Experimental report

06/09/2022

Proposal: TEST-3109 **Council:** 4/2020

Title: Li-Battery plasticizer dynamics

Research area:

This proposal is a new proposal

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Experimental team: Peter FALUS

Local contacts: Peter FALUS

Samples: C4D4N2_1-x: C5H6N2_X with x = 0, 0.2, 0.4, 0.6, 0.8, 1

Instrument	Requested days	Allocated days	From	To
WASP	5	5	11/09/2021	16/09/2021

Abstract:

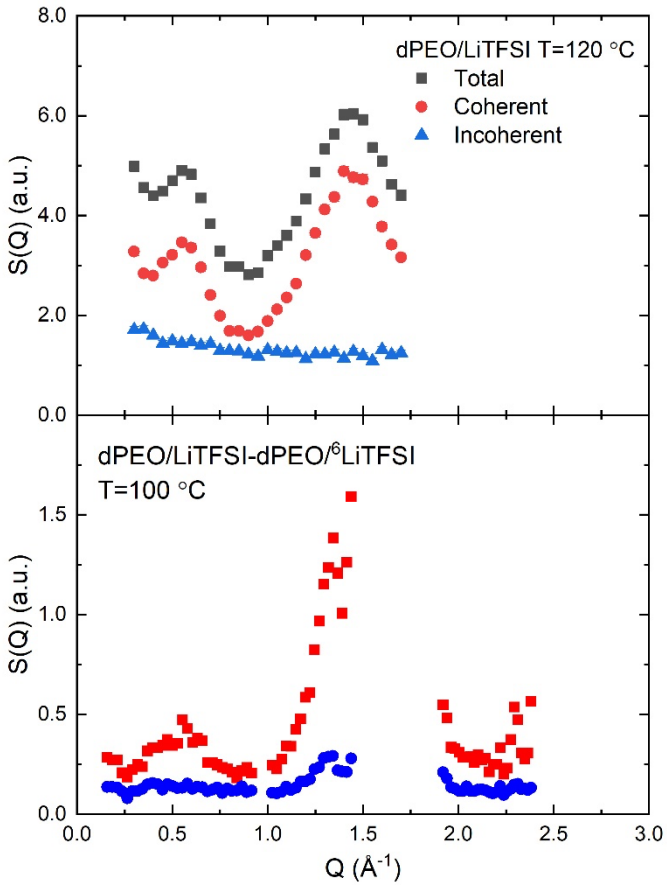

Figure 1 a) Polarized diffraction measurement of dPEO/LiTFSI measured at the NIST Center for Neutron Research. b) Polarized diffraction results for the subtraction dPEO/^{6}LiTFSI-dPEO/LiTFSI, as measured on WASP.

The recently commissioned Wide Angle neutron Spin echo Spectrometer (WASP) at the Institut Laue-Langevin (ILL) offers capabilities to measure the Intermediate Scattering Function (ISF) in the time range from few picoseconds to several nanoseconds in a wide Q - range with unprecedented accuracy and efficiency. In 2021, this spectrometer was employed to collect data on homologues PEO/LiTFSI samples differing only for their isotopic composition as follows: i) $P(EO)_{7.5}$LiTFSI; ii) $P(EO)_{7.5}{}^{6}$LiTFSI; iii) $dP(EO)_{7.5}$LiTFSI; and iv) $dP(EO)_{7.5}{}^{6}$LiTFSI. Here dPEO represents deuterated PEO and Li indicates natural lithium which is composed by ^{7}Li for 92.5 %. An additional dPEO sample was measured as a reference. At this concentration the lithium conductivity is maximum. The molecular mass of the polymer was 13000 Da and 14000 Da for the dPEO and HPEO samples respectively. Two incoming neutron wavelengths, λ, were employed, namely 4 Å and 7 Å, with a $\Delta\lambda\backslash\lambda\approx 15$ %, providing a Q range from 0.41 Å^{-1} to 2.2 Å^{-1} and times from 1 ps to 1 ns, and a Q range from 0.2 Å^{-1} and 1.3 Å^{-1} and times from 7 ps to 7 ns, respectively. Measurements were carried out at 100 °C. The aim of the study was to investigate the dynamics of the lithium ions with respect to their atomic environment, similarly to how the atomic structure of these samples was studied in the past.[1]

Polarized diffraction results obtained by subtracting the data from sample iv to sample iii yield results (Fig. 1 b) in good agreement with previous reports validating the feasibility of the measurement and the possibility to probe the lithium environment. However, unfortunately, the data at Q≈(1.65±0.2) Å^{-1} were not reliable because of an "instrument shadow", which has now been removed. The ISF of the five samples investigated were analyzed yielding results consistent with literature. The ISF of the subtracted spectra (iv-iii) were analyzed using a stretched exponential function, as shown in Fig. 2. Thus, the relative dynamics of the lithium ions with respect to the other atoms was

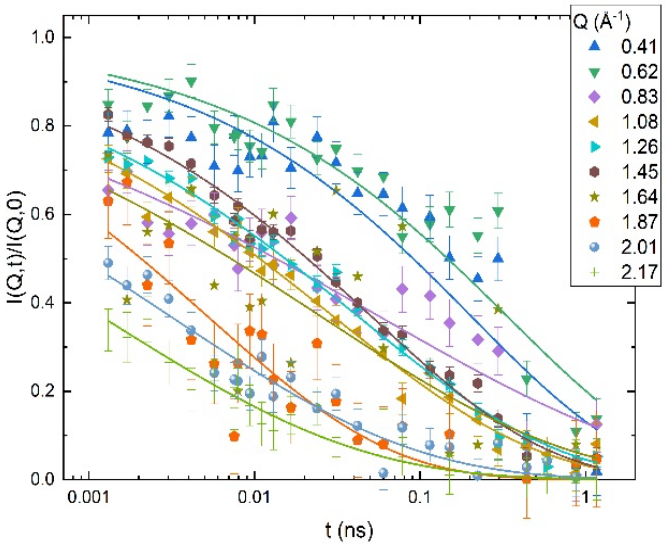

Figure 2: Fitting of ISF of the subtraction of sample iv from sample iii.

measured. Preliminary results indicate that the timescale of the dynamics of Li^+ with respect to the surrounding atoms is 1 to 1.5 times that of the structural relaxation of the PEO chains in the electrolyte (see Fig. 3). Further analysis including MD simulations are underway, with the use of the hydrogenated samples i and ii to extract solely the partial dynamic structure factor of Li-H.[2]

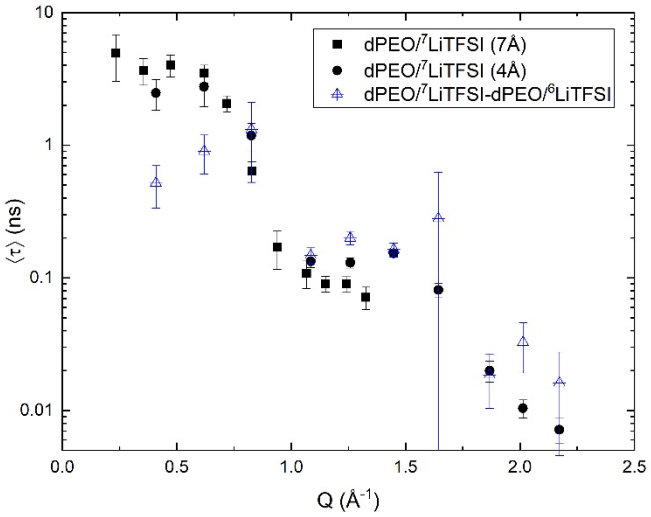

Figure 3: Q-dependence of the measured average relaxation times from the fitting of the ISF.

(1) Mao, G.; Saboungi, M.-L.; Price, D. L.; Armand, M. B.; Howells, W. S. Structure of Liquid PEO-LiTFSI Electrolyte. *Phys. Rev. Lett.* **2000**, *84* (24), 5536-5539. DOI: 10.1103/PhysRevLett.84.5536.

(2) Bertrand, C. E.; Self, J. L.; Copley, J. R. D.; Faraone, A. Nanoscopic length scale dependence of hydrogen bonded molecular associates' dynamics in methanol. *J. Chem. Phys.* **2017**, *146* (19). DOI: 10.1063/1.4983179.