

Identifying Fast Li Ions at the Interfaces in Composites of Ionic Liquids and Li Salts by ^7Li 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 ^7Li NMR spectroscopy, see, *e.g.*, [2], to study both local electronic structures and Li^+ self-diffusion in LiTFSI and $\text{Li}_x\text{EMIM}_{(1-x)}\text{TFSI}$ 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 ^7Li NMR spectra of LiTFSI . A rapid increase in long-range ion conductivity, within two orders of magnitudes, takes place when the 1/2 $\text{EMIMTFSI}/\text{LiTFSI}$ phase starts to melt. This behaviour can also be monitored by temperature-variable ^7Li spin-lattice relaxation (SLR) NMR. If recorded up to delay times of 1000 s, the pronounced bi-exponential ^7Li SLR NMR transients found directly reveal a subset of highly mobile Li ions, partly identified as $[\text{Li}(\text{TFSI})_2]^-$, 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 $\text{LiTFSI}:\text{EMIMTFSI}$ interfacial regions, is responsible for the enhanced ion conductivity observed.

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