Experimental report

28/07/2022

Proposal: **6-07-94** **Council:** 4/2021

Title: Relationship between Segmental Dynamics and Li-ion Conductivity in Polymer and Hybrid Electrolytes for solid-state batteries.

Research area: Materials

This proposal is a resubmission of 6-07-79

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Samples: Poly(trimethylene carbonate)
poly(trimethylene carbonate) + LLZO
poly(trimethylene carbonate) + LiTFSI + LLZO
poly(trimethylene carbonate) + LiTFSI

Instrument	Requested days	Allocated days	From	To
IN16B	5	3	30/08/2021	02/09/2021

Abstract:

The exceptional combination of high energy and power density has made Li-ion batteries the energy storage technology of choice for portable electronic devices and electric vehicles. The next challenge is to implement solid-state electrolyte to allow safer batteries with higher storage properties. Many materials (inorganic or organic) have been studied to that end, but polymer electrolytes (SPE) and their hybrids stands out. Contrary to PEO-based SPE, poly(trimetylene carbonate) (PTMC) synthesized via ring opening polymerization are showing interesting electrochemical properties. The presence of carbonate groups and the higher lithium transference number suggest a different ionic motion mechanism from PEO. Yet, knowledge lacks on the involved molecular-based mechanisms in PTMC. Those mechanisms are key to optimize materials and tackle the conductivity bottleneck in soft electrolytes. In this regard, an interesting option is to consider hybrids composed of PTMC and highly-conducting garnet-type ceramics (e.g. LLZO). Here we propose to investigate i) the relation between ionic conduction and chain dynamics in PTMC polymers and ii) the impact of hybridization on the dynamics.

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The aim of this study is to understand lithium conduction mechanisms inside composite polymer electrolyte (CPE) and solid polymer electrolyte (SPE) made of poly(trimethylene carbonate) (PTMC). PTMC-based electrolytes are showing very interesting electrochemical performances for use as solid-state electrolytes in lithium batteries. Yet, Li^+ dynamics in these materials is still unknown. A comprehensive study of the impact of Li salt and/or nanoparticles addition on the segmental motion of the polymer chains is an important step to unveil the Li^+ dynamics. We expect to get unique insights into the Li-conduction mechanisms by linking the molecular dynamics to conductivity performances, structure and composition of the electrolytes.

Hence, we systematically probe the dynamics in our samples as a function of temperature in order to obtain the onset of motions of interest, their nature and the associated quantitative parameters (mean square displacement, relaxation times, diffusion coefficient, activation energies). We investigated the following three different samples:

- pure PTMC ;
- SPE : PTMC with lithium salt (LiTFSI) ;
- CPE : PTMC with alumina (Al_2O_3) nanoparticles and lithium salt.

All electrolytes have been prepared with the same protocol and dried under vacuum before being sealed under inert atmosphere in Al flat QENS cells. QENS experiments on IN16b spectrometer were carried out with incident wavelength of 6.28 Å covering a Q-range from 0.19 $Å^{-1}$ to 1.9 $Å^{-1}$. Three different temperatures were studied: 233 K below the T_g of materials (approx. 243 K), 293 K and 353 K.

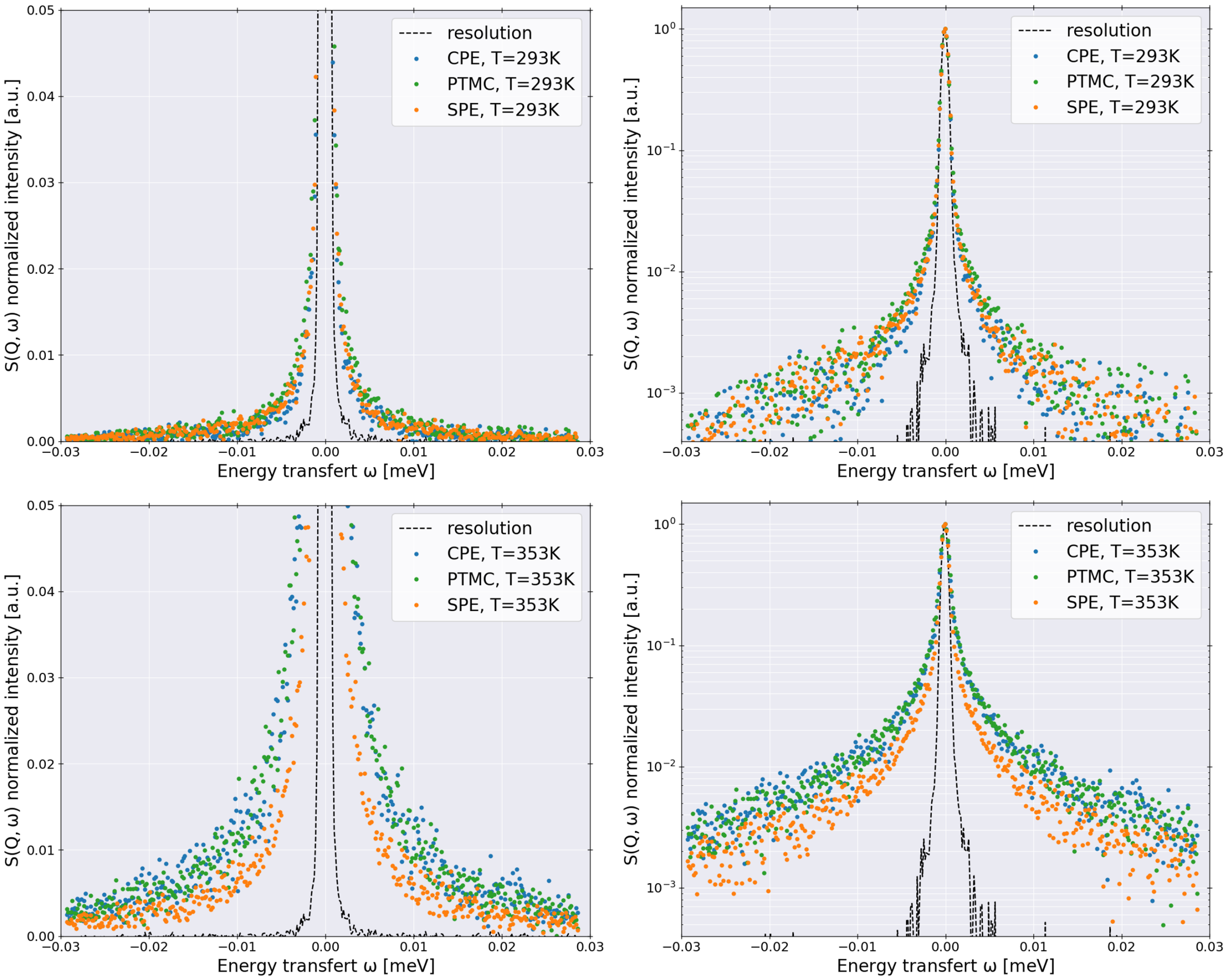

Figure 1: Normalized IN16b spectra obtained at Q =1.13 $Å^{-1}$ and at temperature of 293 K (top row) and 353 K (bottom row).

Figure 1 show the normalized spectra where it is clear that quasi-elastic signal at high temperature from CPE and pure PTMC is more intense compared with the SPE. There is also evidence for a thermal activation of the dynamics as confirmed by the mean-square displacement extracted from IFWS/EFWS showed in Figure 2.

The $S(Q, \omega)$ spectra were fitted using a two Lorentzian component model to account for fast motions (HWHM $\sim 12\,\mu\mathrm{eV}$), and one slower process of interest with a characteristic time of $\sim 400\,\mathrm{ps}$ (HWHM $\sim 0.8\,\mu\mathrm{eV}$) (Fig. 3). The nature of these motions is still discussed as well as a possible correlation with the sample composition. Analysis of complementary data with a faster timescale obtained on IN5 TOF spectrometer are also on-going and might be useful to conclude on a relation between electrolyte composition and the PTMC dynamics.

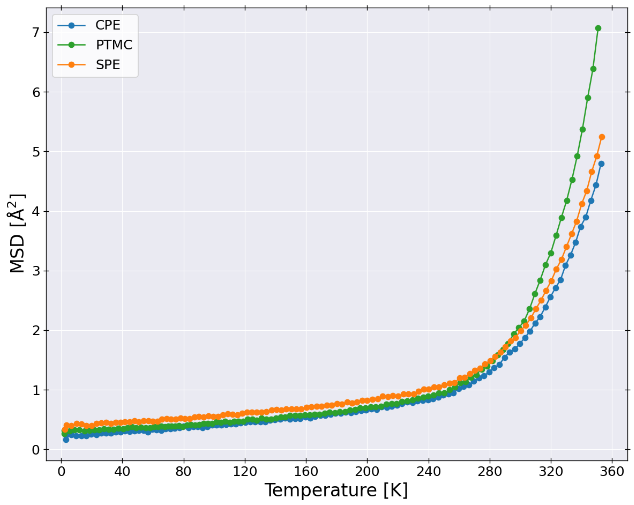

Figure 2: Mean-square displacement obtained with IN16b data

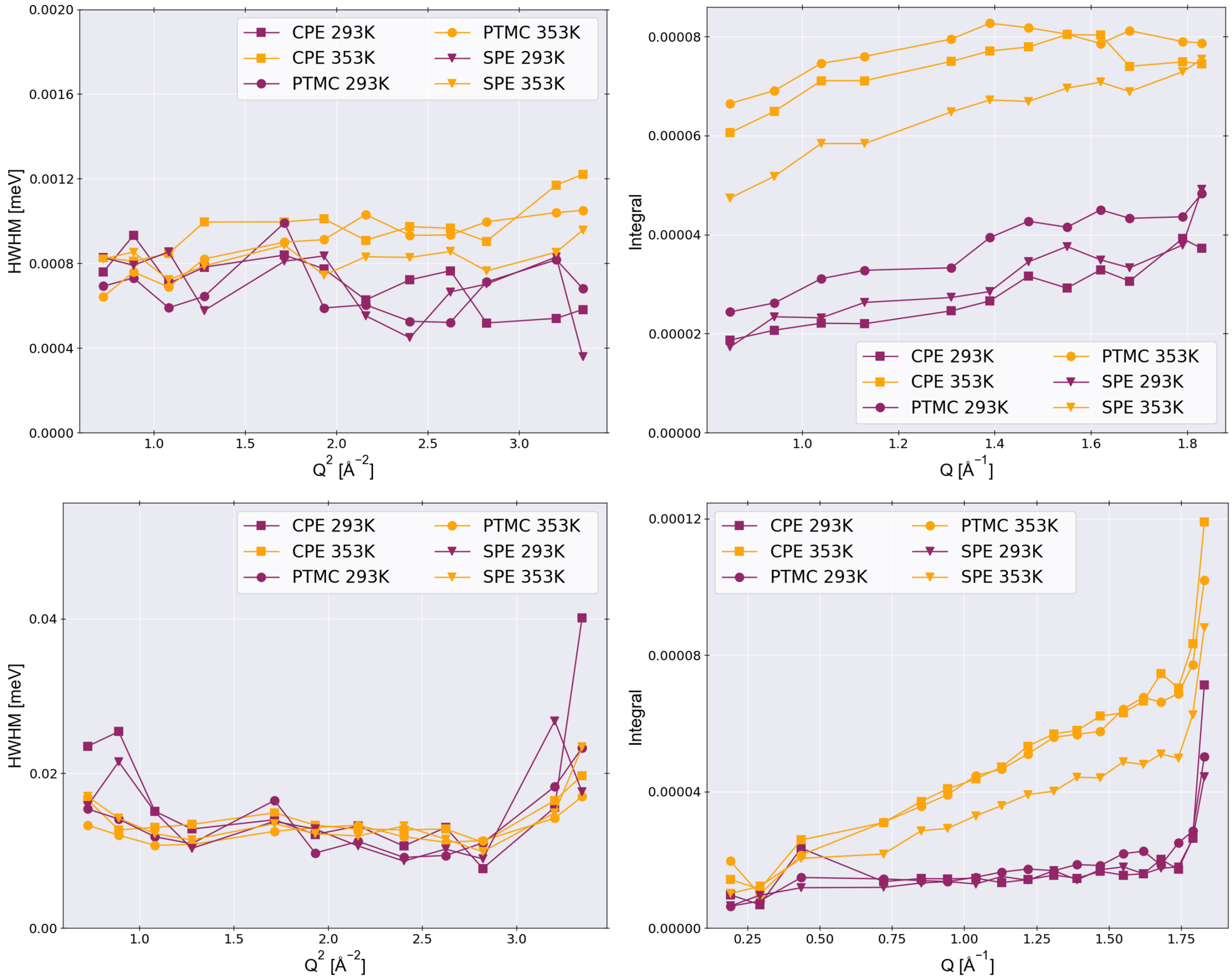

Figure 3: Q-dependance of the fitting result with a two Lorentzian component model.