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Identifying Fast Li Ions at the Interfaces in Composites of Ionic Liquids and Li Salts by ^{7}Li NMR Relaxation Measurements

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New electrolytes are needed in lithium-based battery research in order to increase both safety and electrochemical performance. The mixture of an ionic liquid with a lithium salt represents a conceptually new class of electrolytes for high-temperature lithium batteries, termed “ionic liquid-in-salt” [1]. We used ^{7}Li NMR spectroscopy, see, *e.g.*, [2], to study both local electronic structures and Li^+ self-diffusion in LiTFSI and $\mathrm{Li}_x\mathrm{EMIM}_{(1-x)}\mathrm{TFSI}$ with $x = 0.9$. The NMR spectra, recorded under static conditions, perfectly agree with the results from differential scanning calorimetry. Upon heating to 513 K they clearly reveal several double phase regions; the known solid-state phase transformation of LiTFSI can be well recognized by the change of the quadruple powder pattern of the ^{7}Li NMR spectra of LiTFSI. A rapid increase in long-range ion conductivity, within two orders of magnitudes, takes place when the 1/2 EMIMTFSI/LiTFSI phase starts to melt. This behaviour can also be monitored by temperature-variable ^{7}Li spin-lattice relaxation (SLR) NMR. If recorded up to delay times of 1000 s, the pronounced bi-exponential ^{7}Li SLR NMR transients found directly reveal a subset of highly mobile Li ions, partly identified as $[\mathrm{Li(TFSI)_2}]^-$, which can be well discriminated from the response of pure LiTFSI. Most likely, this Li^+ sub-ensemble, which is anticipated to be located at the LiTFSI:EMIMTFSI interfacial regions, is responsible for the enhanced ion conductivity observed.

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