



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

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### 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  ${}^6\text{Li} \rightarrow {}^7\text{Li}$  tracer-exchange NMR, Li-ion transport pathways within a series of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO)-poly(ethylene oxide) (PEO) composite electrolytes are identified.<sup>1-3</sup>

### Experimental

${}^6\text{Li} \rightarrow {}^7\text{Li}$  tracer exchange: a biased potential was applied to a symmetric cell made with  ${}^6\text{Li}$ -enriched Li metal foil as the electrodes,  ${}^6\text{Li}|\text{composite electrolyte}|{}^6\text{Li}$ , to drive  ${}^6\text{Li}$  ions from one  ${}^6\text{Li}$  electrode to exchange with  ${}^7\text{Li}$  in the composite electrolyte before reaching the other  ${}^6\text{Li}$  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.

${}^6\text{Li}$  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  ${}^6\text{Li}$  Larmor frequency of 73.6 MHz. LiCl with the  ${}^6\text{Li}$  shift at 0 ppm was used as a reference.

### Results and Discussion

The  ${}^6\text{Li}$  MAS NMR spectra of pristine composite electrolytes and those after tracer exchange are shown in Fig. 1. During  ${}^6\text{Li} \rightarrow {}^7\text{Li}$  tracer exchange process,  ${}^6\text{Li}$  ions partially replace  ${}^7\text{Li}$  ions in the composite electrolytes. Therefore, the components comprising Li-ion transport pathways will be preferentially  ${}^6\text{Li}$ -enriched with repeated electrochemical cycling. Quantitative evaluation of the change in  ${}^6\text{Li}$  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.

### Conclusions

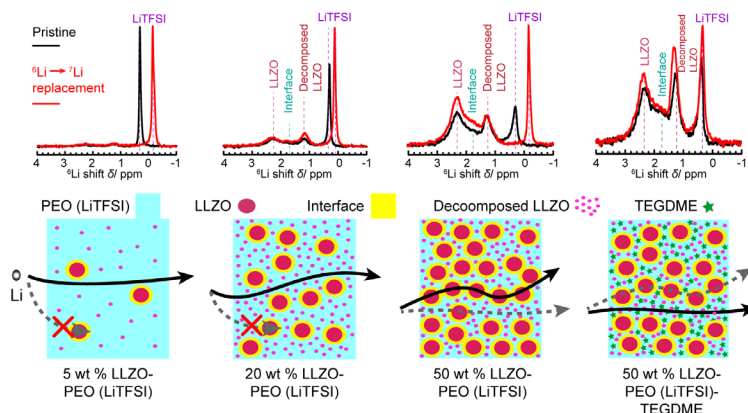
The study has employed tracer-exchange NMR to determine Li-ion transport pathways in typical LLZO-PEO composite electrolytes with various compositions. This study demonstrates that solid-state NMR is a particularly useful tool for determining the contributing factors for ion conduction. The methodology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

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### References

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**Fig.1** Comparison of  ${}^6\text{Li}$  MAS NMR on pristine and tracer-exchanged composite electrolytes and schematic of Li-ion transport pathways.