Investigation of Li Diffusion and Transference Numbers of Ionic Liquid Based Electrolytes by ^{7}Li NMR

Ralf Heinzmann[1], Andreas Hofmann[2], Michael Schulz[2], Sylvio Indris[1]

[1]Institute of Nanotechnology (INT), Karlsruhe Institute of Technology, P.O. Box 3640, 76021 Karlsruhe, Germany

[2]Institute of Applied Materials (IAM-WPT), Karlsruhe Institute of Technology, P.O. Box 3640, 76021 Karlsruhe, Germany

We investigated the conductivity of different ionic liquid based electrolytes together with the Li ion diffusion coefficients determined from field gradient nuclear magnetic resonance spectroscopy. Five different systems were chosen which cover a broad range of conductivities as well as Li ion diffusion coefficients. 1M $LiPF_6$ in EC/DMC (1:1 wt%) is a standard electrolyte used in Li-ion batteries and 0.01M LiCl in H_2O was used as reference system with known ionic conductivity (0.11 S/m) and known diffusion coefficient ($1.03 \cdot 10^{-9}$ m^2/s) at 298 K. Further systems in this study were 0.3M Li-TFSI in MPPyrr-TFSI, 0.5M Li-TFSI in MPPyrr-TFSI/EC (7:3 wt%) and 1.3M Li-TFSI in DMMA-TFSI/PC (1:1 wt%) which consist of Li salts dissolved in mixtures of an ionic liquid and an organic solvent. The highest conductivity over the whole temperature range is obtained for 1M $LiPF_6$ in EC/DMC while the lowest conductivity is observed for 0.01M LiCl in H_2O, caused by the small concentration of Li ions. All systems could be described by an Arrhenius-type behavior with activation energies between 0.16 eV and 0.33 eV. DOSY NMR measurements give diffusion coefficients in the range from $6 \cdot 10^{-12}$ to 10^{-9} m^2/s. From this, transference numbers ranging from 0.76 for 1M $LiPF_6$ in EC/DMC to 0.02 for 0.3M Li-TFSI in MPP-TFSI were derived. These explain the poor performance of 0.3M Li-TFSI in MPP-TFSI in the Li batteries in contrast to 1.3M Li-TFSI in DMMA-TFSI/PC which has an even slightly smaller overall conductivity and still shows reasonable performance in the batteries.