Experimental report

04/09/2022

Proposal:	**EASY-713**	**Council:**	4/2020
Title:	Structural investigation of novel Calcium-based polymer electrolyte		
Research area:	Chemistry		

This proposal is a new proposal

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Experimental team:	
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Samples: PEO-CATFSI

Instrument	Requested days	Allocated days	From	To
D2B	4	4	27/09/2020	28/09/2020

Abstract:

Calcium batteries are considered among the most suitable candidate for post-lithium batteries due to their high charge density and a theoretical specific capacity of 1340 mAh/g and high volumetric capacity of 3833 mAh/mL similar to that of Li1. Ca, considering its reactivity and metal properties, is safer than lithium as it is less prone to burst in flame in contact with air. Additionally, Ca platting-stripping reported so far did not show any dendrites growth demonstrating the safety of such technology especially is coupled to a safe polymer-based electrolyte. However, to date, the electrolyte is still the weak link to develop properly Ca batteries and lot of experiments and modelling approaches are ongoing to find the most suitable candidate in terms of stability windows and ionic conductivity. Structural characterization at low temperature are needed to design by modelling better Ca based polymer electrolyte.

Structural investigation of novel Calcium-based polymer electrolyte

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Novel electrolyte for calcium-polymer batteries has been designed and characterized by our team. Though, in order to fully understand them, modelling is compulsory as several key parameters are still black boxes (calcium coordination, calcium solvation shell, calcium- counter ion interaction strength...). To do so, structural investigation is needed to fit the DFT calculation. FT-IR and Raman spectra have already been measured and computed as a first step, but crystalline structure of the samples would allow us to define what type of species are present in the media and polish our calculations allowing us to model in a better way the calcium polymer electrolytes and teaches us what are the key parameters to improve in order to have great ionic conductivity, mechanical strength etc. To the best of our knowledge, DFT calculation has only been performed on solvant-calcium salt, never on a calcium solid polymer electrolyte.

Solid Polymer Electrolytes (SPE) as compared to liquid organic electrolytes are safer, easier to handle and shape on an industrial scale and finally they can tackle the issues related to dendrite growth leading to safer batteries. However, SPE present poor ionic conductivity at room temperature ca. 1 µS.cm-1, 2 orders of magnitude lower than Goodenough's prerogatives for commercial application and thus too low to enable the cycling of Ca based batteries at room temperature. In addition, the Ca plating/stripping efficiency must be improved, in particular the passive solid electrolyte interphase (SEI) layer formed at the Ca/electrolyte interface has to be controlled (limitation of the electrolyte/Ca reactivity). These limitations hinder the calcium- polymer cells to be further developed.

Our strategy here is to understand better the interaction ongoing in polymer electrolyte designed for Ca batteries. As an example, we are designing polymer electrolyte based on Poly- (EthylenOxide) PEO containing a Ca salt. PEO presents a high donor number and low crystallinity (for some salt concentrations) when coupled to Ca salt giving interest worthy ionic conductivities. The salt dissociation and its mobility are the main parameters fixing the ionic conductivity. These two parameters are largely associated with the specific interactions between the ionic species and polymer matrix, the divalent character of the Ca2+ should have a large impact on them. The faster approach to come to this point is to use Density Functional Theory (DFT) and/or Molecular Dynamics (MD) but the models are more efficient if we input a structural model in it.

We used neutron diffraction on two different samples, one salt mixed with PEO and another one mixed with deuterated PEO to ensure a better statistic and avoid hydrogen saturation. A solid state synthesis route was employed with the melting of a polymer at 100°C followed by the salt incorporation inside the polymer host prior to be cooled down to RT at 10°K/min.

Unfortunately, the synthesis of other samples (to have several ratio of PEO/Ca salt) failed in the laboratory, since the materials were not pure. So, we focused our investigation on both materials that we considered pure for the investigation. Additionally, we measured a sample with a Li salt instead of a Ca salt to see the difference caused by the metal carrier in the structure.

For both samples Ca and Li salt mixed with PEO, we did the measurement at 77K to ensure that the structure is frozen during the measurement. As can be seen in Figure 1, numerous peaks are obtained leading us to conclude that the samples are still not pure making any refinement feasible. Additionally, only little difference is found between the Ca based sample compared to Li based sample which makes us believe that the structural properties are not far away whatever the charge carrier employed.

As a first conclusion we can say that the divalent nature of Ca compared to Li seems to not affect the structure of the materials. To complete our investigation, we performed a similar investigation at the MSPW beamline at Alba at low temperature on the same sample to maybe identified a more "clean" structure (Figure 2).

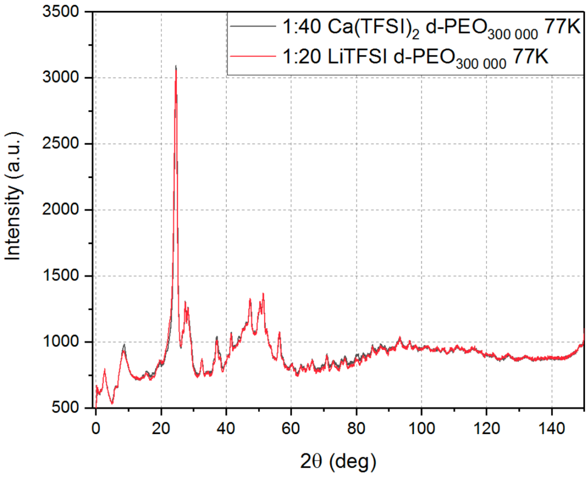

Figure 1. Neutron diffractogram obtained at D2B beamline for both PEO-Ca and PEO-Li based sample measured at 77K.

Based on the results obtained at the synchrotron source, we decided to perform an ab initio calculation using FullProf Treor and Dicvol option. Taken the 20 most intense peak, the ab initio calculation gave us up to 7 phases to be further tested in our theoretical model. Among them a monoclinic one seems interesting (α = 90°, β = 119°, γ = 90°, a = 10.7, b = 7.90, c = 9.95).

This phase is currently tested and simulated to see if it can fit to our electrochemical ionic conductivity measurement and to our laboratory Raman spectra.

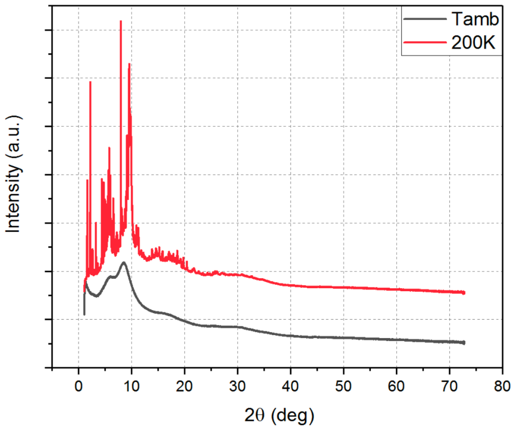

Figure 2. X-ray diffractogram obtained at MSPW beamline at ALBa for the PEO-Ca based sample measured at room temperature at and 200K.

Work fully performed at ILL
Proposal-number: DIR-220
Instruments: D2B