation of lithium conductive oligomeric and polymeric structures.

Here a computational approach based on DFT is presented, aiming at the design of new SEI-forming additives and show-casing how small changes in the chemical structures of sulfur-based compounds can affect both the reduction potential and the composition of the created SEI-layer. Based on the computations a few promising candidates for future LIB research are suggested.
Single Li\textsuperscript{+}-ion conducting poly(tetrafluoroestyrenesulfonate) – polyether block copolymer electrolytes

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Lithium-ion battery technologies based on liquid electrolytes have been greatly successful for consumer electronics. However, the intrinsic instability of liquid electrolytes typically requires special safety measures which result in increased cost and reduced energy (power) density, which is especially problematic in automotive applications. In single-ion conductors (SICs), the anions are tethered to a solid polymer and only the Li\textsuperscript{+} is transported in the electrolyte. Hence, the use of polymeric SICs potentially solves many of the issues originating from the use of liquids and free salts [1,2]. On the other hand, it remains a challenge to improve the conductivities of SICs which are usually low because of a low degree of ion-dissociation and slow dynamics of the polymer chains.

In the present work we have prepared a series of BAB-type triblock copolymer conductors having a central polyether block with two flanking poly(tetrafluoroestyrenesulfonate) blocks in various block ratios were designed and synthesized via atom transfer radical polymerization and thiolation/oxidation (Figure 1). The polyether block consisted of either poly(ethylene oxide) (PEO) or poly(ethylene oxide-co-propylene oxide) (PEOPO). Because of the highly electron-withdrawing character of the fluorinated aromatic rings, Li\textsuperscript{+} can be expected to be highly dissociated and conducted through the dynamics of the polyether chains. Partial PEO crystallinity reduced the conductivity below approx. 45 °C. According to both thermal and morphological characterizations, the miscibility of the blocks increased above this temperature which greatly enhanced the ion conductivity. The SIC with the highest lithium ion conductivity in the series reached 1.5×10\textsuperscript{-5} S cm\textsuperscript{-1} at 60 °C.

Figure 1. Structure of a BAB triblock copolymer containing PEO (A) and poly(tetrafluoroestyrenesulfonate) (B) blocks [3].

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References
Computational and Experimental Approach to PVDF-HFP/Ether-modified Polysiloxane semi-IPNs as Solid Polymer Electrolyte Membranes

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For all-solid-state batteries the development of solid polymer electrolytes (SPE) with sufficient mechanical and electrochemical properties is crucial. In this context, the preparation of semi-interpenetrating networks (IPNs) is an attractive approach since a chemical or even electrostatic crosslinked polymeric host, such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) forms a matrix which is interpenetrated by a viscous and ion-conducting macromolecule. Especially, liquid ether-modified polysiloxanes are suitable candidates as conducting component due to their ionic conductivity, thermal stability, and broad variability of physicochemical properties.[1]

For semi-IPN SPE membranes consisting of PVDF-HFP, polysiloxane-comb-propyl(triethylene oxide) (PSx) and lithium bis(trifluoromethane)sulfonimide (LiTFSI) prepared by solution casting technique, an ionic conductivity of \(7.7 \times 10^{-5} \text{ S cm}^{-1}\) at room temperature was reached with 15 wt.% LiTFSI. The electrochemical stability window ranges from 0.5 V to 4.6 V vs. Li/Li\(^+\) reference electrode.[2] However, the comb-structured PSx with its non-polar methyl- and dipolar ether-functionalties attached to the Si-O-backbone is amphiphilic and fluorophobic, wherefore the miscibility with the fluorous PVDF-HFP is inhibited, causing a porosity of \(\approx 20\%\) in resulting semi-IPN SPE membranes as well as a rough surface areas which limit contact with electrode materials.[3] Computational methods, such as the conductor-like screening model - for real solvents (COSMO-RS)[4], a quantum chemical-based thermodynamic prediction model, were used to investigate the molecular interactions and to support experimentally observed miscibility effects.

References
Analysis of a PEO:LiTFSI polymer electrolyte confined in porous alumina by impedance spectroscopy

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The segmental motion of polymer chains in polymer:salt complexes is the origin of ionic conduction in these materials. Slow relaxation times as a result of the high molecular weight of chain segments, particularly above the entanglement limit, limits the ionic conductivity at ambient temperature.

It is well known that confinement of polymers in alumina membranes can lead different chain conformations and chain alignments or suppress crystallization [1]. Previous studies by Teeters and coworkers investigated a PEO:lithium triflate polymer electrolyte, with high-molecular PEO (4.000.000 g/mol), infiltrated into porous alumina membranes. The results show a clear dependence between the pore diameter and the ionic conductivity as well as the glass transition temperature was found and ascribed to the partial suppression of crystalline domains and the interactions of the polymer with the pore walls [2][3].

In this study, this phenomenon was further investigated utilizing a PEO with moderate molecular weight (20.000 g/mol) and the commonly used LiTFSI electrolyte salt was melt-infiltrated into alumina pores ranging from 18 – 150 nm in pore diameter. The prepared membranes were characterized by electrochemical impedance spectroscopy (EIS).

References:
Analysis of Lithium Dendrite Formation by Atom Probe Tomography

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Employing lithium metal anodes would increase the energy density of lithium batteries significantly, but so far severe safety issues mainly related to the uneven stripping/plating, dendrite creation, upon charge/discharge has been limiting. Polymer electrolytes are one obvious option to mechanically hinder the growth of the dendrites. Our knowledge of the initial stages of dendrite formation is however quite limited. Here we attack this by using a tool-box of modern microscopy techniques; first a threshold for the dendrite formation as a function of battery cycling parameters and choice of electrolyte was located by using scanning electron microscopy (SEM) (Figure 1). Second, an in situ lift-out method within a focused ion beam (FIB) – SEM workstation was used to extract volumes with dendrites and position these on supporting holders. Finally, atom by atom analysis and reconstructions of dendrites and their surroundings were made using three-dimensional atom probe tomography.

Figure 1. A scanning electron microscope image of the early steps of lithium dendrite formation.
Preparation of physical ion-gels using self-assembly of ionomer block-copolymers

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Here, we report tough ion gels containing ionic liquids (ILs) by using the self-assembly of an amphiphilic ABA triblock copolymer with ionic interaction. The ABA triblock copolymer, consisting of poly(acrylic acid) (PAA) as a solvato-phobic A segment and poly(methyl methacrylate) (PMMA) as a solvato-philic B segment, exhibits gelation in 1-ethyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)amide ([C$_2$ mim][NTf$_2$]) ionic liquid by self-assembly of the PAA segments. To enhance the mechanical property of the ion gel, we introduced ionic interaction to the solvato-phobic segment by neutralization of PAA segments using metal hydroxide. The PAA segments were partly neutralized by LiOH, to prepare poly(acrylic acid-r-lithium acrylate) (P(AA-r-LiA)), which can form ion clusters through the ionic interaction in the cross-linking points. Due to the strong ionic interaction, the energy for pulling-out the polymer chain from the physical cross-linking points is expected to be enhanced. In this study, the mechanical property and ionic conductivity of P(AA-r-LiA)-b-PMMA-b-P(AA-r-LiA)) (LML)/[C$_2$ mim][NTf$_2$] ion gel (Fig. 1) were investigated.

![Fig. 1 The structures of LML (left), AMA (center), and SMS (right).](image)

PAA-b-PMMA-b-PAA (AMA) (Fig. 1) was synthesized by an ATRP method. LML was prepared by partial neutralization of AMA using LiOH in a THF/water mixed solvent at room temperature. AMA/[C$_2$ mim][NTf$_2$] and LML/[C$_2$ mim][NTf$_2$] ion gels were prepared by mixing the polymer and IL (weight fraction of polymer = 20wt%) with a co-solvent. Transparent and self-standing ion gels were obtained after evaporation.

Tensile tests of both AMA and LML (the ratio of neutralization = 20mol%) ion gels were conducted (Fig. 2), and for comparison, the mechanical property of a PST-b-PMMA-b-PST (SMS) /[C$_2$ mim][NTf$_2$] ion gel (Fig. 1) [1], which has been reported by our group, was also investigated. The elastic moduli of the all ion gels were almost the same, indicating that the cross-linking density did not change due to the same length and ratio of solvato-phobic and solvato-philic segments. Whereas, higher fracture energy of LML ion gel was observed compared with that of AMA and SMS ion gel. This result indicates that the mechanical toughness of the cross-linking point was improved owing to strong aggregation by the ionic interaction as expected.

Ionic conductivity measurements were conducted for the LML, AMA and SMS ion gels (Fig. 3). At all measured temperatures, the conductivities of all ion gels were the same order of magnitude. These results imply that the AMA and LML ion gels have a similar microstructure to that of the SMS ion gel.

In this presentation, we will discuss the effect of partial neutralization in the solvato-phobic PAA segment on the mechanical properties and ionic conductivities.

References
Effect of Alkoxy Substituted Aryl-Thiourea as Dopant in Carboxymethyl Cellulose (CMC) in Affecting Its Conductivity Behaviour

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Essentially linear featuring alkoxy substituted aryl-thiourea derivatives provide wide range of electronic properties as they involve rigid π-systems on their structures. In this contribution, two novel thiourea derivatives with general formula A-ArC(O)NHCS(NHAr-D were successfully synthesized which A is noted as aryl group containing chloro (-Cl) A1 and nitro (-NO2) A2 substituents. In which, acts as the polar head group (acceptor, A) while D represented as –OC6H2n+1, the alkoxy chain tail acts as donor, D. Due to its D-π-A system, alkoxy thiourea derivatives are applied as dopant in Carboxymethyl Cellulose (CMC) host material in order to form a conductive biopolymer electrolyte thin-film. The formation of biopolymer-thiourea complex has been analyzed through Fourier Transform Infrared (FTIR) spectroscopy and X-ray Diffraction (XRD) to determine the interaction between CMC and thiourea derivatives in the form of thin films as well as Electrical Impedance Spectroscopy (EIS) for their ionic conductivity behavior. In turn, quantum chemical calculation using Gaussian 09 software was used to govern the relationship between experimental and theoretical analysis of the CMC-thiourea complexes with conductivity. The highest conductivity at ambient temperature is 1.44 x 10⁻⁷ S cm⁻¹ for CMC-thiourea complexation featuring chloro substitution (A1). It is proven that the results of theoretical studies meet good agreement with the experimental results obtained in this study. Indeed, biopolymer electrolyte materials featuring thiourea derivatives as dopant have great potential to be developed as electrical conductor. Due to these findings, these so-called molecular wires candidate has opened wide possibilities to be applied in many micro-electronic devices in the near future. Figure 1 below depicts the general molecular structure of synthesized thiourea derivatives

![Figure 1](image)

Figure 1. General molecular structure of thiourea derivatives as ionic dopant in CMC host.

Keywords: thiourea, carboxymethyl cellulose, conductive thin film
About the Interactions Controlling Nafion’s Viscoelastic Properties and Morphology

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Interactions controlling the viscoelastic properties of Nafion are identified by investigating morphological changes induced through stretching at a wide range of controlled temperature and relative humidity [1]. ²H-goniometer NMR exploiting the pseudonematic effect [2, 3] in D₂O containing membranes provides information on induced anisotropy on the 70 nm scale while Small Angle X-ray Scattering (SAXS) is used to reveal local structural correlations on the low nanometer scale [4]. Under highly humidified conditions, stress is suggested to be mainly transmitted through the robust polymeric domain with shearing mainly occurring within the soft aqueous domain. Since the latter deteriorates the uniformity of the flat aqueous domain thickness, also the structural nano-correlation decays. With decreasing relative humidity, where the weakly hydrated ionic domain is thought to form an increasingly stable Coulomb structure, and with increasing temperature reducing the elastic modulus of the polymeric domain, shearing is suggested to preferentially occur within the mechanically weaker polymer aggregates leaving the nano-scale structural correlation intact. Structural anisotropy on the 70 nm scale, as evidenced by a residual ²H quadrupolar splitting, is only observed after stretching. Un-stretched Nafion is virtually isotropic on this scale, i.e. any genuine anisotropy of Nafion’s morphology must be on a significantly smaller scale.

Nanoconfinement of LiBH$_4$ for High Ionic Conductivity in Lithium Ion Batteries

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Efficient energy conversion and storage is crucial for development of systems based on renewable energy sources. For electricity storage, Li-ion batteries are commonly used in electronics devices but require many improvements to obtain longer life-time and higher energy densities. The current use of organic liquids and gels electrolytes limits these improvements because of lithium dendrites formation, reducing the lifetime of the battery and which can possibly be hazardous due to risks of short circuits.

An alternative to current state-of-art lithium-ion batteries could be solid-state batteries of higher stability and no risks of electrolyte leakage. LiBH$_4$ is a promising material for solid-state batteries as it is lightweight and stable electrochemically up to 5 V. Similar to other metal borohydrides, LiBH$_4$ exists in different polymorphs. While the orthorhombic phase (Pnma), stable at room temperature has a low ionic conductivity ($\sim$10$^{-5}$ mS cm$^{-1}$ at 30 °C), the hexagonal phase (P6$_3$/mmc), stable above 110 °C, has a much higher ionic conductivity ($\sim$1 mS cm$^{-1}$ at 120°) [1]. Confinement of LiBH$_4$ in mesoporous SiO$_2$ allows obtaining fast ionic conductivity even at room temperature. Figure 1 shows Arrhenius plot of ionic conductivities of bulk LiBH$_4$ and nanoconfined SiO$_2$. For LiBH$_4$ the clear increase of the conductivity at 110 °C is due to the phase transition.

The origin of the high ionic conductivity in the nanoconfined LiBH$_4$ is due to an interfacial layer created between the borohydride and the walls of the SiO$_2$ pores. Better knowledge of the mechanisms behind the formation of this interface as well as the effect of the mesoporous SiO2 structure parameters (pore size, surface area,...) are crucial for improving even further the ionic conductivity of the low temperature solid electrolytes to be use in solid-state lithium ion batteries.

![Figure 1. Nanoconfined LiBH$_4$ in SiO$_2$ scaffold [1]](image)

![Figure 2. Arrhenius Plot of bulk LiBH$_4$ (red triangles), SiO$_2$ - LiBH$_4$ nanocomposites (circles and squares) and physical mixtures (green diamonds). Red symbols indicate measurements taken during heating and blue during cooling [1]](image)

References

Electrochemical performance of PEDOT polymer electrode on rechargeable organic battery

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Rechargeable organic battery is beneficial in terms of low cost, renewability, safety, higher theoretical capacity and environmentally friendly [1,2]. Currently, various organic structures are prepared for rechargeable organic batteries but investigation for new organic electrode material is still limited. Herein, we studied about electrochemical performance of PEDOT which has Tioehter structure, high discharge capacity and high energy density as anode material [3]. The PEDOT was composited with Super-p carbon in order to improve the electrical conductivity. The structure and morphology were analyzed by FT-IR, FE-SEM and EDS. By SEM and EDS analysis the coated PEDOT-carbon composite electrode is confirmed with uniform distribution. When the organic electrode is charged and discharged, sulfur atom in electrode have interacted with PF6- (or Li+) in electrolyte. The discharge capacities of PEDOT anode was 530.25 mAh/g and 495.84 mAh/g for 1 and 5 cycles at 0.1 C.

Figure 1. SEM image of PEDOT anode

References


Protic Organic Ionic Plastic Crystals: Fast Solid-State Proton Conductors

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High temperature polymer electrolyte membrane fuel cells (PEMFCs) operating between 100 °C and 200 °C are desirable because they offer significant benefits, such as improved electrode kinetics, simpler water and heat management, and better tolerance to fuel impurities, leading to higher overall system efficiencies [1]. However, state-of-the-art high temperature PEMFCs suffer from leakage problems associated with liquid electrolytes, such as H$_3$PO$_4$ and protic ionic liquids.

Recently, organic ionic plastic crystals (OIPCs) [2–6], which are unique electrolyte materials due to their superior properties such as intrinsic ionic conductivity, non-flammability, negligible vapor pressure, plasticity (mechanical flexibility), high thermal stability, and wide electrochemical window, are promising ionic conductors for electrochemical devices. While the OIPCs used as electrolytes for PEMFCs should be proton-conducting, they are often doped plastic crystals, which employ acids, protic ionic liquids or bases as the dopants for doping the matrix of certain neat plastic crystals.

In order to obviate the use of dopants that may be incompatible with the host matrix of plastic crystals, we have developed some highly proton-conductive pure plastic crystals which are protic OIPCs (abbreviated as "POIPCs", Figure 1) [3–6] and in essence are solid protic organic salts formed by proton transfer from a Brønsted acid to a Brønsted base. In this talk, we will present our recent work on some pure POIPCs with wide plastic crystalline phases as novel, fast solid-state proton conductors for the realization of all-solid-state high temperature PEMFCs [3–6]. The physicochemical properties of POIPCs, including thermal, mechanical, structural, morphological, thermodynamic, crystallographical, spectral and ion-conducting properties, as well as proton conducting mechanisms, isotope effects and fuel cell performances, are studied comprehensively in both fundamental and device-oriented aspects.

Figure 1. Schematic of POIPC-based fuel cells.

References
A Flexible, All-Solid-State Lithium Battery Based on a Reinforced-Concrete Inspired Si/Carbon Architecture

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The emerging microelectro-systems, such as wearable electronics or implantable biomedical devices, call for the good mechanical strength of on-board power sources and their simultaneous high energy and power densities within a limited footprint area. To avoid the inherent safety concerns of the mobile electrolyte, such as liquid leakage upon mechanical loading and the design inflexibility, it is highly desired to develop a solid-state electrolyte, with the thorough consideration of ionic conductivity and interfacial contact resistance that can be integrated into the full cell. In this study, we developed a flexible, all-solid-state lithium-ion battery based on the integration of a novel reinforced-concrete inspired Si/carbon structure as the anode, a LiTFSI salt dissolved copolymer (poly(e-Caprolactone) and poly(trimethylene carbonate), 80:20 by molar ratio, as the solid electrolyte, as well as a 25-µm thick lithium iron phosphate electrode as the cathode. The determination of the electrochemical behavior of each component and of the integrated full cell systems allows highlighting of the merits of using the proposed polymer electrolyte and its consequences on the stabilized cycle behavior of the Si/carbon anode. When galvanostatically evaluated, without using the separator and current collectors, the all-solid-state battery exhibits a remarkable cyclability (~0.05 % capacity fading per cycle) for 200 cycles and high Coulombic efficiency (95% for the 1st cycle and more than 99.5 % from the 5th cycle onwards), and tolerates the short-circuiting problem. Befitting from the intimate coupling of the components and the good tensile strength of the reinforced-concrete architecture, the full cell demonstrate good capacity retention under the drastic flexing states.
Innovative And Functional Materials For Green And Safe Large-Scale
Li/Na-based Energy Storage

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The modern life style that we are enjoying depends on energy storage systems in which the role of Li-
on batteries (LiBs) is peerless. However, state-of-the-art LiBs are approaching the verge of possible
technological imagination in energy density. Some researchers argue that next-gen secondary batteries
should switch to heavier elements such as Na [1]. Indeed, when it comes to gigantic energy storage
systems for the electricity grid and/or other non-portable applications where size does not matter, Na-
on batteries (NiB) can be an intelligent choice. Nevertheless, research on NiBs’ components is at the
very beginning, and it is necessary to develop novel types of materials, both novel safe polymer
electrolytes and high energy electrodes as well as novel production process thereof.

In this work, an overview is provided on both truly solid and quasi-solid polymer electrolytes
specifically conceived and developed for Na-ion secondary cells, based on polyethylene oxide (PEO),
acrylates/methacrylates and/or their mixtures. Eventually, pyranose ring based natural additives and/or
low volatile plasticizers are added along with supporting sodium salts to improve specifically defined
characteristics. Both standard casting and smart photopolymerization techniques have been explored
[2]. Moreover, due to the versatile nature of free radical photo-polymerisation multiphase electrode-
electrolyte composites are produced [3]. In this process, an appropriate liquid reactive mixture
comprising monomers, salts and eventually additives, which constitutes the polymer electrolyte
precursor, is drawn into a thin film over the electrode material. Therefore, the liquid reactive mixture
can penetrate into the electrode voids to achieve an intimate contact between the electrode/electrolyte
surfaces, during film formation. It is then in-situ polymerised to form, in a single step, a self-standing
electrode intimately connected to the Li+/Na+ ion conducting electrolyte membrane, with an efficient
interpenetration of the two surfaces. By this one-pot process, we are able to optimize the interfacial
properties between nanostructured electrodes and polymer electrolytes, thus obtaining high performing
electrochemical cells. Lab-scale Li/Na-ion polymer cells are assembled with different nanostructured
electrode materials (e.g., LiFePO4, TiO2 nanotubes, Ga2O3 nanorods and graphene-wrapped mixed
transition metal oxides) and tested for their long-term cycling ability and rate capability,
demonstrating that safe, durable and high energy density devices conceived for green-grid storage and
operating at ambient and/or sub-ambient temperatures can be a reality in the near future.

References
Mechanical Stabilization of Solid Polymer Electrolytes through Gamma Irradiation

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Recent research efforts into solid polymer electrolytes (SPEs) beyond the polyether paradigm have broadened the research field with new materials that offer improvements in performance as well as opportunities for tailoring materials for specific applications. In particular materials based on polycarbonates and polyesters have shown to fulfil this promise, as shown for systems based on both the poly(ethylene carbonate) [1,2] and the poly(trimethylene carbonate) [3,4] backbone structures. This has ultimately led to the development of SPEs that can be used in Li batteries operational at room temperature. [1,4]

Since ion conduction in these materials – at least at moderate salt concentrations – is coupled to the polymer chain dynamics, the performance of these electrolytes is inherently a compromise between mechanics and ion dynamics. While this is not necessarily an issue at room temperature, it becomes notable at elevated temperatures and we have observed migration of the electrolyte during long-term battery operation under such conditions, ultimately leading to failure of the electrolyte membrane to act as a separator between the electrodes with concomitant battery failure.

A solution to this is to chemically crosslink the material in order to stabilize it mechanically. For the poly(ec-caprolactone-co-trimethylene carbonate) host material we have already successfully used in high-performance Li battery cells, [4] this can be done through $\gamma$-irradiation. [5] Here, we have explored this treatment in the context of SPEs and show the effects of $\gamma$-irradiation on the mechanical properties, ionic conductivity and battery cell performance at room temperature and beyond.

![Figure 1. Viscoelastic properties (left) and ionic conductivity (right) of pristine and $\gamma$-irradiated SPEs.](image)

References
Towards Safer Sodium-Ion Batteries
via Organic Solvent/Ionic Liquid Based Hybrid Electrolytes

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Our society is in urgent need of more efficient, affordable and environmentally friendly energy storage technologies. While lithium-ion batteries (LIBs) is undeniably the main track of development and outstanding at present, complementary technologies are needed for managing applications such as renewable energy integration. One particularly appealing alternative is to explore the feasibility of a technology analogous to LIBs – sodium-ion batteries (SIBs) – using the basic LIB know-how and with sodium being more abundant and less expensive.

As in any battery technology, the electrolyte choice is as important as that of the electrodes to ensure successful operation. Considering both safety and “environmental impact” ionic liquids (ILs) have emerged as an interesting option for LIBs. ILs exhibit both non-volatility and non-flammability, but unfortunately their high viscosities and comparatively low conductivities are expected to considerably limit the rate performance. Mixed electrolytes, i.e. with ILs as additives/co-solvents to an organic electrolyte, are a compromise suggested to improve the safety – while still providing an appreciable conductivity. Here, the possibility of expanding this strategy to SIBs has been explored.

We here present a systematic study of several electrolytes consisting of a sodium salt (NaTFSI) dissolved in mixtures of ILs and organic solvents. The physico-chemical and electrochemical characterisation includes ionic conductivity, viscosity, density, cation coordination and solvation, various safety measures; self-extinguishing time and flash point, and electrochemical stability window. Imidazolium (BMImTFSI/EMImTFSI) and pyrroolidinium (PYR13TFSI) ILs were used as additives to optimized ethylene carbonate: propylene carbonate (EC:PC) electrolytes, while hard carbon (HC) was used as anode. Hybrid electrolytes with 10 to 50% of IL content were found to have ionic conductivities on par with comparable organic solvent based electrolytes, but with highly enhanced safety properties. A systematic Raman spectroscopy study of the cation coordination and solvation before and after electrolyte safety tests by ignition suggest that IL cations and TFSI remain stable when ignited, while the organic solvents are preferentially consumed. Finally, the SEIs formed when using hybrid electrolytes have better both mechanical and electrochemical properties than the SEIs obtained using pure IL based electrolytes. For a half-cell with a HC electrode and a 0.8 m NaTFSI in EC0.45:PC0.45:PYR13TFSI0.10 hybrid electrolyte encouraging results were obtained; ca. 182 mAhg⁻¹ at C/10 over 40 cycles.
Ion-conductive properties of poly(ethylene oxide-co-ethylene carbonate)/
Li salt electrolytes

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Solid polymer electrolytes (SPE) are expected to be useful as an electrolyte for batteries because of its safety, flexibility and lightweight. Poly(ethylene oxide) (PEO) and its derivatives have usually low glass transition temperatures \( T_g \) and those electrolytes exhibit relatively high ionic conductivity. However, PEO-based electrolytes suffer from low Li transference numbers \( (t_I) \), less than 0.3. To overcome these problems we recently suggested polycarbonates, such as polylethylene carbonate) (PEC), as a new polymer matrix for SPE. However, PEC-based electrolytes have a issue with low ionic conductivity relative to PEO-based electrolytes at low salt concentrations, because of the high \( T_g \) of the original polymer. In this study, we focus on the copolymerization of ether and carbonate units as novel candidates for the electrolytes. The ether/carbonate copolymers can be obtained with suitable ratio by the optimization of the polymerization condition. We investigated the influence of the ether units on the ion-conductive properties of poly(ethylene oxide/ethylene carbonate) (P(EO/EC))-based electrolytes. The electrolytes were prepared with lithium bis(fluorosulfonylimide) (LiFSI). The LiFSI content in the electrolyte varied from 5 to 160 mol\% to an average monomer unit of each EO and EC unit. We found that the \( T_g \) of neat copolymers and the electrolytes decreased with increasing the contents of EO unit, while the conductivity for the electrolytes increased with increasing both EO unit and salt concentration. The \( t_I \) of P(EO/EC) electrolyte having EO unit of 53% and 80mol% of LiFSI had high \( t_I \) of 0.65 at 60 °C. This value was very high and comparable with that of the PEC-based electrolytes. The dissociation states of Li ions is essential to reveal ion-conductive properties of P(EO/EC) electrolytes, so the measurement of FT-IR was carried out. The results of characterization of FT-IR spectra suggest that Li ions interact preferentially with carbonate groups but hardly interact with ether groups in P(EO/EC)-based electrolyte. However, the conductivity of electrolytes having high EO unit (70%) decreased than lower EO unit at the high salt concentrations (>60 mol%). The \( T_g \) of the electrolyte for EO unit 70% also increased than that of electrolyte for EO 53% at high concentrations. The FT-IR spectra of electrolyte (EO unit 70%) suggest that that EO units interact with Li+. Thus, the P(EO/EC) electrolytes showed novel ion-conductive behavior which has advantages of both EO and EC-based electrolytes. The copolymerization of EO and EC units provide a novel guideline for SPEs.

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Molecular Layering in Electric Double Layers of PEGDME Based Lithium Electrolytes

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In "soggy sand" electrolytes, addition of ceramic particles to lithium salt containing liquid lithium electrolyte leads to dissociation of ion pairs due to preferential adsorption of anions on the oxide particle surface and increase in counter ion concentration, consequently enhancing cation (lithium) conductivity.[1-2] This study deals with interfacial structuring of pure and lithium triflate (LiTf) containing polyethylene glycol dimethyl ether (PEGDME-150) on the surface of mica using a number of complementary techniques such as surface force apparatus (SFA), infrared spectroscopy (IR), Zeta potential measurements and impedance spectroscopy.

The presence of different ionic species and thermodynamic of ionic association in the bulk LiTf+PEGDME-150 electrolyte containing 1 vol% of ball-milled mica particles (~150 μm) have been studied using IR. The triflate stretching band reveals the concentration dependence of free ions, Li-Tf ion pairs and dimers, as previously observed in the case of pure LiTf+PEGDME-150.[3] Addition of mica to LiTf+PEGDME-150 enhances the ion pair dissociation resulting in higher concentrations of free ions in agreement with the soggy sand theory.[2] Preferential anion adsorption is additionally confirmed by negative Zeta potential values at all mica volume fractions.

Initial SFA force-distance profiles of pure PEGDME-150 in contact with mica indicate no layering or interaction on the surface. However, pronounced interfacial structuring evolves in time (first observed after 30 min) with compression profiles indicating immobilized polymeric brush like structures (up to 10 nm in size) on the mica surface, most probably a consequence of complexation of surface K+.

Similar behavior is found for up to 0.2M LiTf containing PEGDME-150. Upon increase in concentration of LiTf, the interfacial structure changes drastically with appearance of the molecularly structured electrical double layer below (15 nm thickness). Taking into account the speciation found by IR and mica particle charge, inner Helmholtz layer most likely consists of solvated triflate anion (up to 4 nm) while the outer LiTf concentration dependent Helmholtz layer consists of ion pairs. Molecular layering in concentrated LiTf+PEGDME-150 electrolytes has proven to be similar to charge compensations recently found in pure ionic liquids.[4]

References
Numerical analysis on the concentrated solution based vanadium ion crossover in all-vanadium redox flow batteries

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The transport phenomena of species through the ion exchange membrane of the all-vanadium redox flow battery (VRFB) can be described using multicomponent diffusion equations, i.e. Stefan-Maxwell equations. In this work, a three-dimensional, transient, non-isothermal VRFB model is further developed based on the concentrated solution theory for ions with high concentration. The model accounts for electrochemical reactions, heat generation, species/heat transport, and furthermore, interactions between vanadium ions (V2+, V3+, VO2+ and VO2+) are included based on the Stefan-Maxwell equations. Using the model, we investigate the effect of interactions between vanadium ions on the crossover behavior through the membrane during charge and discharge cycle. The model is applied on the single straight channel, and simulation results provide the change of vanadium ion crossover in form of multi-dimensional contours in the components of VRFB and polarization curves along the time. This work can contribute on the basic understanding of the behavior of highly concentrated solutions and be helpful for optimization of design and operation of VRFBs.
Poly (ethylen oxide)-lithium bis(trifluoromethanesulfonyl)imide N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PEO-LiTFSI-Pyr$_{14}$TFSI)-based solid electrolytes for lithium sulfur battery

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Rechargeable lithium ion batteries having high energy density, power density, long cycle life, as well as low memory effect, are widely used in various applications ranging from mobile electronics to automotive. However, it suffers a drawback from severe safety issues, emerging from the volatile and flammable nature of carbonate-based liquid electrolytes that are typically used in lithium ion batteries. All-solid-state lithium metal polymer batteries are flexible thin films not only facilitate the assembly and versatility in battery design, but also enable significant improvements in terms of safety and performance [1,2]. In this study, we prepared a poly (ethylen oxide)-lithium bis(trifluoromethanesulfonyl)imide N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PEO-LiTFSI-Pyr$_{14}$TFSI)-based polymer electrolytes with a high ethylene-oxide/Li-ion ratio (EO/Li=20). The PEO-LiTFSI-Pyr$_{14}$TFSI solid-state electrolyte is applied to lithium sulfur battery to improve safety and cycle life. PEO-LiTFSI-Pyr$_{14}$TFSI polymer electrolytes achieved $10^{-6}$ S/cm at room temperature and ionic conductivity is increased with increasing temperature to $10^{-4}$ S/cm at 70 °C.

![Ionic conductivity vs temperature](image)

**Figure 1.** Temperature dependence of ionic conductivity of (PEO-LiTFSI-Pyr$_{14}$TFSI)-based polymer electrolytes.

**References**
Ionic Liquid-Based Gel Polymer Electrolytes for Lithium Microbatteries: Correlation Between Structural And Electrochemical Properties

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This project focuses on the study of new electrolytes for microbatteries that can be used through a wet deposition process. Our strategy consists in confining a mixture of an ionic liquid (IL) and a lithium salt in an organic membrane in-situ polymerized by UV-initiated reaction. This method is suitable for microbatteries manufacturing process and offers many advantages compared to classical vacuum deposition methods (PVD, CVD). The process indeed allows high deposition rate, low cost, and a highly conformal film consistent with 3D textured or high roughness substrates.

The lithium salt LiTFSI was first dissolved in the ionic liquid N-Propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr13TFSI). The effect of lithium salt concentration was investigated by measuring the bulk conductivity and the lithium transference number by diffusional NMR. The presence of lithium ions in the electrolyte (investigated by Raman spectroscopy) and the cycling performance of the battery was demonstrated.

Transparent and flexible ion-gels were then obtained by confining the optimal electrolytic solution in an organic matrix by photo-induced radical polymerization of a PEO-based methacrylate precursor. The initial solution contained 30%wt of the monomer and 70%wt of the IL solution. Self-standing films with good mechanical strength (G’= 0.3MPa) and a thermal stability up to 300°C were obtained.

Figure 1. Images of the gelled electrolyte as a free-standing membrane (a) and integrated in a microbattery stack —top view (b) and cross section SEM image view (c).

The final membrane displayed an excellent ionic conductivity of 8.10^{-4} S.cm^{-1} at 25°C, comparable to some liquid electrolytes and significantly better than the standard solid electrolyte used in microbatteries (LiPON), whose conductivity is about 2.10^{-6} S.cm^{-1}.

Then LiCoO2/ion-gel/Li coin cells were assembled and batteries were successfully cycled at different C rates (C/10, C/5, C/2) between 3 and 4.3V at 25°C. At C/10, its total capacity was equal to 80% of the reference capacity obtained with a standard liquid electrolyte (EC:PC:DMC 1:1:3 + 1M LiPF6). However, at higher C rates, the capacity decreased significantly due to an important ohmic drop. Indeed, the mobility of the lithium ions scanned by diffusional NMR, drastically decreases after UV curing, pointing out their immobilization by the PEO polymer network.

This technique, coupled with impedance spectroscopy, X-ray diffraction and differential scanning calorimetry, suggests that part of the lithium salt dissolved in the ionic liquid is chelated by the solid matrix and lithium ions are thus restrained from migrating during the cell polarization. Interesting improvements of the battery performance were found by decreasing the cross-linking agent concentration and using a dissociating co-solvent. The nature of the interactions between Li+ and the polymeric network and their influence on the electrochemical performance will be discussed.
Measurement of Lithium Transference Numbers in Poly(Ethylene Oxide) Based Electrolytes by Combination of Potentiostatic and Galvanostatic Polarization Methods

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Among all solid electrolytes considered for use in lithium ion batteries, systems based on poly(ethylene oxide) PEO allow to obtain relatively high values of ionic conductivity as well as good mechanical and chemical stability. However, efficient operation of the rechargeable cell depends not only on value of conductivity, but also on lithium transference numbers ($t^+$). The $t^+$ values reported for PEO-based electrolytes indicate that anions have significant share in overall charge transport. Moreover, different experimental methods used for calculation of lithium transference numbers often give inconsistent results.

In our work, lithium transference numbers of electrolytes comprising linear PEO and LiN(CF₃SO₂)₂ salt have been measured using two electrochemical methods. Initial measurements performed by Bruce and Vincent [1] method have shown that, in order to obtain reliable and repeatable results, significant modifications of measurement procedure need to be introduced. The new method combines potentiostatic [1,2] and galvanostatic [3] polarization methods which allows for compensation of various experimental artifacts observed in measurement of cells with lithium electrodes. Analysis of the results can be performed using either approaches of Evans et al. [1], Watanabe et al. [2] or Ma et al. [3].

Measurements of PEO:LiN(CF₃SO₂)₂ electrolytes with different amount of lithium salt performed by new procedure have shown that, in contradiction to some earlier predictions, the values of $t^+$ do not exhibit a continuous decrease upon increase on concentration of salt (Fig. 1.). The lithium transference numbers reach a minimum for electrolytes with composition close to that of the PEO₆:LiN(CF₃SO₂)₂ stoichiometric complex, but increase significantly upon further increase of concentration of lithium salt. This indicates possibility to obtain efficient lithium ion transport even in electrolytes with high concentration of salt.

References

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Thermal simulations of Polymer Electrolyte 3D Li-Microbatteries

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High charge and discharge rates are desired properties of the Li-ion batteries in both macro- and micro-scale (i.e. a footprint area of \(<1 \text{ mm}^2\)). In this context, a rise of the cell temperature due to ohmic heating and irreversible electrochemical reactions can take place, leading to performance limitations and safety issues. Investigation of the behavior of the thermal effects in the cell provides possible explanations of the limiting factors of cell performance and suggests improvements to obtain enhanced performance and safety of the battery.

Here we present extensive simulations with a fully coupled thermal-electrochemistry model of the 3D microbattery (3D-MB) using Finite Element Methodology (FEM). 3D-batteries, where the current distribution is much less uniform than in their 2D counterparts, are expected to possess more inherent problems of thermal distribution. Both pillar shaped and concentric electrode arrangements have here been investigated for these 3D-MBs, using LiCoO\textsubscript{2} (LCO) as a positive and graphite as a negative electrode. In both architectures, polymer electrolytes with LiPF\textsubscript{6} salt were used. Electrode and electrolyte material parameters (i.e. diffusion coefficient and ionic conductivity) have thereafter been varied and different C-rates used to benchmark the performance of these 3D-MB cells. The initial model was validated towards reported results of Li-ion battery systems in literature [1,2].

FEM simulations of the 3D-MB during operation provide complete 3D time dependent descriptions of the thermal behavior of the cells. Temperature distribution and gradient (Fig. 1) in the cell are highlighting critical regions, most likely leading to performance bottlenecks and safety hazards. Furthermore, the simulations clearly demonstrate the highest heat sources occur near the regions with most active charge transfer processes, which are located at different spots during battery operation, thereby providing a tool for optimization of the cell geometry in terms of both performance and safety.

![Figure 1. Snapshots from the discharge cycle of the simulated cell.](image)

Amelioration of Copolymer Electrolytes for Dye-sensitized Solar Cells Incorporated with Binary Salt and Ionic Liquid

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Dye-sensitized solar cells (DSSCs) have attracted a huge amount of interest from researchers worldwide due to their unique properties of easy fabrication and handling, low cost and reasonable high power conversion efficiency (PCE). One of the major factors limiting the development of this application is the short lifetime of the cells due to the volatilization of the liquid electrolytes which is traditionally used. With this challenge in mind, polymer electrolytes were prepared to replace the liquid electrolytes in the fabrication of DSSCs. We used a novel approach which is the addition of binary iodide salts to improve the efficiency of the copolymer electrolyte based DSSCs. Binary salt systems utilize the different characteristics of the different salts to optimize the enhancement in the polymer electrolytes. The highest ionic conductivity obtained for the binary salt system was 1.89 mS cm⁻¹ which is a sample containing KI: TPAI = 3:1 mass ratio. The DSSC fabricated with the same sample also shows highest PCE value of 5.53% with maximum short circuit density (Jsc) of 14.07 mA cm⁻², open circuit voltage (Voc) of 0.60 V and a fill factor of 65% under the standard light intensity of 100 mW cm⁻² irradiation of AM 1.5 sunlight. The ionic conductivity studies and PCE of the DSSCs shows that the binary salts system having better performance compared the single salt system. The cells have also been studied under different illumination condition and it was found that the photocurrent density of the cells is not only limited by the charge diffusion inside the samples. Electrochemical impedances studies of these cells have been performed to understand more on the electrical properties of the DSSCs. Tafel measurements which were carried out with two symmetrical Pt electrode shows that the dual salt system has higher electrocatalytic activity.
Optimization of formic acid electro-oxidation on Pt electrode modified with electrosynthesized polymer and Pt nanoparticles


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Obtaining of modified electrodes with Pt nanoparticles dispersed onto nano-wires of poly (3,4-ethylenedioxythiophene) (PEDOT), to be tested in formic acid electrocatalysis, to be compared with previous works is reported. The nanowires are synthesized by cyclic voltammetry from 0.01 mol L\(^{-1}\) monomer and 0.1 mol L\(^{-1}\) tetrabutylammonium hexafluorophosphate in acetonitrile, on Pt|PEDOT|mesoporous silica electrodes previously modified by electrochemical methods [1-3]. The silica film is prepared at fixed potential, to then act as a template, directing the growth of PEDOT nanowires (PEDOT-nw) inside the pores. Subsequent removal of the template without damaging the polymer nano-structure deposited on the electrode is the main contribution of this work, which has significantly exceed the previous results. Thus, when analyzing the electrode modified with PEDOT-nw (PtPEDOT|PEDOT-nw) by scanning electron spectroscopy, images of a surface are observed as a "brush" with nw diameter between 20 and 25 nm. Its voltammetric response realizes an increase of p-doping load 500 times with respect to solid films, without change reversibility [1]. The subsequent insertion of Pt nanoparticles (np-Pt), based on the p-doping process to prepare PtPEDOT|PEDOT-nw/np-Pt electrode, show that the catalytic activity of these nanostructured electrodes remarkably improved against electro-oxidation of HCOOH: the oxidation requires with much higher current density than that obtained in all these previous studies. Furthermore, the amount of Pt required is much lower [2, 3], so that the simplicity of the electrochemical techniques used, and a significant decrease in the cost of obtaining these devices, ensures that now has an electrode properties insurmountable for the catalytic oxidation of HCOOH, which has great relevance in fuel cells.

![Figure 1. (A) PEDOT-nw SEM micrographs. (B) Cyclic voltagram during formic acid oxidation on modified electrodes: (——) Pt|PEDOT|PEDOT-nw; (——) Pt|PEDOT|PEDOT-nw/np-Pt and. Working solution: 0.100 mol L\(^{-1}\) KPF\(_6\), 0.100 mol L\(^{-1}\) HCOOH in H\(_2\)O. Scan rate, 0.010 V s\(^{-1}\).](image)

Acknowledgements
Financial support through FONDECYT grant number 1141158 is gratefully acknowledged. A. M. R. Ramírez thanks CONICYT for a doctoral scholarship folio: 21130607.

References
Proton Conducting Membranes for Energy Applications

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Proton conducting membranes are one of the most crucial components in several electrochemical applications such as fuel cell, flow battery and CO2 reduction etc. Nafion, with high proton conductivities and proven stability is the most commonly used proton conductors. However, operation condition of the Nafion membranes and derivatives was limited under 100°C due to the presence of water being an essential condition for its high proton conductivity. Thus, solid-state anhydrous proton conductors are being sought.

The organic ionic plastic crystals (OIPCs) have emerged as a novel solid-state ionic conductor, with unique plastic phase that ensure good mechanical flexibility and improved contact between electrodes an electrolyte. [1] In addition, intrinsic ionic conductivity, non-flammability, good thermal stability and wide electrochemical windows are all desirable properties obtained by OIPCs. [1-3] Forsyth and MacFarlane groups have developed knowledge of the proton transport behaviour in electrolyte materials which are important for the design and development of novel solid electrolytes for electrochemical device application.

\[
\text{Figure 1. Structure of DMEDAH Tf and DMEDAH Tf}_2
\]

In this work, we investigate thermal properties, phase behavior, ionic conductivity and proton transport behavior of the protic organic salts DMEDAH Tf and DMEDAH Tf, in order to achieve a fundamental understanding of the relationship between chemical structure/composition of protic organic salt based electrolyte and their proton conductivity.

References
Cross Linking – A Viable Technique For All Solid State Lithium Batteries
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Semi-interpenetrated network Solid Polymer Electrolytes (SPEs) were fabricated by UV-induced cross-linking of poly(ethylene glycol) diacrylate (PEGDA) and divinylbenzene (DVB) within a poly(ethyleneoxide) (PEO) matrix (Mv = 5 x 10⁶ g·mol⁻¹), comprising lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI), at a molar ratio of [EO]/[Li⁺]–30. The increase of polymer rigidity and stiffness (high shear modulus) due to crosslinking are assumed to improve the material resistance towards dendrite growth [1-3]. The DVB cross-linker incorporation was found to influence significantly the crystallinity of the PEO matrix, with a decrease in the melting temperature (Tm) of the membrane. Moreover, the influence of the DVB concentration on the ionic conductivity was determined for the different polymer electrolytes at different temperatures. The resulting SPEs showed a high electrochemical and mechanical stability as well as practical conductivity values exceeding 10⁻⁴ S·cm⁻¹ at 70°C. Cycling performance of these semi-interpenetrated SPE’s have been shown with Li metal polymer using intercalation cathode and in an all solid state Li sulphur battery. This approach (crosslinking) could be extended towards preparing easily processable and scalable single ion conducting SPEs with improved properties for all-solid-state batteries.

Figure 1. A schematic illustration of UV induced preparation of semi-interpenetrated network based on PEO matrix

References
Polymer Electrolyte Actuators based on Homogeneous Networks using Tetra-arm Polyether

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Polymer electrolyte actuators are electrochemical devices, and have been attracting much attention due to advantages such as lightweight, flexibility, and cost-effectiveness. Although many studies relating to polymer actuators using hydro-gels and organo-gels as the polymer electrolytes have been reported, they have serious issues such as limited operating conditions and poor mechanical properties due to the solvent evaporation and polymer network defects, respectively. Regarding the polymer electrolyte for the actuator, we have developed polymer electrolytes, so-called “ion gels” [1], [2], which are comprised of ionic liquids (ILs) and polymer networks. The ion gels are self-standing and flexible materials with maintaining the characteristics of ILs such as low-volatility and high ionic conductivity. Therefore, we have proposed the polymer actuators that can operate in wide range of temperatures and even under reduced pressures by using the ion gels as an electrolyte (Fig. 1) [2].

Taking cycle performance of the actuator into account, high mechanical toughness of the ion gels is required. We have focused on tetra-arm poly(ethylene glycol) (tetra-PEG) gel [3] as the polymer electrolyte (Fig. 2). Owing to the homogeneous three-dimensional network structure, tetra-PEG network can retain much amount of IL even at a lower polymer concentration with good mechanical properties. We have previously reported that the polymer actuators using tetra-PEG ion gels showed rapid response and high durability [4].

Polymers, which are well-known as ion conductive polymers, can dissolve lithium salts due to the coordination of ether oxgens to lithium cations. Here, we will compare the performance of tetra-PEG/ionic liquid actuators with that of tetra-PEG/Li salt actuators. Ion transport properties in these two polymer electrolytes are completely different, depending on the difference in the interaction between the cations and ether oxygen atoms. We will discuss the effect of doped salts into the tetra-PEG networks on the bending behavior of actuators.

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References
Electrochemical Studies of Plasticized Chitosan-Ammonium Bromide Based Polymer Electrolytes for Supercapacitor

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The science of energy storage is an important branch of technology nowadays, as portable electronic devices such as laptops, mobile phones, digital cameras and tablets are becoming increasingly multifunctional which demands high power energy resources. The studies on electrochemical devices include the performance of the devices, electrode materials and electrolytes. Ion conducting polymer electrolytes have become an interesting area in solid state ionics due to their prospective application in solid state electrochemical devices [1]. Research on polymer electrolytes are mainly focused on the improvement in ionic conductivity and mechanical strength, as well as chemical, thermal and electrochemical stabilities of the electrolytes to fullfill their potential application in electrochemical devices [2, 3]. Previously, conductivity studies of chitosan-ammonium bromide (NH4Br) based electrolytes have been carried out [4]. In this work, further characterizations are reported and the highest conducting electrolyte is used in the fabrication of a supercapacitor. These electrolytes are prepared via solution cast technique. The impedance measurements of the electrolytes are conducted using HIOKI 3532-50 LCR HiTESTER from room temperature to 358 K in the frequency range of 50 Hz to 5 MHz. From the impedance measurement, the dielectric and electrical properties of the electrolytes are determined. From transference number of ion (t_ion) measurement, ion is found as the dominant conducting species. Linear sweep voltammetry (LSV) results from different scan rates confirm the suitability of the highest conducting electrolyte to be used in the fabrication of a supercapacitor. The supercapacitor is characterized using galvanostatic charge-discharge and cyclic voltammetry (CV) measurements.

References
Diffusion of Li Ions in Amorphous and Crystalline Phases in PEO$_2$:LiCF$_3$SO$_3$ Polymer Electrolytes

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The PEO$_2$:LiCF$_3$SO$_3$ polymer electrolyte has attracted significant research due to high conductivity and enhanced stability in lithium polymer batteries. Most experimental studies have shown that amorphous PEO lithium salt electrolytes have higher conductivity than the crystalline ones. Other studies, however, have shown that crystalline PEO salt complexes can conduct ions [1-3]. As a result, further theoretical investigations are warranted to help conduction in amorphous regions versus conduction in crystalline polymer. In this work, we use density functional theory and ab initio molecular dynamics simulations to investigate the atomic-scale mechanism of lithium ion transport in polymer electrolytes and to obtain the amorphous structure of PEO$_2$:LiCF$_3$SO$_3$. The diffusion pathways and activation energies of ions in both crystalline and amorphous PEO$_2$:LiCF$_3$SO$_3$ are identified. In crystalline PEO$_2$:LiCF$_3$SO$_3$, the activation energy for the low-barrier diffusion pathway is approximately 1.0 eV. In the amorphous phase, the value is 0.6 eV. This result would support the experimental observation that amorphous PEO$_2$:LiCF$_3$SO$_3$ has higher ionic conductivity than the crystalline phase.

References
Imidazolium-Based mono and Dicationic Ionic Liquid Sodium Polymer Gel Electrolytes

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Sodium and sodium-ion batteries (NIBs) have attracted extensive attention for large scale energy storage applications owing to the natural abundance, relatively low cost and very suitable redox potential (E°Na+/Na- ≈ -2.71 V vs. SHE), making them a viable alternative to lithium ion batteries, specially for stationary applications [1,2]. In this context, ionic liquid polymer gel electrolytes have been widely investigated as promising candidates in sodium batteries because of their excellent properties such as safety, mechanical stability and flexibility [3]. In this work, we report on the synthesis, thermal, structural and electrochemical characterization of sodium polymer gel electrolytes based on imidazolium-based mono and dicationic ionic liquids, a P(VDF-HFP) polymer matrix and NaTFSI as sodium salt. Results obtained indicate that gel electrolytes, based on 0.2 M sodium mono and dicationic ionic liquids are thermally stable at temperatures up to 280 °C, well above working conditions of rechargeable batteries. Regarding ionic conductivity data, it has to be pointed out that, as expected, values are lower than those corresponding to the liquid electrolyte (Figure 1); room temperature values range from 9.2x10⁻² to 2.2x10⁻⁴ S.cm⁻¹, the higher values corresponding to the monocationic ionic liquids with the shorter side chain. The cathodic scan, performed by cyclic voltammetry test, shows a reversible process at about 0.5 V vs. Na⁺/Na for all tested electrolytes. On the other site, the linear sweep voltammetry test evidences extended anodic stability of the electrolyte (up to 5 V vs. Na⁺/Na).

Figure 1. Ionic conductivity vs. temperature of pure ionic liquid (IMI-60) and Na-doped ionic liquid electrolyte (EIMI-60) compared with EMI based gel electrolyte (GEIMI-60).

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References
A new concept for solvent-free lithium polymer electrolytes that enables next-generation energy storage devices

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Ionic Materials (“Ionic”) has invented a novel polymer with a new approach with extremely high ionic conductivity at room temperature (~1mS/cm) and over a range of temperatures, even surpassing that of a standard liquid carbonate-based electrolyte at -40°C. Ionic’s polymer has the potential to revolutionize energy storage by facilitating significant improvements in battery performance, cost, and safety, which could in turn speed the electrification of transportation and benefit a wide variety of other applications. This solid polymer can be reliably extruded into very thin films, is non-flammable, has attractive mechanical properties for lithium dendrite suppression, is electrochemically stable against Li, and is compatible with a variety of different anodes and cathodes. The polymer electrolyte is based on an inexpensive semicrystalline commercially available polymer and Li salts familiar to the battery and polymer electrolyte communities. The ionic transport mechanism is unlike that which characterizes the polyethers, which work primarily in the amorphous state and rely on visco-elastic behavior, where secondary bonds are beginning to break. In these new materials, the ion mobility is completely decoupled from polymer host motion, as verified by differential scanning calorimetry and nuclear magnetic resonance (NMR). In fact NMR pulsed gradient measurements reveal Li self-diffusion coefficients at room temperature that are an order of magnitude higher than in the ceramic ion conductors of the Li10GeP2S12 class.

This novel polymer has numerous potential benefits across a range of battery chemistries. Solid state, lithium metal anode batteries are of particular interest to Ionic due to their extremely high capacity and potential to reduce cell costs below $100/kWh – a commonly cited tipping point for the mass adoption of electric vehicles.
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# Programme Overview

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<th>Time</th>
<th>Sun</th>
<th>Mon</th>
<th>Tue</th>
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<td>8.10-8.20</td>
<td>Welcome</td>
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<td>8.20-9.00</td>
<td>PL1 - Angell</td>
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<td>PL3 - Balsara</td>
<td>PL4 - Kreuer</td>
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<td>9.00-9.30</td>
<td>K1 - Cui</td>
<td>K3 - Sokolov</td>
<td>K5 - Borodin</td>
<td>K6 - Di Noto</td>
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<td>9.30-10.00</td>
<td>I1 - Tominaga</td>
<td>I7 - Popovic</td>
<td>I13 - Schönhoff</td>
<td>I16 - Smotkin</td>
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<td>I2 - Zukowska</td>
<td>I8 - Popall</td>
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<td>I3 - Snyder</td>
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<td>O2 - Commarieu</td>
<td>O7 - Marzantowicz</td>
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<td>Advisory Board Meeting</td>
<td>Concluding Remarks - 15 min</td>
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<td>I5 - Edman</td>
<td>I11 - Bouchet</td>
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<td>Wackerl, Lassagne, Ivanova, Luo</td>
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