Experimental report

06/09/2022

Proposal:	**7-03-201**	**Council:**	10/2020
Title:	Li-ion diffusion mechanism in sulfide-based electrolytes for solid-state Li-ion batteries by high resolution QENS		
Research area:	Materials		

This proposal is a new proposal

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Samples: Li6PS5Cl
Li10SiP2S12

Instrument	Requested days	Allocated days	From	To
IN16B	5	2	01/07/2021	03/07/2021

Abstract:

Solid electrolytes are one of the very few viable solutions that could stimulate a breakthrough in the battery safety, since contrary to organic-based electrolyte solid electrolytes are not flammable. Unfortunately, thei conductivity is generally very low compared to the liquid ones leading to the development of novel solid-state electrolytes so call super ionic conductors. Based on glass ceramics electrolyte, the thiosulfates solid electrolyte can deliver an ionic conductivity of ca.15 mS/cm as close as the one of liquid based electrolyte. However, to date, lot of questions remain regarding the relationship between the structure of the solid electrolyte and the Li-ion dynamics within the crystal, a process only sporadically investigated due to the lack of adequate technique. Here we propose to use quasielastic neutron scattering (QENS) to probe several solid electrolytes from the Li-S-P family to determine the Li-ion diffusion mechanism in the crystal, and to couple this molecular-level information to the ionic conductivity measured by electrochemical methods. Coupling both approaches will lead to a deeper understanding of the lithium ion superionic conductors.

Li-ion diffusion mechanism in sulfide-based electrolytes for solid-state Li-ion batteries by high resolution QENS

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Sulfide-based materials are currently under intense investigation for application as non-flammable electrolytes in solid state lithium batteries since the safety of the battery can be drastically enhanced with them.[1] Unfortunately, solid electrolytes suffer from low ionic conductivity compared to the usual liquid electrolytes, and thus strategies to overcome this issue are examined by looking for alternative materials with different ratios of Li, P and S. Li3PS4 (75 Li2S-25 P2S5), a state of art sulfide-based solid electrolyte from the quasi-binary Li2S-P2S5 system with an ionic conductivity of ca. 0.2 mS/cm, was recently overcome by several other solid electrolytes with ionic conductivity up to 17mS/cm for the argyrodite family. Li10SiP2S12 (hereafter called LSiPS) and Li6PS5Cl (LPSCl), are known to be among the most attractive sulfide-based solid electrolyte owing to their impressive ionic conductivity and their stability vs. Li metal anode.[2] Known to be a glass ceramic solid electrolyte, both materials are crystalline as can be seen from the collected neutron diffractogram at D2B beamline earlier September 2020 but only few Braggs peak are present in the IN16B Q-range.

We initially planned to study two solid electrolyte materials belonging to the argyrodite family, LiPS and LiPSCl, which we have already investigated from the structural and electrochemical point of view, using ^{7}Li. However it was not possible to purchase the ^{7}Li materials and only two days were allocated to demonstrate that a QENS signal is measurable on IN16B. We therefore focus our measurements on LiPSCl only.

Figure 1 shows elastic and inelastic (at 3 μeV window scan) performed with LiPSCl sample between 300K (no conductivity is measured below 300K) and 380K. It clearly shows that some dynamics enters the energy window of IN16B (decrease of EFWS and increase of IFWS intensities). The statistics is too poor and the temperature range too narrow to fit the IFWS and extract an activation energies and a characteristic time according to the model developed by Frick et al. [3]

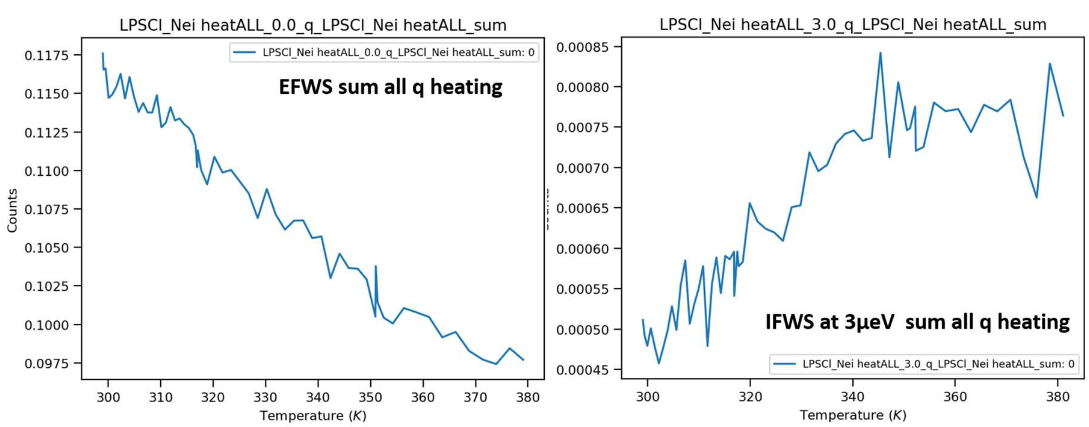

Figure 1. Elastic (left) and Inelastic (right) Fixed Window Scan measured on IN16B from 300 K to 380K.

We performed then QENS measurements at 300K, 353K and 380K. Figure 2 shows the QENS signal obtained for LiPSCl at 300K at high Q together with the Q dependence of the HWHM, Γ, of the quasielastic signal. Γ(Q) increase with Q which is a typical signature of a diffusive motion. Γ(Q) is fitted with a random jump diffusion model and the diffusion coefficient has been extracted.

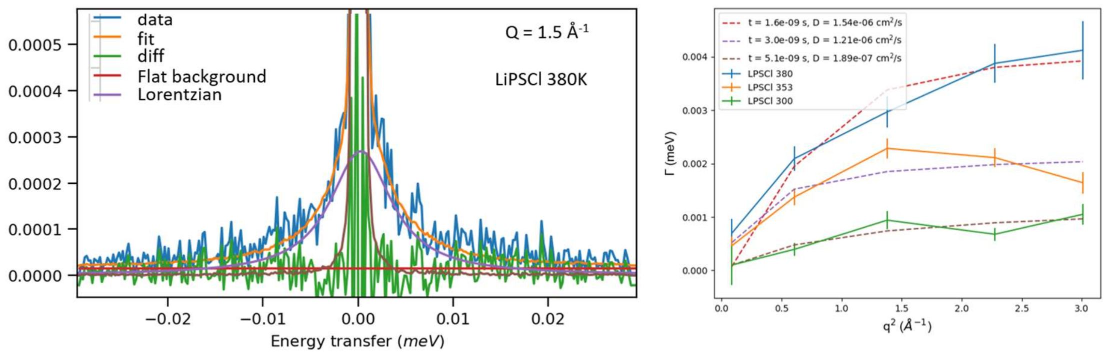

Figure 2. Fitted S(Q,w) spectra of LiPSCl at 380K with a Lorentzian, an elastic line and a flat background. Γ(Q) is fotted with a radom jump diffusion model.

This first experiment demonstrate that a QENS signal is measurable on IN16B with no isotopic substitution thanks to the excellent signal to noise ratio of the instrument.

The extracted diffusion coefficient and characteristic time will be compared to conductivity measurements and NMR.

1. L. R. Mangani and C. Villevieille, *Journal of Materials Chemistry A*, 2020, **8**, 10150-10167.
2. B. Zhang, L. Yang, L.-W. Wang and F. Pan, *Nano Energy*, 2019, **62**, 844-852.
3. Frick, B., Combet, J. & van Eijck, L.. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 669, 7–13 (2012).