

Novel semi-solid electrolytes for Li-based batteries

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Electrolytes of relevance for high performance batteries have to fulfill a variety of restrictive criteria: Not only is high Li^+ conductivity a necessary condition to avoid too high losses, also an anion contribution as low as possible is desired as otherwise concentration polarization occurs [1]. Furthermore, the electrolyte should be mechanically stable. Beyond that, it should wet the electrodes, which is particularly crucial if nano-structured electrodes are used, as best achieved by liquid electrolytes. It goes without saying that the electrolytes must be — at least kinetically — stable against the electrode phases and of course not being too costly or environmentally problematic. Based on our theoretical and experimental work we offer two solutions.

1) One elegant material class are the “soggy sand electrolytes” which we proposed. They show a semi-solid consistency but can still penetrate nano-structures (cf. Fig. 1 and Fig. 2c).

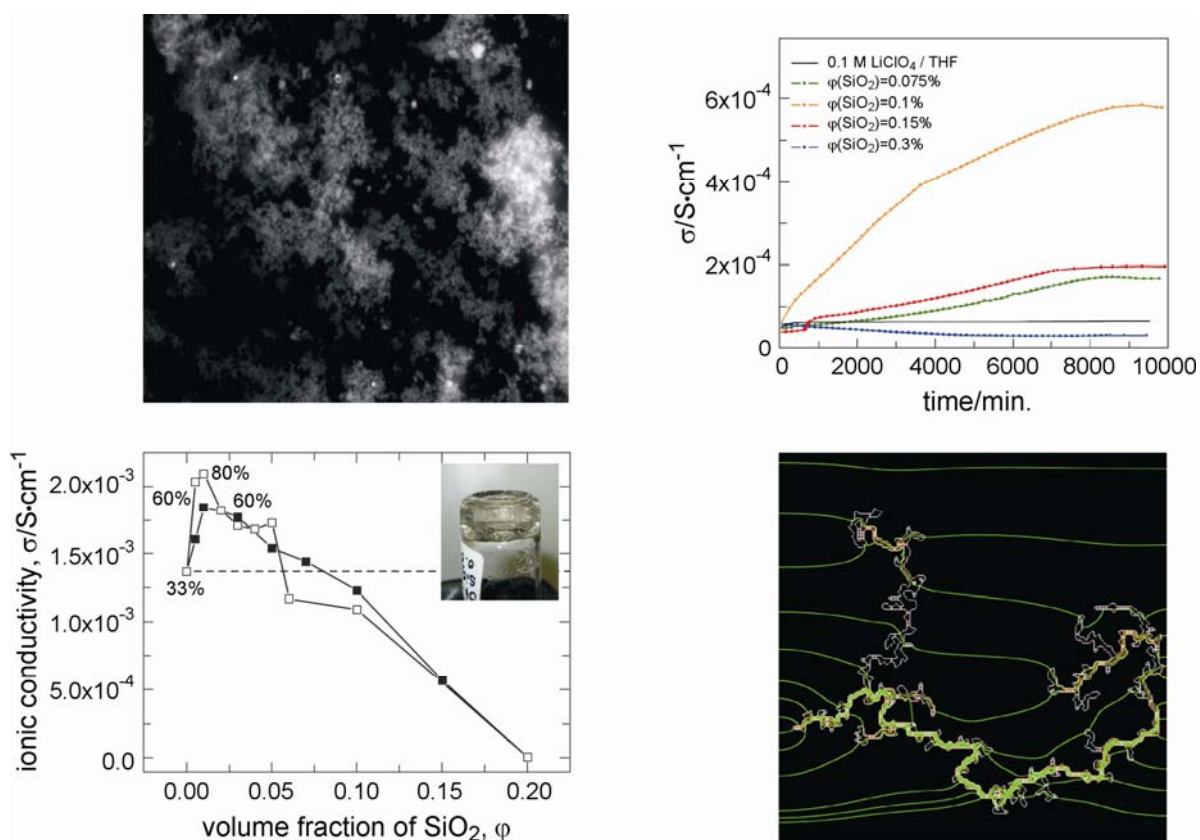


Figure 1: The figure shows a confocal microscopy picture of the silica network during formation process (top, left hand side), the time evaluation of the overall ion conductivity (top, right hand side), the steady-state conductivity for soggy sand electrolytes (together with cationic transference numbers) as a function of silica content (bottom, left hand side) and the current lines along clusters and within electrolyte as obtained from modeling (bottom, right hand side).

They derive from usual liquid salt containing liquid solvents by adding fine-dispersed nano-particles that are surface-acidic enough as to adsorb the anions. Since as a consequence of adsorption ion pairs are dissociated within the space charge zone they show under certain conditions higher Li^+ conductivities than the pure electrolyte. The same is true for the transference number. In this way transference numbers can be increased from typically 40% to 80%, as indicated in Fig. 1c. Recent work of us concentrated on borate esters and particular on oligo methylene glycol as solvent.

A critical point is network stability in these soggy sand electrolytes. Recently the combination of a variety of methods such as laser confocal spectroscopy, rheological measurements, electrochemical investigations together with Monte-Carlo and Finite Element calculations allowed us to achieve quite a complete picture [2].

The initially rather stable colloidal dispersion develops into a percolating network (see Fig. 1a). This network formation could be followed by in-situ conductivity measurements (see Fig. 1b). Studying the kinetics of network formation is certainly an achievement that is of general interest in many other areas of physics and chemistry such as colloid chemistry and physics.

Once the network is formed it coarsens via surface diffusion which is a self-decelerating process (as the number of next neighbors appears in the activation energy) and in some cases practically comes to a stand-still (see stationary curve 1c). This is obvious from the experiment as well as from Monte-Carlo simulation. Figure 1d displays current-lines calculated via finite-elements using a typical fractal cluster from Monte-Carlo simulations. The time-dependence of the calculated (2D) conductivity semi-quantitatively matches the experimental (3D) results.

2) An even more efficient immobilization of the anions is naturally achievable by covalent bonding (see Fig. 2b). Here we ion-exchange the proton in proton-conducting polyelectrolytes (Fig. 2a) by Li^+ . We used novel sulfonated poly(phenylene-sulfone) polymers invented by us earlier. Conductivities achieved in this way are even better than in the previous case and the transfer number is practically 100%. As the necessary exchange of water by organic solvents leads to partial dissolution, the consistency is, as in the previous case, semi-solid guaranteeing good contact to the electrodes [3].

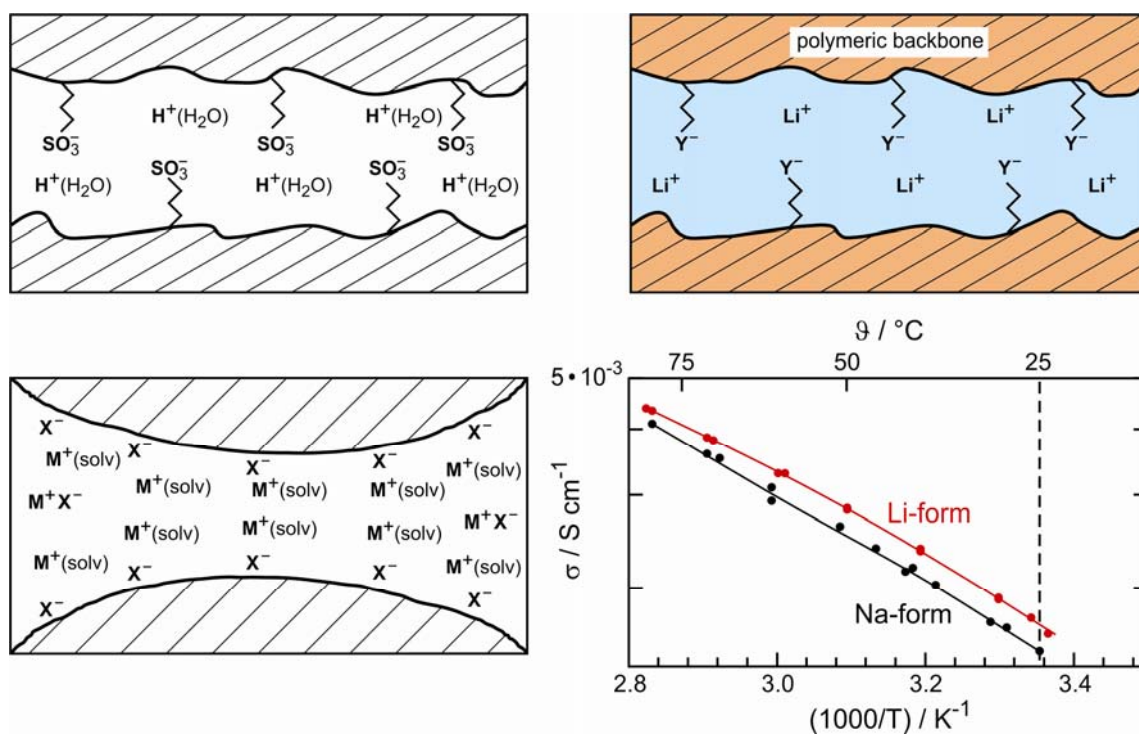


Figure 2: Similarity of the local situation in polymeric proton conductors (top left hand side) with the soggy sand electrolytes (bottom, left hand side). Ion exchange of proton vs. lithium ion (top, right hand side) leads to excellent pure cation conductors (bottom, right hand side).

A future challenge is a detailed understanding of the concentration and mobility of free and bound species and their behavior during polarization which can be achieved on the basis of the concept of “conservative ensembles” which was constructed as to handle transport of species which undergo fast internal reaction processes [4]. In order to achieve this we are combining impedance measurements, polarization measurements, PFG-NMR measurements for F- and Li-nuclei as well as modeling.

References:

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