**New Insights into Li-Ion Transport in Composite Electrolytes**

Zheng, J. (FSU, Chemistry & Biochemistry); Feng, Z. (Oregon State U., Chemical, Biological & Environmental Engineering); Chan, C. (Arizona State U., Materials Science & Engineering); Hu, Y.-Y. (FSU, Chemistry & Biochemistry, NHMFL) and Huang, K. (U. of South Carolina, Engineering & Computing)

**Introduction**

The current generation of rechargeable Li-ion batteries (LIBs) employ liquid electrolytes, which are toxic, flammable and corrosive, resulting in significant safety issues. To address these safety issues in addition to improving the energy density of LIBs, solid electrolytes are considered as a promising solution. Ceramic–polymer composite electrolytes are promising for improved ionic conductivity, good stability and compatibility with electrodes, and excellent mechanical properties that cannot be achieved with conventional ceramic or polymer ion conductors. In composite systems, Li ions can transport via the polymer matrix, inorganic fillers, the organic-inorganic interfaces, or a combination of the three. Li-ion transport pathways, together with active Li-ion concentration and Li-ion mobility, determine the ionic conductivity of Li electrolytes. Thus, exploring the mechanism of Li-ion transport is crucial, but challenging. With 6Li → 7Li tracer-exchange NMR, Li-ion transport pathways within a series of Li7La3Zr2O12 (LLZO)-poly(ethylene oxide) (PEO) composite electrolytes are identified.1–3

**Experimental**

6Li → 7Li tracer exchange: a biased potential was applied to a symmetric cell made with 6Li-enriched Li metal foil as the electrodes, 6Li|composite electrolyte|6Li, to drive 6Li ions from one 6Li electrode to exchange with 7Li in the composite electrolyte before reaching the other 6Li electrode. The direction of the applied potential was switched at 5 min intervals. The test was carried out on a LANHE (CT2001A) battery testing system.

6Li magic-angle spinning (MAS) NMR experiments were performed on a Bruker Avance III-500 spectrometer with a 2.5 mm Bruker HXY triple-resonance probe. The sample was spun at 25 kHz and the spectra were collected at the 6Li Larmor frequency of 73.6 MHz. LiCl with the 6Li shift at 0 ppm was used as a reference.

**Results and Discussion**

The 6Li MAS NMR spectra of pristine composite electrolytes and those after tracer exchange are shown in Fig. 1. During 6Li → 7Li tracer exchange process, 6Li ions partially replace 7Li ions in the composite electrolytes. Therefore, the components comprising Li-ion transport pathways will be preferentially 6Li-enriched with repeated electrochemical cycling. Quantitative evaluation of the change in 6Li amount for each component within the composite electrolyte will reveal the preferred pathways for Li-ion transport.

The results are depicted in the schematic diagram of Li-ion pathways. With low LLZO content (< 20 wt %), LLZO-PEO (LiTFSI) composites behave as a polymer electrolyte modified by LLZO. With increasing amount of LLZO to a critical point, LLZO particles connect to form a percolated network, thus LLZO-PEO (LiTFSI) composites function as a ceramic electrolyte. Moreover, with the additive, tetraethylene glycol dimethyl ether (TEGDME), Li-ion conduction is mainly through TEGDME-modified polymer phase. The presence of TEGDME additive in PEO has been shown to significantly enhance Li-ion conduction.

**Fig.1** Comparison of 6Li MAS NMR on pristine and tracer-exchanged composite electrolytes and schematic of Li-ion transport pathways.

**Conclusions**

The study has employed tracer-exchange NMR to determine Li-ion transport pathways in typical LLZO-PEO composite electrolytes with various compositions. This study demonstrates that solid-state NMR is a particularly useful tool for determining the contributing factors for ion conduction. The methodology and results from this work will facilitate the development of high-performance composite electrolytes for rechargeable solid-state batteries.

**Acknowledgements**

Financial support from NSF DMR-1553519, CBET-1340269, DMR-1508404, and the AAAS Marion Milligan Mason Award. Work was performed at the NHMFL supported by NSF DMR-1157490 and the State of Florida.

**References**

[1] Zheng, J., *et al.,* Angew. Chem. Int. Ed., **55**, 12538-12542 (2016). [2] Zheng, J., *et al.,* J. Mater. Chem. A, **5**, 18457–18463 (2017). [3] Yang, T., *et al.,* ACS Appl. Mater. Interfaces, **9**, 21773–21780 (2017).