Development of silicon polymer electrodes for all-solid-state lithium-ion batteries

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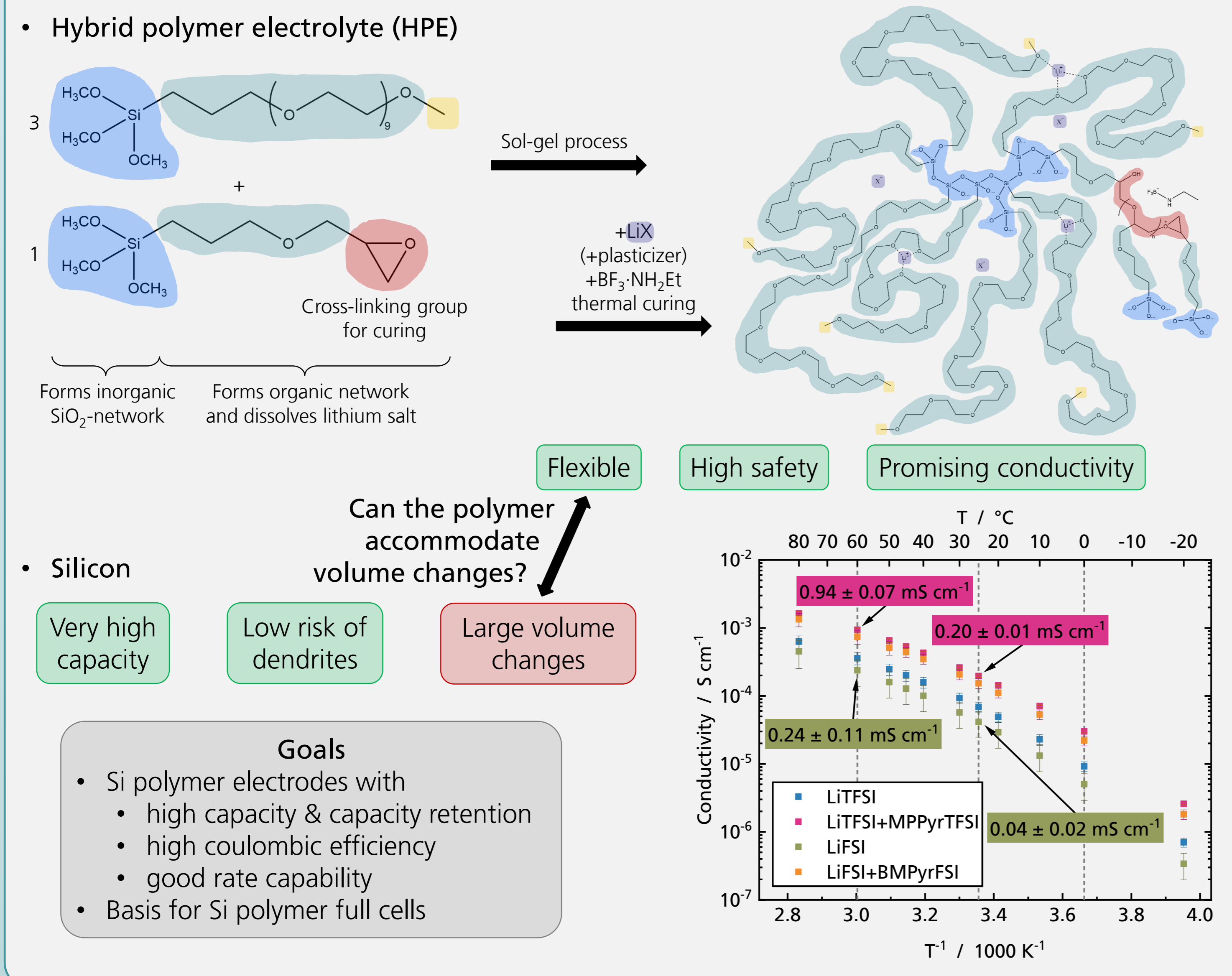[b]Chemical Technology of Materials Synthesis, Faculty of Chemistry and Pharmacy, Julius-Maximilians-University Würzburg, Röntgenring 11, 97070 Würzburg, Germany
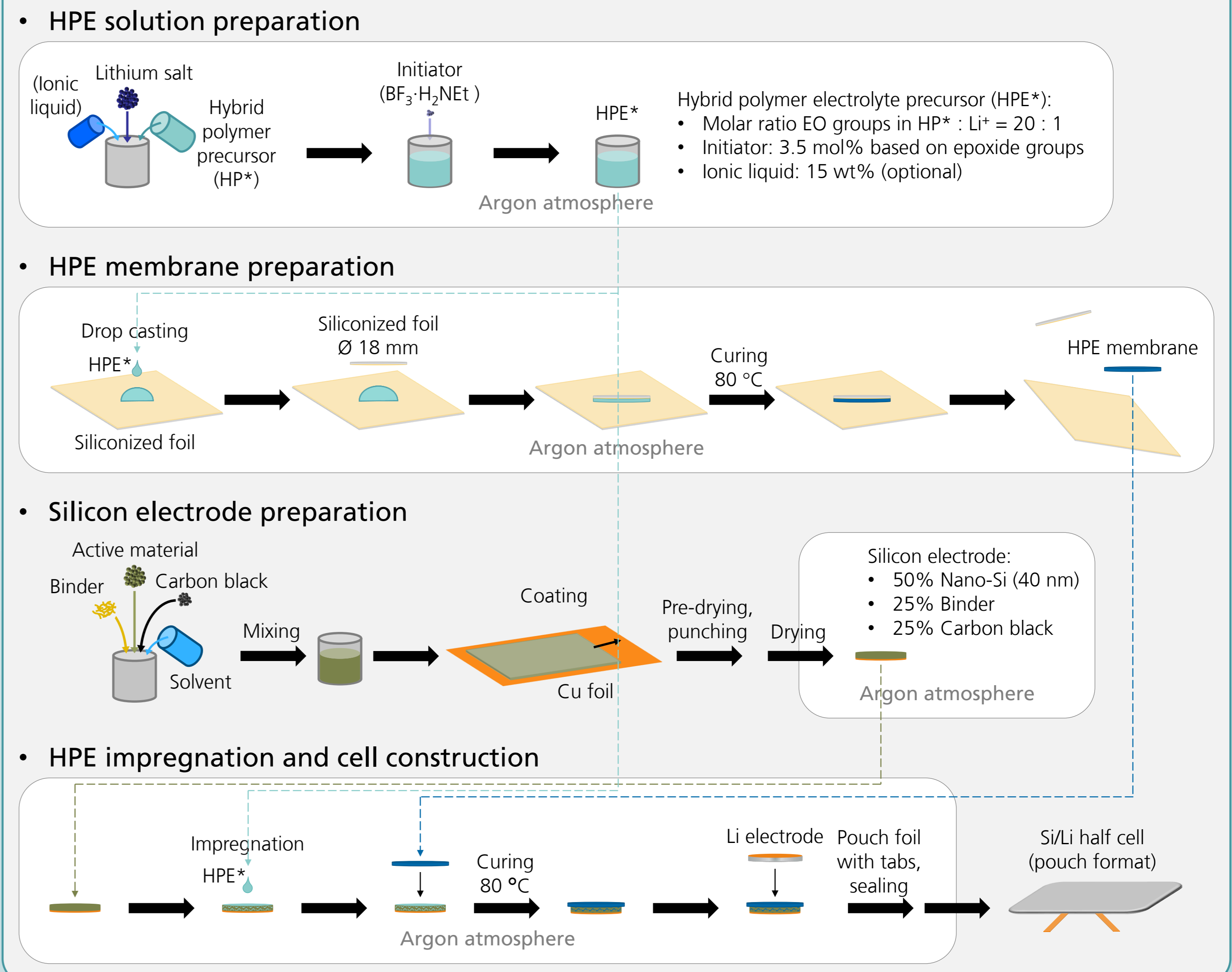
Introduction

The growing market for battery electric vehicles has resulted in an increasing demand for battery materials that meet the requirements of low cost, high safety, long lifetime and high energy density [1]. Solid-state batteries offer an opportunity for enhancement in several of these areas. For example, the absence of a flammable, toxic and potentially leaking liquid electrolyte clearly enhances battery safety [2]. To achieve a high energy density, the positive and negative electrode materials must have high specific capacities along with a high and low reduction potential, respectively. For the negative electrode, silicon fulfills these criteria with a very high theoretical specific capacity of 3579 mAh g^{-1} [3] and a suitable delithiation potential of approx. 0.4 V vs. Li/Li$^+$ [3,4]. Also, in contrast to lithium metal electrodes, silicon electrodes are significantly less prone to the dendrite growth that would cause safety issues and limit the cycle life. The main challenges of silicon electrodes in cells with a liquid electrolyte result from the large volume changes of silicon during (de)lithiation. A flexible polymer electrolyte may help to compensate these volume changes and thereby minimize the related issues like disintegration of the electrodes and irreversible loss of lithium.

In this work, the development of nano-silicon polymer electrodes is presented. The anode contains a hybrid inorganic-organic polymer electrolyte (HPE). The HPE used in this work is based on a molecular hybrid polymer with polyether organic domains and an inorganic SiO$_2$ network [5]. The electrochemical performance of the silicon polymer electrodes is examined in solid-state cells with a lithium counter electrode. The rate capability, capacity retention as well as side reactions in the first cycle are identified as challenges to be addressed in the HPE-based cells. Different approaches like the variation of the conductive salt and the use of plasticizers are implemented.
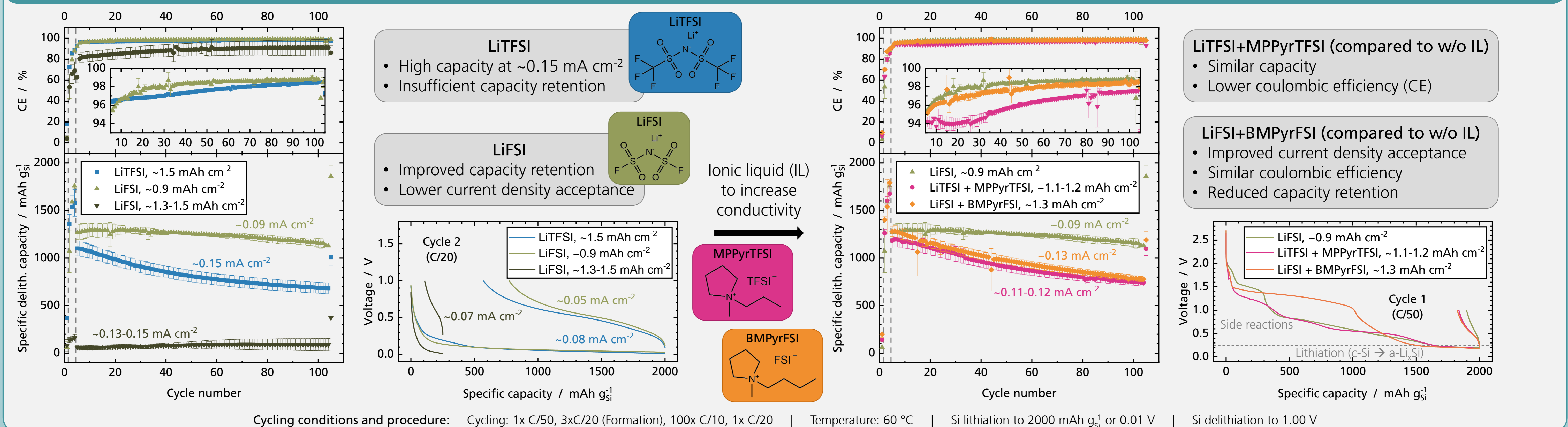
Hybrid polymer electrolyte and silicon

Electrolyte, electrode and cell preparation

Influence of conductive salt and ionic liquid

Cycling conditions and procedure: Cycling: 1x C/50, 3xC/20 (Formation), 100x C/10, 1x C/20 | Temperature: 60 °C | Si lithiation to 2000 mAh g$_{Si}^{-1}$ or 0.01 V | Si delithiation to 1.00 V

Conclusions and outlook

Silicon polymer electrodes were successfully prepared via an infiltration-based route and tested in cells with a hybrid polymer membrane as electrolyte and a lithium counter electrode. Electrodes with an areal capacity of 0.9–1.5 mAh cm^{-2} achieve a high capacity of approx. 1000–1400 mAh g$_{Si}^{-1}$ at a C-rate of C/10. The use of LiFSI instead of LiTFSI as conducting salt significantly improves the capacity retention, however, at the expense of reduced current density acceptance due to the lower conductivity of the LiFSI-containing HPE. The addition of an ionic liquid increases the electrolyte conductivity at 60 °C from (0.36±0.08) to (0.94±0.07) mS cm^{-1} in the TFSI$^-$-based HPE and from (0.24±0.11) to (0.74±0.17) mS cm^{-1} in the FSI$^-$-based HPE. In the TFSI$^-$-containing Si/Li cells, the IL leads to a decrease of the coulombic efficiency while in the FSI$^-$-based cells, the IL does not significantly influence the CE. The capacity retention is not as good as in the LiFSI-containing cells without IL.

In addition to the simultaneous achievement of a high current density acceptance and a good capacity retention, significant side reactions and a low CE in the early cycles are the main challenge to be addressed. This is particularly important with regard to the transition from half cells to full cells, where the lithium inventory is limited. Assuming that the side reactions consume lithium, effective strategies to counter the lithium loss are critical. Therefore, further steps will include full cell testing to investigate the role of a limited lithium inventory. In case lithium loss is confirmed to inhibit long-term cycling in full cells, further additives, pre-lithiation of the silicon electrode and overdimensioning of the positive electrode will be considered to reduce or compensate lithium loss.

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