Peeking across grain boundaries in a solid-state ionic conductor

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Solid-state-batteries potentially offer an increased Li-ion battery energy density and safety as required for large-scale production of electrical vehicles. Charge transport across grain boundaries is often a limiting step to exploiting the potential bulk conductivity of a solid-electrolyte material. Electrochemical Impedance Spectroscopy (EIS) is the technique commonly used to quantify this transport across grain boundaries, but it is an indirect method of measurement which makes use of a circuit to fit the data and often data obtained is difficult to interpret and fit accurately. Solid-state NMR is a versatile and non-destructive technique used to characterize the structure and dynamics of materials. It has been demonstrated that it is possible to follow Li transport across the electrode-electrolyte interface, both with solid and liquid electrolytes, allowing for the quantification of interfacial charge transport. For bulk Li ionic conductors, quantification of charge transport with NMR across grain boundaries remains difficult since individual solid electrolyte grains appear 'identical' from an NMR point of view.

The argyrodite Li_6PS_5X (X=Cl, Br) solid electrolyte belongs to the family of sulfur based solid electrolytes, which have become extremely popular recently since their conductivity approaches that of liquid electrolytes. The chlorine and bromine containing Li_6PS_5Cl and Li_6PS_5Br which have an identical structure, exhibit comparable bulk conductivity observed from EIS and solid-state NMR relaxometry measurements, although there are indications that Li_6PS_5Br may be electrochemically more stable than its Cl containing counterpart. Despite their structural similarity, when measured with ^{6}Li NMR, their resonance peaks have different chemical shifts, due to the difference in Li shielding of the halogen dopants. Exploiting this property with two-dimensional ^{6}Li-^{6}Li exchange NMR on a mixture of Li_6PS_5Br and Li_6PS_5Cl, we are able to observe Li-exchange between particles of these two materials across grain boundaries, allowing the direct and unambiguous quantification of this charge transport process.

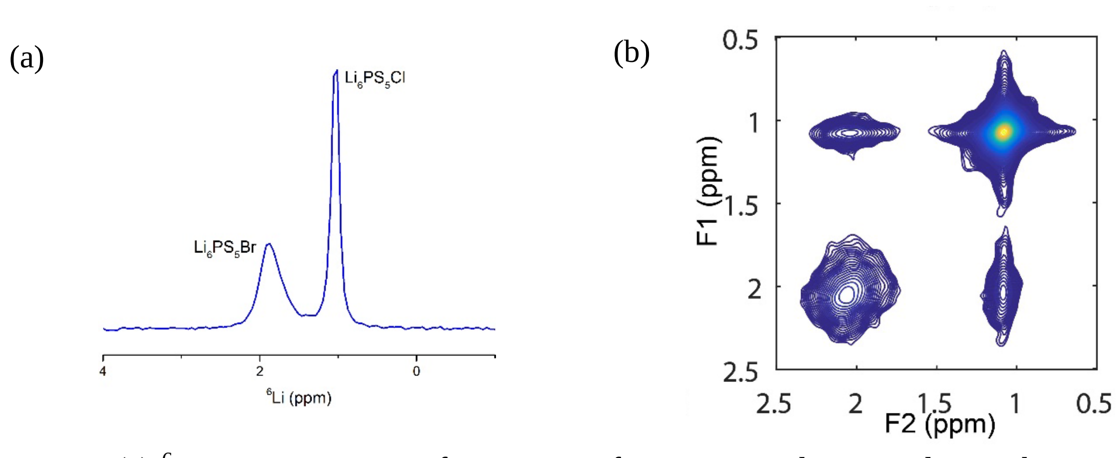

Figure 1 (a) ^{6}Li MAS spectrum of a mixture of Li_6PS_5Br and Li_6PS_5Cl at 12 kHz spinning. (b) 2D ^{6}Li-^{6}Li exchange NMR spectrum of the mixture from (a) at a mixing time of 1s.