Technische Universität Braunschweig

BATTERIETAGUNG 28.-30. März 2022 | LENA | BLB Battery LabFactory Braunschweig | iPAT Institut für Partikeltechnik

Comparison of integrated active and passive fillers for the enhancement of the ionic conductivity of polymer-based electrolytes for solid-state batteries

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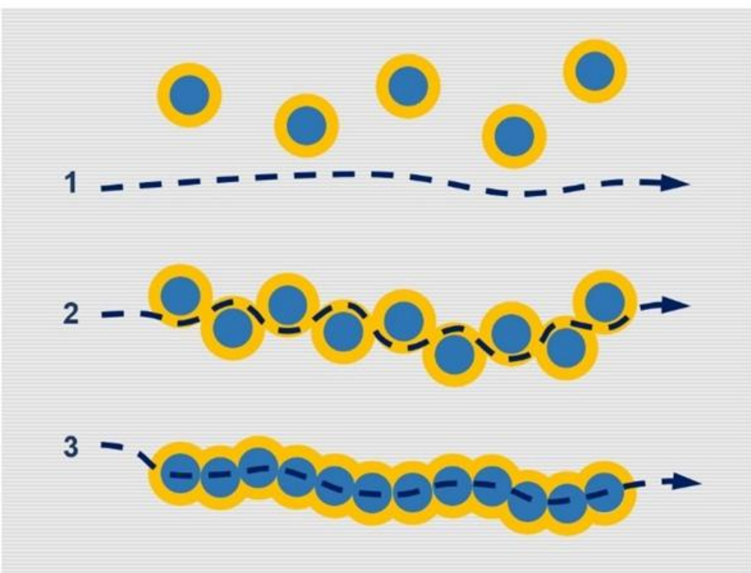
Introduction

Hybrid solid electrolytes (HSEs) containing ceramic filler particles in a polymer matrix can combine the advantages of organic and ceramic materials. Thereby, ceramic fillers can be divided into two categories.

Passive fillers: Li-deficient and do not directly participate in the Li⁺ transport process. Improving the ionic conductivity of the polymer electrolyte by suppressing its crystallization, especially for polyethylene oxide (PEO)

Active fillers: Containing Li-ions in their structure, contributing to the long-range Li-ion transport while improving the mechanical and electrochemical properties. e.g. $Li_7La_3Zr_2O_{12}$ (LLZO); good Li-ion conductivity ($\sigma \leq 10^{-3}$ S cm^{-1}), stable against the Li metal electrode, and wide potential window



Possible Li⁺ pathway in HSEs [1]

With passive fillers:
Path 1: Through the polymer
Path 2: Through the SCR

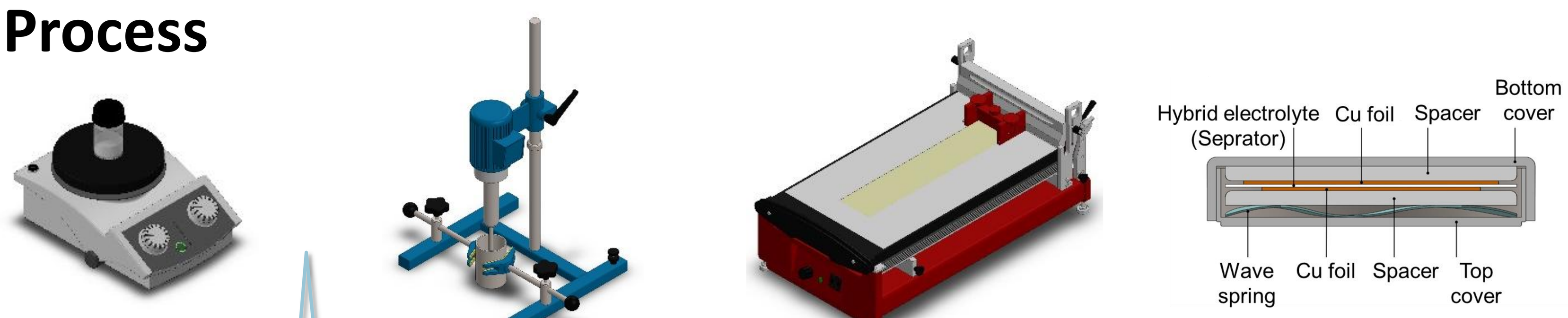
With active fillers:
Path 1: Through the polymer
Path 2: Through the SCR
Path 3: Through the ceramic particles

Polymer | Li⁺ pathway | Ceramic fillers | Space Charge Region (SCR)

- This work demonstrates a comprehensive evaluation of the ionic conductivity and transport pathways of Li⁺ in HSEs by comparing the integration of passive and active fillers into PEO-based electrolytes.

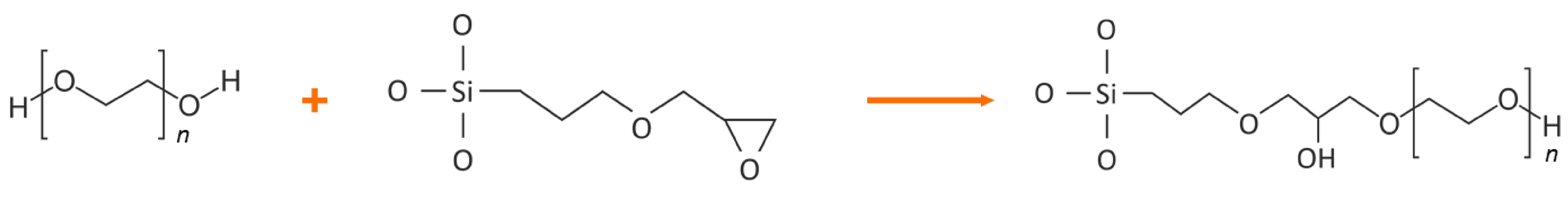
Preparation of Electrolytes

Process



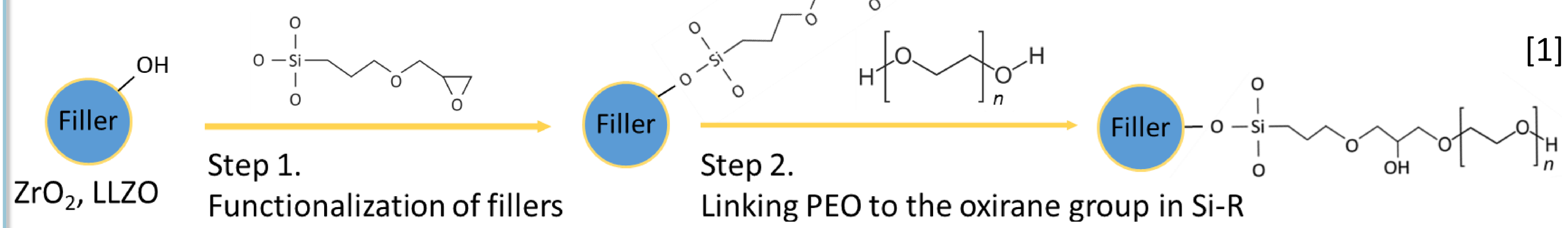
Precursor preparation | Sonication | Tape casting | Coin cell building

- Filler-free polymer electrolytes (PEO-GMPTS)

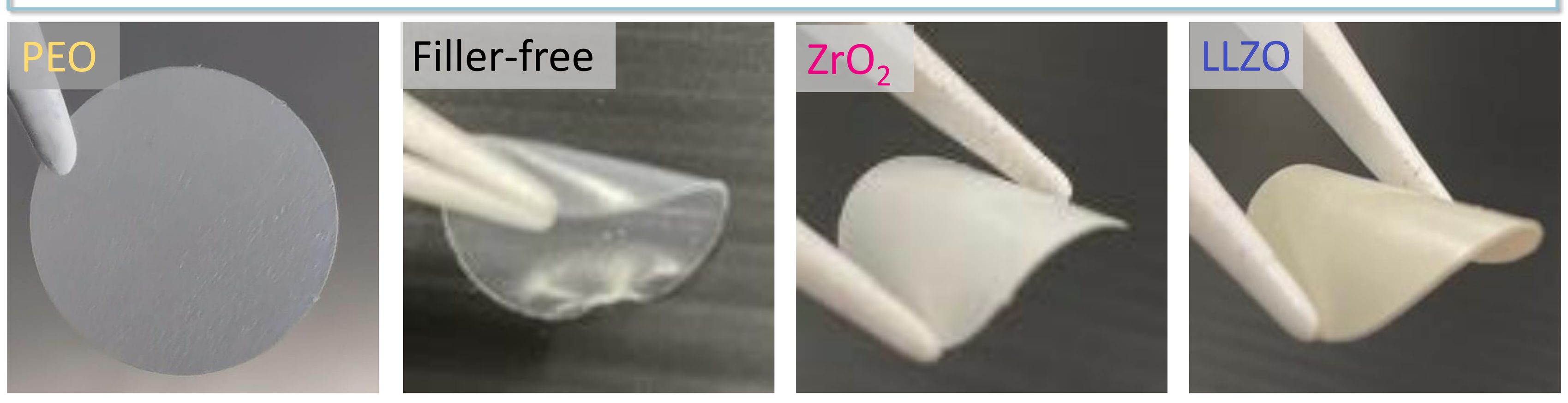


Polyethylene oxide (PEO) | (3-glycidyloxypropyl)trimethoxysilane (GMPTS, Si-R)

- Hybrid electrolytes (PEO-ZrO_2-GMPTS & PEO-LLZO-GMPTS)

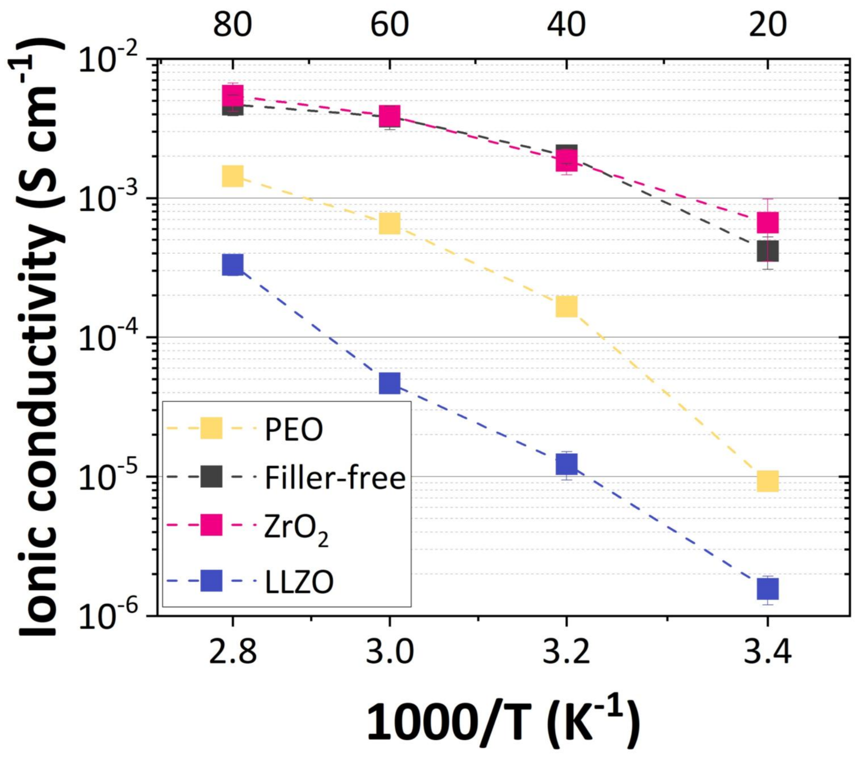


ZrO_2 and LLZO were selected as passive and active fillers for the comparison. The surface of both fillers was modified with ligands to reduce their interfacial resistance to the polymer. 15 vol.% of fillers were added into the polymer.



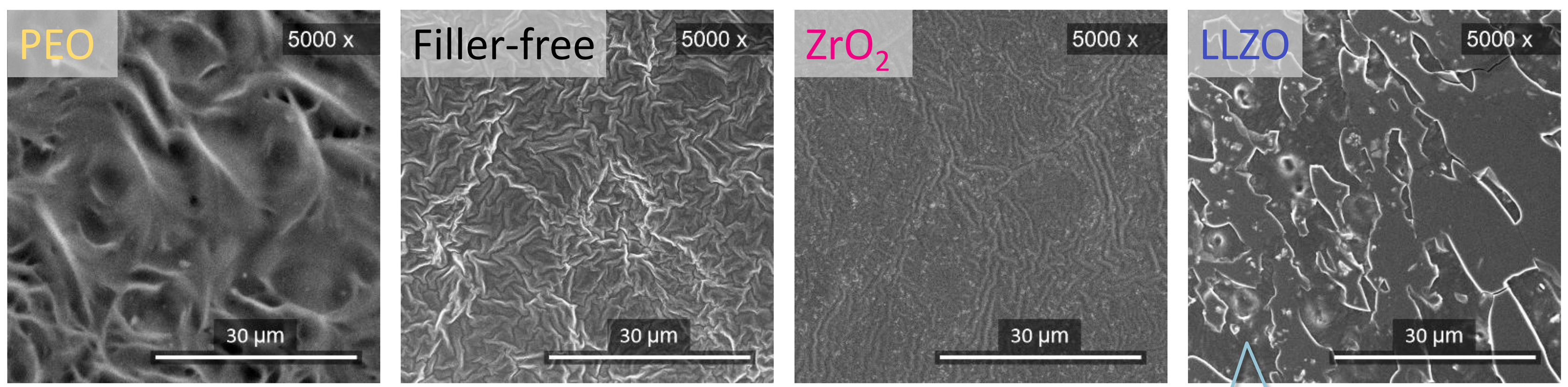
Filler-free vs. Passive vs. Active fillers

Ionic conductivity of electrolytes

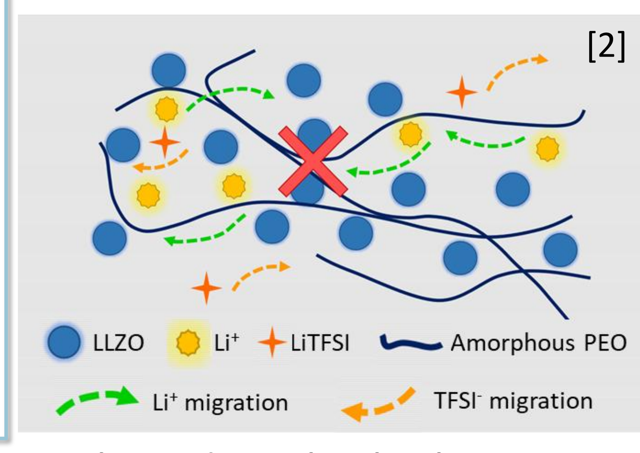


- Filler-free samples which only contain PEO–GMPTS have higher ionic conductivity than the pure PEO electrolyte especially at 20 °C and 40 °C.
- HSE with ZrO_2 fillers shows the highest ionic conductivity, while HSE with LLZO fillers has the lowest.

Morphologies of electrolytes



- Filler-free electrolyte containing the ligands shows fibrous structure
- HSE with ZrO_2 fillers has a homogenous and uniform distribution of particles within the fibrous structure
- HSE with LLZO fillers shows a glassy surface with poor distribution of particles



- The low ionic conductivity of LLZO-based HE is attributed to the high content of heavy LLZO fillers with non-uniform distribution
- The excessive LLZO fillers blocked the Li⁺ transport path within the PEO

Conclusions

- Effects of LLZO and ZrO_2 fillers and silane ligands on the overall performance of PEO-LiTFSI-based hybrid solid electrolytes were investigated
- Ionic conductivity: $\sigma_{LLZO} < \sigma_{PEO} < \sigma_{Filler\text{-}free} < \sigma_{ZrO_2}$
- Ion transport mechanism is still dominated by the polymer phase
- The addition of silane ligands into polymer electrolyte impedes the crystallization of PEO, enhancing ionic conductivity at RT
- Fillers with a large volume content and high density interfere with Li-ion transport due to non-homogeneous distribution

References

[1] E. Kuhnert, L. Ladenstein, A. Jodlbauer, C. Slugovc *et al.*, Lowering the Interfacial Resistance in $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$|Poly(Ethylene Oxide) Composite Electrolytes. *Cell Reports Physical Science* 201.20

[2] G. Tian, *Study on lithium ion migration in the composite solid electrolyte for lithium metal batteries*. Dissertation, Karlsruher Instituts für Technologie, 2018.

Acknowledgement

We would like to acknowledge the funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany´s Excellence Strategy – EXC 2163/1 -Sustainable and Energy Efficient Aviation – Project-ID 390881007.

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