Concentration Dependent Self-Diffusion Coefficients of Aqueous Electrolyte Solutions in Bulk Phase and Confined in Porous Glasses Measured by Pulsed Field Gradient NMR

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1. Introduction

In current realisations of high-power lithium-ion batteries one of the main safety deficiencies is generated by the liquid electrolyte, which, e.g., expands at increasing temperatures and therefore damages the internal cell structures of the battery [1]. Efforts for building a dry electrolyte by making use of ion conducting solids were not able to reach satisfying lithium-ion conductivities at ambient temperatures, see e.g. [2]. Thus, these kinds of materials are not applicable in high-current battery applications. A new concept could be realised for instance via a micro- and/or mesoporous solid where the pore space is filled with an ion conducting media. This would combine the mechanical and thermal stability advantages of a solid with the advantage of the high ion conductivity in liquid electrolytes.

To design such a material, one has to understand the phenomena of the high ion conductivity in fluids and elucidate the physical mechanisms of the ion transport. Additionally, the surface of the porous media needs to be modified in such a way that a bulk-like ion transport mechanism is supported inside the meso- and/or micropores of the solid.

2. Experimental

The pulsed field gradient (PFG) nuclear magnetic resonance (NMR) method [2] has been used to study the molecular water self-diffusion and the ionic self-diffusion in aqueous electrolyte solutions of alkali metal chlorides for bulk solutions and for these solutions confined in porous glass monoliths. The PFG NMR offers the possibility to clearly distinguish between the individual NMR-active atomic nuclei. Therefore, it provides a discrete observation of the individual diffusing species.

An innovative ansatz, which combines well-known fundamentals with *a priori* concepts, is given to derive a comprehensive description for the dependence of the self-diffusion coefficient on the alkali metal chloride concentration. The developed model was successfully fitted to the PFG NMR data in order to emphasize the applicability of the presented model.

3. Results

For the concentration dependency of the self-diffusion coefficients in alkali metal chloride electrolytes, the so far known theoretical predictions, e.g. [4,5], are found to be inaccurate. The presented novel model is validated by the experimental data as measured by PFG NMR diffusiometry (see exemplary Fig. 1). Analogue to the investigation of polystyrenes dissolved in benzene and confined by macroporous acrylate-based monoliths [6], the characteristic concentration dependencies found in the bulk solutions remain unchanged if the electrolyte self-diffusion occurred in the porous glass monoliths. However, the self-diffusion coefficients were reduced in the monoliths by a constant factor, which is independent of the alkali metal chloride concentration. This constant factor represents the tortuosity of the porous glass monoliths.

The presented results outline a set of initial values needed for further improvements of the porous glass in such a way that it will be possible to operate as a semi-dry electrolyte in a high-power lithium-ion battery setup.
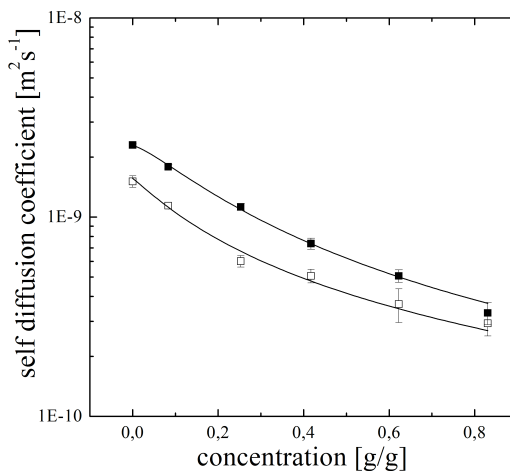

Fig. 1: Concentration dependent self-diffusion coefficient of water in LiCl(aq) in bulk (full symbols) and confined by porous glass monoliths (open symbols). The solid lines represent a fitting by the novel model. If the electrolyte is confined by the porous glass, the bulk self-diffusion coefficients were reduced by a factor of about 1.5 which represents the tortuosity factor.

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