

Probing Li-ion transport in Li₆PS₅X (X=Cl, Br)-based solid-state batteries

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Current flammable liquid organic electrolyte can cause serious problems due to leakage and can cause gas evolution when operating at elevated temperatures and at higher voltages.^{1,2} Unlike the liquid electrolyte, a solid electrolyte does not suffer from these drawbacks and in addition, improves the thermal and mechanical stability of the battery while providing the possibility to work in a higher voltage window under extreme conditions.³ The halogen doped Li₆PS₅X (X=Cl, Br, I) evolved from the Argyrodite Li₇PS₆ solid-electrolyte and was first reported by Diesroth and co-workers exhibiting a promising Li-ion conductivity of the order of 10⁻³~10⁻² S/cm, approaching the conductivity of liquid electrolyte.⁴ Deiseroth *et al.*⁵ studied possible three-dimensional lithium ion diffusion pathways and the temperature dependence of ionic conductivity using the AC impedance method. However in most cases the individual contributions arising from grain boundaries and bulk particles towards resistance i.e. towards ionic conductivity cannot be decoupled. Solid-state NMR is a powerful tool which allows the measurements of diffusion of Li-ions only in the bulk.⁶⁻⁸

Here, we propose a novel method to probe Li-ion transport in all-solid-state cells using Li₆PS₅X (X=Cl, Br) solid electrolyte. ⁷Li spin-lattice relaxation NMR method is applied to give us lithium hopping rates and bulk diffusion coefficients in Li₆PS₅X (X=Cl, Br) solid electrolyte. Moreover, 1D- and 2D- Exchange Spectroscopy (EXSY) measurements are also performed to provide quantitative information on the Li-ion dynamics between the Li-containing cathode (Li₂S) and Li-ion solid electrolytes (Li₆PS₅Cl and Li₆PS₅Br), providing important information for the development of solid-state batteries research. This work demonstrates the ability of exchange NMR between distinguishable Li-ion sites in the electrode and the solid electrolyte to quantify unambiguously the amount and timescale of Li-ion transport over the solid electrolyte-electrode interface in bulk solid state batteries. Thus, this approach is a valuable support to the development of interface design strategies necessary for future high performance all-solid-state batteries.

References

- [1] Hu, M.; Pang, X.; Zhou, Z. *Journal of Power Sources* **2013**, *237*, 229.
- [2] Campion, C. L.; Li, W.; Lucht, B. L. *Journal of The Electrochemical Society* **2005**, *152*, A2327.
- [3] Roth, E. P.; Orendorff, C. J. *Electrochemical Society Interface* **2012**, *21*, 45.
- [4] Deiseroth, H.-J.; Kong, S.-T.; Eckert, H.; Vannahme, J.; Reiner, C.; Zaiß, T.; Schlosser, M. *Angewandte Chemie International Edition* **2008**, *47*, 755.
- [5] Deiseroth, H.-J.; Maier, J.; Weichert, K.; Nickel, V.; Kong, S.-T.; Reiner, C. *Zeitschrift für anorganische und allgemeine Chemie* **2011**, *637*, 1287.
- [6] Wilkening, M.; Heitjans, P. *ChemPhysChem* **2012**, *13*, 53.
- [7] Wagemaker, M. *Structure and Dynamics of Lithium in Anastase TiO₂*; TU Delft, Delft University of Technology, 2003.
- [8] Wagemaker, M.; van de Krol, R.; Kentgens, A. P. M.; van Well, A. A.; Mulder, F. M. *Journal of the American Chemical Society* **2001**, *123*, 11454.