Lithium ion containing block copolymer membrane for lithium ion microbatteries

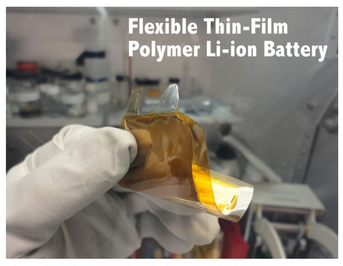
Majid Rasool, Simon Schaper, Ezzeldin Metwalli, Peter Müller-Buschbaum

Technische Universität München, Physik-Department, Lehrstuhl für Funktionelle Materialien, James-Franck-Straße 1, 85748 Garching
simon.schaper@ph.tum.de

Motivation

Lithium ion batteries with solid state electrolyte

- Safer than liquid electrolyte
- High energy density
- Roll-to-roll processing possible
- Flexible form factor
- Lightweight
- No memory effect
- Ultra thin
- Integrating devices



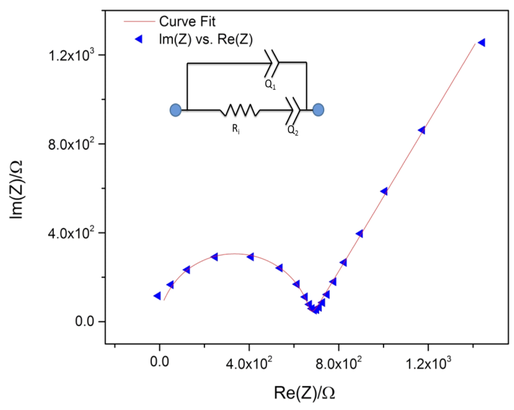
http://sadoway.mit.edu/research/thin-film-polymer-batteries


http://www.globalsolar.com/

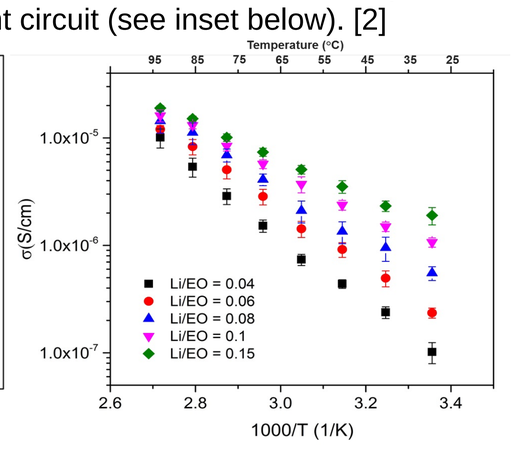

http://www.bmw.de/de/neufahrzeuge/bmw-i/i3/2015/erleben.html

Impedance Spectroscopy

- Measurements for different Li/EO ratios as well as for different temperatures.
- Debye circuit with constant phase elements instead of ideal capacitors chosen to be a suitable equivalent circuit (see inset below). [2]

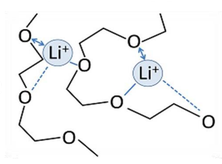


Nyquist plot for polymer membrane with Li/EO ratio of 0.06 [1]



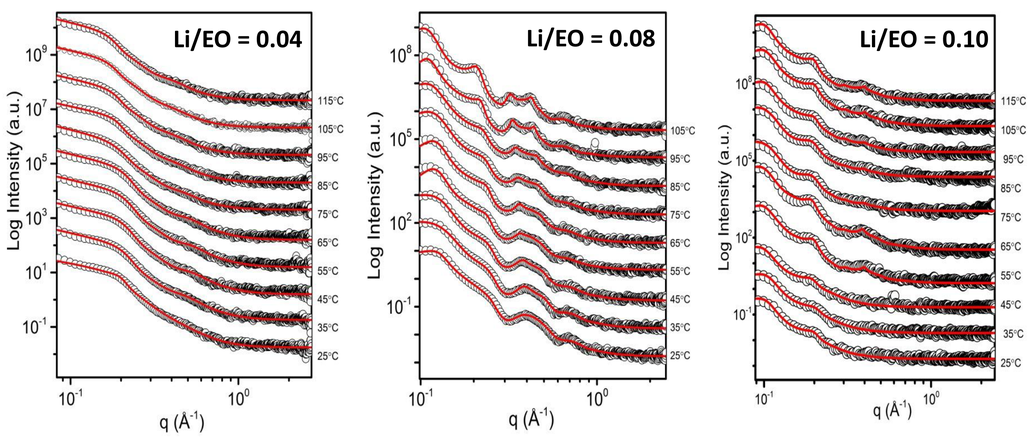
Ionic conductivity profiles of PS-b-PEO by varying the Li/EO ratios at different temperatures. [1]

➢ Results indicate an increasing conductivity with increasing temperature and LiTFSI content due to the hopping of Li ions within the polymer chain: [4]

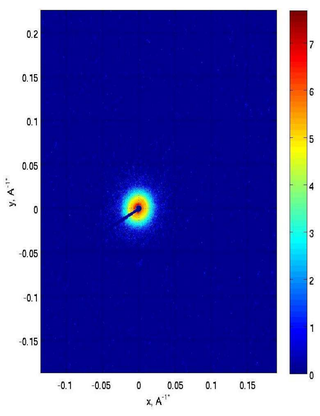


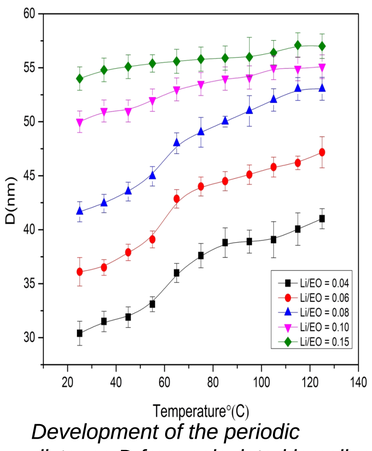
Film morphology (SAXS)

- Small angle X-ray scattering (SAXS) measurements were carried out to analyze the inner morphology of the lithium-polymer hybrid films.
- SAXS profiles were fitted using a model assuming lamellar morphology of the PS-*b*-PEO films.
- Two main structural peaks are observed, which shift to lower *q*-values with the increase of temperature, indicating an expanded periodic distance
- The increased domain spacing at high temperatures is due to the melting of PEO crystals can be seen the WAXS results.

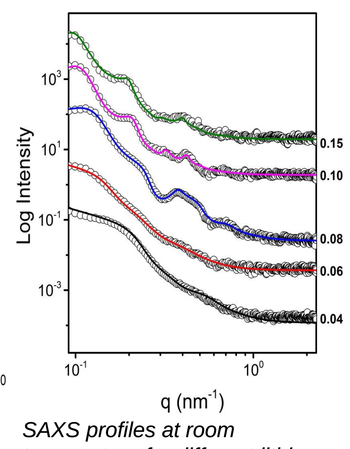


SAXS heating profiles for different temperatures and Li/EO ratios [1]


SAXS 2D scattering pattern of PS-b-PEO with Li/EO =0.04 at room temperature [1]



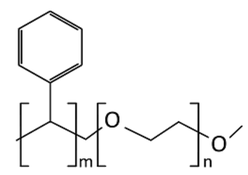
Development of the periodic distance D from calculated lamellar model while heating [1]

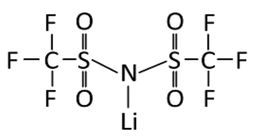


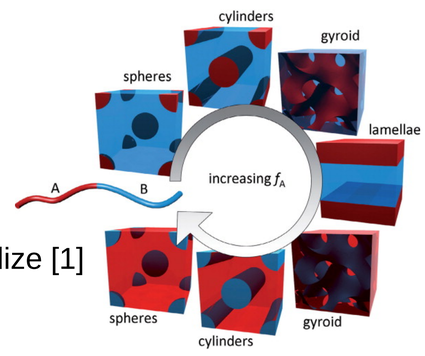
SAXS profiles at room temperature for different lithium salt concentrations [1]

Materials and structure

- **PS-*b*-PEO**
  - Poly(styrene-block-ethylene oxide)
  - Diblock copolymer (total M_w = 91.5 kg/mol)
  - Mechanically stable glassy PS domains (M_w = 30 kg/mol)
  - Lithium conducting PEO part (M_w = 61.5 kg/mol) tends to crystallize [1]
- **Lithium salt LiTFSI**
  - Bis(trifluoromethane) sulfoimide







Morphology of a block copolymer with different volume fractions f_a [6]

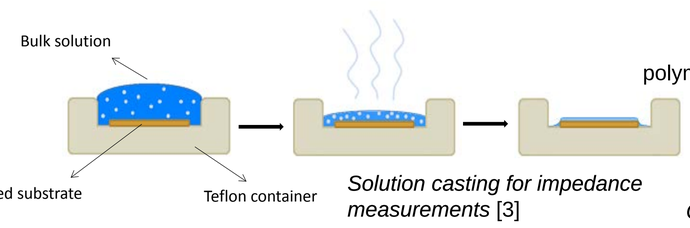
Sample Preparation

- Li-polymer hybrid films with various Li/EO ratios were prepared via solution casting using THF (tetrahydrofuran) as solvent.
- All preparation steps were performed under inert gas in a glove box due to the hygroskopic nature of the LiTFSI salt.

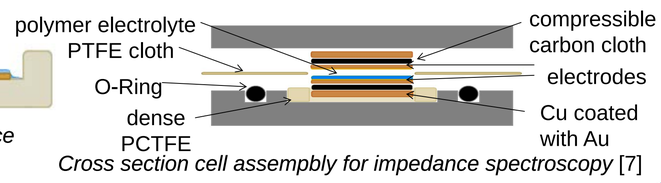

(THF)


Sample between two mica windows for SAXS/WAXS measurements [1]


Cell assembly for impedance spectroscopy [1]



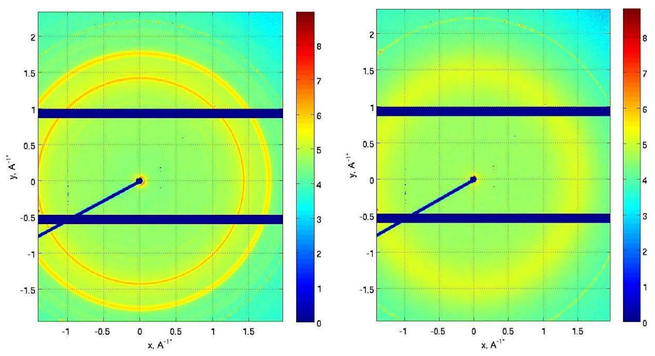
Solution casting for impedance measurements [3]



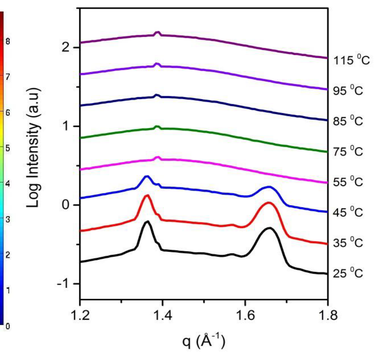
Cross section cell assembly for impedance spectroscopy [7]

Crystallinity (WAXS)

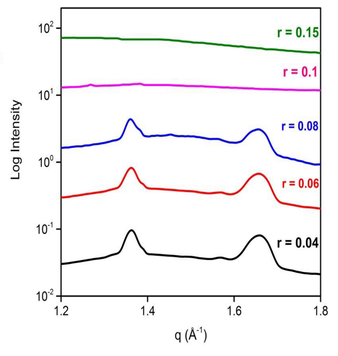
- Wide angle X-ray scattering (WAXS) measurements carried out to analyze the influence of Li salt and temperature on the crystallinity of the PEO blocks.
- At low temperatures, crystalline peaks at 1.3 and 1.6 Å^{-1} are observed, which are assigned by crystals of PEO blocks, at high temperatures (>55°C), the PEO crystals melt. [5]
- With increasing salt concentration PEO crystallization is suppressed by the incorporated lithium ions.



2D WAXS detector image for Li/EO ratio 0.06 and T=25°C (left) and T=55°C (right) [1]



WAXS 1D cuts for Li/EO ratio 0.06 with increase in T [1]



WAXS profiles for different lithium concentrations at T=25°C [1]

Outlook

- Addition of TiO_2 nanoparticles (size: 2-8 nm) to the system to prevent PEO crystallization.
- Different PS-*b*-PEO polymer with larger molecular weight
- Solution casting
- Ultra thin films via spin coating
- All contents dissolved in the same solvent (THF and methanol)
- Porous titania nanostructured films as future electrode
- Ultra thin solid state polymer electrolyte lithium ion batteries

WAXS heating profiles for Porous titania film based on PS-b-PEO block copolymer electrolyte. Sample was made with 100nm Titania film with solution casting of BCP solution with lithium salt concentration of r = 0.08 (left) and r = 0.15 (right) [1]

References

1. M. Rasool, *Block copolymer electrolyte based membrane for lithium ion micro batteries*, E13 TUM (2014)
2. R. A. Huggins. *Advanced Batteries. Materials Science Aspects*, Springer (2009)
3. Brunner, S., *Diplomarbeit: Blockcopolymere für Anwendungen als Feststoffelektrolyte in der Energiespeicherung*, in *Physik department E13* 2013, TU München.
4. Yao, Z., *Solid State Electrochemistry Peter G. Bruce.* Materials and Manufacturing Processes, 1998. **13**(3): p. 475-476.
5. L. Zhu, et al., *Phase structures and morphologies determined by self-organization, vitrification, and crystallization: confined crystallization in an ordered lamellar phase of PEO-b-PS diblock copolymer.* Polymer, 2001. **42**(13): p. 5829-5839.
6. I.Botiz et al., *Materials Today* **13**, 42-51 (2010)
7. A. Eberle. *Charakterisierung von Festelektrolyten über Impedanzspektroskopie*, Diploma Thesis, Lehrstuhl für Technische Elektrochemie, TU München (2011)