Batteries: Solid state and polymer electrolytes

On the path to safer and more versatile lithium-ion batteries (LIBs), solid electrolytes are a key factor in research and development. The common and widely used liquid electrolytes offer a good ionic conductivity (Dudley et al., 1991) and can deal with changing porous interfaces as they can easily fill gaps which occur due to volumetric changes of the active materials in the electrodes during cycling. However, liquid electrolytes like ethylene carbonate (EC) and dimethyl carbonate (DMC) are usually toxic and flammable as well as unstable against dendritic growth, so an additional (polymeric) separator needs to prevent short circuits in the LIB cell adding passive volume and weight.

One alternative to liquid electrolytes are polymer electrolytes which are often based on poly(ethylene oxide) (PEO). As polymer electrolytes serve as lithium-ion conductor as well as separator and are easy processable from solution, a higher flexibility in cell design and thin film batteries is possible. However, the lithium-ion conductivity is lower in polymer electrolytes than in liquid electrolytes but also lower than in recent solid-state electrolytes based on sulfides (Kato et al., 2016).

We investigate the performance and ionic conductivity of PEO based block copolymer electrolytes in bulk and thin-film geometry. Particular interest lies in the morphology – ionic conductivity correlation of high PEO fraction polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) amphiphilic diblock copolymers. The mechanically stable, hydrophobic, but not conducting PS block is covalently bond to the soft, hydrophilic, and lithium-ion conducting PEO block. Therefore, PS-b-PEO undergoes a microphase separation on the nanometer scale which can influence the ionic-conductivity massively. PEO is amorphous above 60°C but crystallizes at room temperature decreasing the lithium ions' mobility, which is dependent on the polymer chains flexibility. The addition of the right lithium salt in a suitable amount prevents this crystallization but also changes the morphology of the PS-*b*-PEO. These morphology effects were studied effectively with x-ray scattering experiments in thin-film (Metwalli et al., 2011) and in bulk (Metwalli et al., 2015) geometry. It the latter case also the correlation between ionic conductivity and morphology was proven and an ideal molar ratio of lithium-ion to ethylene oxide monomers of 1:10 was found. Hence, the temperature as well as the amount of lithium salt significantly influence the conductivity, morphology, and performance of these polymer electrolytes.

However, there is still need for a further increased ionic conductivity. The addition of ionic liquids to PEO based block copolymer electrolytes can increase their ionic conductivity up to a match with the values of liquid ones at elevated temperatures (Metwalli et al., 2018). In this three component system (PS-*b*-PEO, lithium salt, ionic liquid), not only the morphology but also an additional complexation of the lithium salt with the PEO block, leading to new crystalline structures, affects the ionic conductivity. Only the proper ratio of all three components leads to increased ionic conductivities due to more flexibility in the ion-conducting, ionic liquid doped PEO blocks.

In-operando small-angle X-ray scattering studies reveal the morphological impact of the polymer electrolyte during cycling of a lithium-ion battery (Möhl et al., 2018b). The results show that a more disordered morphology of a high PEO content PS-*b*-PEO polymer electrolyte is favorable for the cell's performance stability, while annealed, well ordered PS-*b*-PEO polymer electrolyte cells have a rather unstable performance.

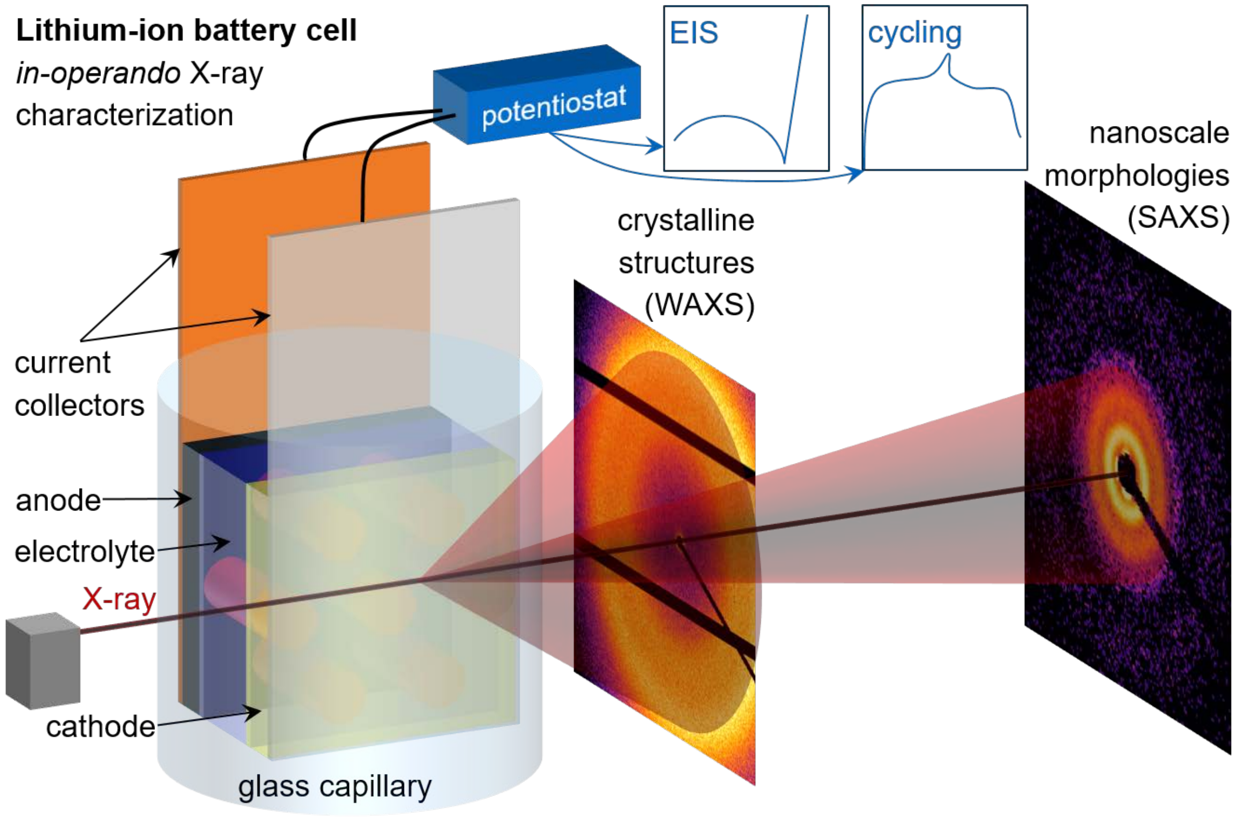

Figure 1: Sketch of the *in-operando* X-ray scattering setup: Small- and wide-angle X-ray scattering (SAXS / WAXS) is measured simultaneously to electrical impedance spectroscopy (EIS) or cycling of a lithium-ion battery capillary cell.

In-operando small-angle neutron scattering (SANS) on single ion polymers, where the anion is covalently bond to the polymer so the only free moving charge carrier in the electrolyte is the lithium ion, reveal a dependence of the electrolyte's morphology on the (dis-)charge current (Möhl et al., 2018a). However, the investigated cells using lithium metal as anode show a displacement in the polymer electrolyte morphology. The cells stay stable for more than 200 cycles. This resistance against dendritic growth and dissolution of the lithium-iron-phosphate cathode even at elevated temperatures of 90°C is remarkable for the stability of the future polymer electrolytes for lithium-ion batteries.

Active collaborations in the material research area of the TUM.Battery network path the way to the future of the lithium-ion battery.

Selected publications:

387. **G.E.Möhl, E.Metwalli, P.Müller-Buschbaum**
In operando Small Angle X-ray Scattering investigation of nanostructured polymer electrolyte for lithium-ion batteries
ACS Energy Lett. 3, 1525-1530 (2018) link

369. **E.Metwalli, M.V.Kaeppel, S.J.Schaper, A.Kriele, R.Gilles, K.N.Raftopoulos, P.Müller-Buschbaum**
Conductivity and morphology correlations of ionic-liquid/lithium-salt/block copolymer nanostructured hybrid electrolytes
ACS Appl. Energy Mater. 1, 666-675 (2018) link

363**. G.E.Möhl, E.Metwalli, R.Bouchet, T.N.T.Phan, R.Cubitt, P.Müller-Buschbaum**
In operando small angle neutron scattering study of single-ion copolymer electrolyte for Li-metal batteries
ACS Energy Lett. 3, 1-6 (2018) link

297. **E.Metwalli, M.Rasool, S.Brunner, P.Müller-Buschbaum**
Lithium-salt-containing high-molecular-weight polystyrene-block-polyethylene oxide block copolymer films
ChemPhysChem 16, 2881-2889 (2015) link

175. **E.Metwalli, M.Nie, V.Körstgens, J.Perlich, S.V.Roth, P.Müller-Buschbaum**
Morphology of lithium-containing diblock copolymer thin films;
Macromol. Chem. Phys. **212**, 1742-1750 (2011) link

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Metwalli, E.; Kaeppel, M. V.; Schaper, S. J.; Kriele, A.; Gilles, R.; Raftopoulos, K. N.; Müller-Buschbaum, P. Conductivity and Morphology Correlations of Ionic-Liquid/Lithium-Salt/Block Copolymer Nanostructured Hybrid Electrolytes. *ACS Appl. Energy Mater.* **2018,** *1* (2), 666–675. DOI: 10.1021/acsaem.7b00173.

Metwalli, E.; Nie, M.; Körstgens, V.; Perlich, J.; Roth, S. V.; Müller-Buschbaum, P. Morphology of Lithium-Containing Diblock Copolymer Thin Films. *Macromol. Chem. Phys.* **2011,** *212* (16), 1742–1750. DOI: 10.1002/macp.201100112.

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Möhl, G. E.; Metwalli, E.; Bouchet, R.; Phan, T. N. T.; Cubitt, R.; Müller-Buschbaum, P. In Operando Small-Angle Neutron Scattering Study of Single-Ion Copolymer Electrolyte for Li-Metal Batteries. *ACS Energy Lett.* **2018a,** *3* (1), 1–6. DOI: 10.1021/acsenergylett.7b01025.

Möhl, G. E.; Metwalli, E.; Müller-Buschbaum, P. In Operando Small-Angle X-ray Scattering Investigation of Nanostructured Polymer Electrolyte for Lithium-Ion Batteries. *ACS Energy Lett.* **2018b,** *3* (7), 1525–1530. DOI: 10.1021/acsenergylett.8b00763.