

Transport Processes in Soft Ionic Materials

Monika Schönhoff

Institute of Physical Chemistry, University of Muenster, Germany

In the search for advanced electrolytes in Li ion batteries, ternary polymer gel electrolytes consisting of ionic liquid, polymer and Li salt are suitable materials to yield a compromise between sufficient conductivity and mechanical stability. The transport processes are however influenced by complex mutual interactions of the molecular constituents. Multinuclear NMR of ^7Li , ^{19}F and ^1H employing dynamic NMR methods provides excellent means for detailed quantitative analysis of the local dynamics, diffusivities and electrophoretic mobilities. Here, we report on systems based on the poly(ionic liquid) PDADMATFSI [1] to address the question in how far charged chains are superior polymeric constituents in ternary gels in terms of their ability to enhance Li^+ conduction.

Polyelectrolyte multilayers (PEM) prepared by Layer-by-Layer (LbL) self-assembly are, due to their inherently low thickness, interesting candidates for applications as ion conductors. With this motivation we are studying fundamental charge transport properties by impedance spectroscopy. With protons as charge carriers, the dc conductivity shows a strong exponential dependence on humidity [2]. Furthermore, PEM are soft and easily swellable in suitable solvent environment, which provides further functionalities, such as tunable molecular uptake and release, triggered by pH variation. Furthermore, we have shown that polyelectrolytes can exhibit exponential or linear growth behavior in dependence on the assembly pH [3].

When mixing oppositely charged polyelectrolytes, a solid polyelectrolyte complex (PEC) phase or a liquid, viscous coacervate phase can be formed. Here, we study frequency-dependent rheological or impedance spectra on coacervates or solid PEC, resp., where unique scaling concepts can be demonstrated: In analogy to the time-temperature superposition principle a concept of time-humidity superposition was established for PEC [4], and a scaling concept of time-pH superposition in the case of coacervates made from weak polyelectrolyte. These concepts imply that spectra are just shifted along the axes to be superimposed to a "master curve". The validity of the latter scaling concept implies identical dynamic mechanisms being relevant in coacervates formed at different pH, in spite of their different viscosities and degrees of dissociation on the chains of the weak polyelectrolyte PAA.

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