Experimental report

09/09/2022

Proposal: EASY-870 **Council:** 10/2020

Title: Impact of the synthesis condition on solid electrolyte

Research area: Materials

This proposal is a new proposal

Main proposer: Claire VILLEVIEILLE

Experimental team:

Local contacts: Emmanuelle SUARD

Samples: Li6PS5Cl

Instrument	Requested days	Allocated days	From	To
D2B	5	5	16/05/2021	17/05/2021

Abstract:

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. 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 was recently overcome by Li-Cl-P-S system, known to be among the most attractive sulfide-based solid electrolyte owing to its impressive ionic conductivity and its stability vs. Li metal anode. However, lot of impurities can be formed during synthesis at high temperature. We would like here to measure two samples synthesize in 2 different manners to check the crystallinity as the literature model seems to not fit properly to this phase.

Impact of the synthesis condition on solid electrolyte

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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. 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 was recently overcome by Li-Cl-P-S system, known to be among the most attractive sulfide-based solid electrolyte owing to its impressive ionic conductivity and its stability vs. Li metal anode. However, lot of impurities can be formed during synthesis at high temperature. We would like here to measure two samples synthesize in two different manners to check the crystallinity as the literature model seems to not fit properly to this phase.

Argyrodite solid electrolytes, especially Li6PS5Cl are declared to be the most promising sulfide based solid electrolyte owing to its electrochemical stability windows, better than most of Li-s-P solid electrolyte family member but also due to its high ionic conductivity at room temperature.

To date, at our laboratory, we thoroughly explorer two different kind of commercial based argyrodite materials. Despite being reference both like Li6PS5Cl structure, they deliver totally different electrochemical results in term of ionic conductivity and in term of electrochemical stability windows. Preliminary investigation in our X-ray laboratory reveals the presences of known impurities for this synthesis, mainly Li2S and LiCl (know the lower the ionic conductivity) but the refinement indicates that the amount of both impurities is rather low in both commercial products.

The quality of our X-ray diffractometer was not helping to address this point. We performed a similar investigation at the synchrotron facilities but once again the refinement was not leading us to a valuable conclusion but pointed out that the Li content might be different in both case which could explain the difference in ionic conductivity.

We thus decided to investigate the samples by means of neutron diffraction to understand the difference in the structure of both materials.

As can be seen in Figure 1, the sample can be indexed in the ICSD card belonging to the cubic Li6PS5Cl material in the F –4 3 m space group. Impurities can be seen in the range up to 50° indexed as Li2S and LiCl. At higher theta values, the large peaks visible are attributed to the sample holder used for the measurement.

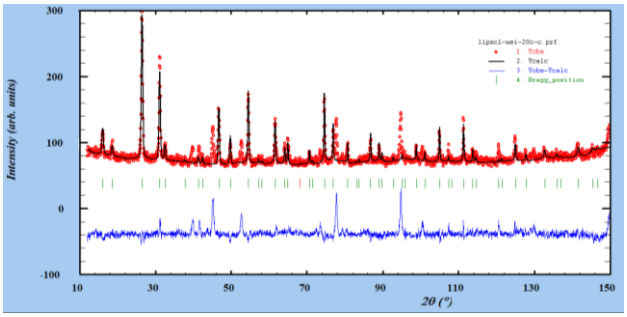

Figure 1. Neutron diffractogram obtained at D2B beamline for the first commercial sample.

Surprisingly, the Biso parameters are very high for Li and S position putting doubt about the synthesis quality. Also, the Li site seems to be not fully occupied. Bot information are counter intuitive first of all, the impurities are normally insulating so they should decrease the ionic conductivity of the sample, second point is that less Li than planned should also lead to a lower ionic conductivity; However, this sample has the expected ionic conductivity.

Similar approach was performed on the second commercial sample as can be seen in Figure 2. Less impurities can be found on the sample, and the Li content is full for this sample. Additionally, as for the other sample, the Biso stays high for Li and S.

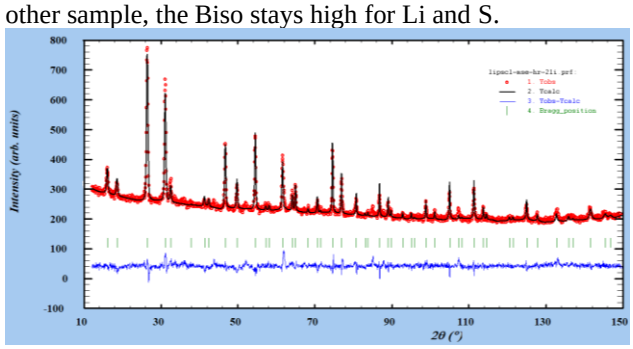

Figure 2. Neutron diffractogram obtained at D2B beamline for the first commercial sample.

At this stage, Fourier maps are currently being performed to ensure that the structural model used from the literature is fully relevant for this purpose. A paper is currently being written to explain the difference between the two materials and to correlate this to the electrochemical data obtained.

Work fully performed at ILL
Proposal-number: Easy 870 and
Instruments: D2B