

Block-Co-Polymers as Superionic Polyelectrolyte Membrane Materials in Lithium Ion Batteries

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Abstract

Block copolymers have shown great potential in the development of advanced materials for energy storage and conversion applications, such as lithium batteries and polyelectrolyte membranes. One of the key features of block copolymers is their ability to self-assemble into well-defined nanostructures, which can be controlled through the choice of polymer composition, molecular weight, and processing conditions. In addition to their structural properties, the ion conductivity of block copolymers is also an important consideration for their use in energy devices. One of the challenges in the development of high-performance block copolymers is achieving optimal ion conductivity while maintaining structural stability. Polyethylene oxide (PEO) is a popular block copolymer segment in polyelectrolyte membranes due to its excellent ion conductivity properties. We find that the addition of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), a commonly used electrolyte salt, affects the self-assembly and structural properties of the block copolymer, and leads to very high ion conductivities of $> 4 \cdot 10^{-2}$ S/cm at room temperature.

Materials

- PI-PS-PEO block-co-polymers were synthesized via sequential living anionic polymerization
- Solid polymer electrolyte membranes were prepared by slowly casting PI-PS-PEO/LiTFSI-THF solutions in a dry argon stream
- Due to embedding LiTFSI transparent pure polymer membranes became white electrolyte membranes

Electron Microscopy (CRYO-STEM)

- Samples were prepared by cryo ultramicrotomy.
- Care was taken, to keep samples in nitrogen atmosphere to protect them against air and moisture
- Sections were stored in liquid nitrogen and transferred to the TEM using a cryo transfer holder
- Neat block-co-polymer shows structure of hexagonal ordered cylinders
- A phase transformation to a gyroid structure is observed, when LiTFSI at a ratio of Li:PEO=4,2:1 is added
- The bicontinuous gyroid morphology is ideal to provide continuous conduction paths

(Cryo-) 4DSTEM

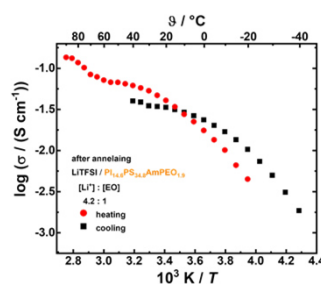
- A series of virtual STEM images of the neat block-co-polymer and the LiTFSI loaded sample was taken and analysed:
 - summed diffraction pattern from all scanning points in the 4D-STEM dataset. The red ring angular range corresponds to the counterpart indicated in grey in c)
 - virtual STEM image reconstructed from the 4D-STEM dataset by integrating the intensity within the red ring in a) at each scanning point
 - STEM scattering intensity plot as a function of the scattering vector: the blue and orange curves correspond to the averaged scattering intensity from the two polymer phases. Each point was measured around the given scattering vector with an integration width of 7 nm^{-1} . The difference between them is given in the black curve. The angular range with the highest positive difference (indicated in grey) match very well with the strongest peaks in the WAXS plot in d)
- A contrast change at $6,2 \text{ nm}^{-1}$ was observed for LiTFSI loaded polymers

WAXS

- Wide-angle X-ray diffraction shows a crystalline PI-PS-PEO/LiTFSI/THF-phase^[1] in all block-co-polymers loaded with LiTFSI
- For different salt concentrations the same characteristic peak positions are observed
- Correlation of 4DSTEM data and WAXS measurements clearly indicates the Li-containing phase

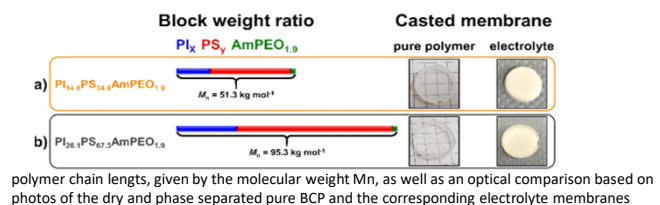
Conductivity

- The ion conductivity for the polymer membranes was determined by electrochemical impedance spectroscopy
- Membranes were annealed with several -20°C to 90°C annealing cycles
- For $[\text{Li}^+:\text{EO}]_n = 4.2$ at room temperature (20°C) a remarkably high conductivity of $4 \cdot 10^{-2}$ S/cm is measured
- High ion conductivities together with low activation energies are a known characteristic for super-ionic Li^+ -conductors
- Achieving high ion conductivity requires low energy barriers and high concentration of mobile ions

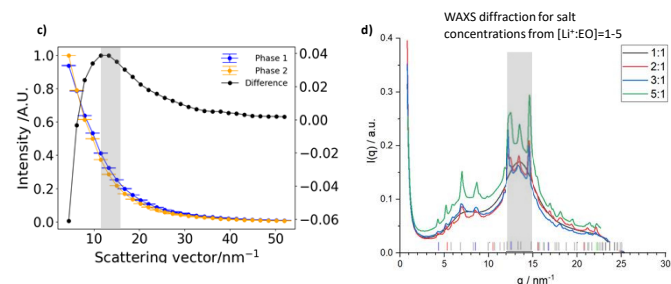
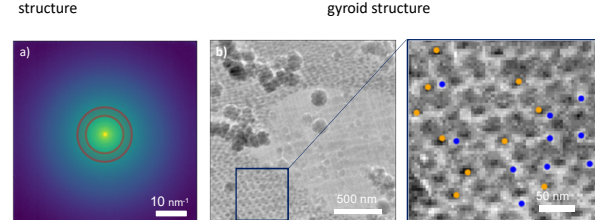
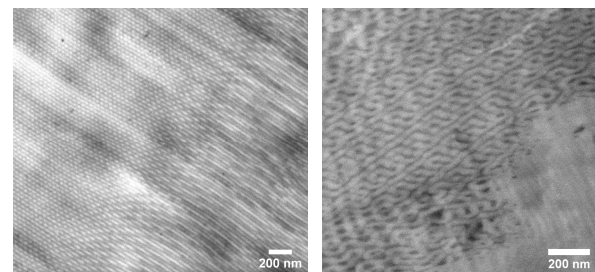


References

- [1] Zhou, Z.; Zou, R.; Zhang, P. Deciphering the role of tetrahydrofuran residue in the poly(ethylene oxide)/LiTFSI hybrid used for secondary battery electrolyte, *Giant*, 6, 100056 (2021).



polymer chain lengths, given by the molecular weight M_n , as well as an optical comparison based on photos of the dry and phase separated pure BCP and the corresponding electrolyte membranes



Conclusion

- We found that increasing the LiTFSI concentration leads to phase separation, whereby a solid polymer PEO/LiTFSI/THF-phase is formed.
- Increasing the salt concentration has two synergistic effects:
 - the formation of a superionic PEO/LiTFSI/THF phase
 - a phase transition from the hexagonal cylinder phase to a gyroid bicontinuous network providing continuous conduction paths.
- Both effects concomitantly lead to exceptionally high Li^+ ion conductivities in the range of 0.01 S/cm to 0.1 S/cm ,

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