Experimental report

10/05/2019

Proposal: 6-02-589 **Council:** 4/2018

Title: Dynamics in super-concentrated acetonitrile/LiTFSI electrolytes

Research area: Materials

This proposal is a continuation of 1-04-108

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Samples: Acetonitrile/LiTFSI

Instrument	Requested days	Allocated days	From	To
IN16B	4	4	05/07/2018	06/07/2018
			18/09/2018	21/09/2018

Abstract:

Studies have shown that highly concentrated Li-salt to acetonitrile solutions show a remarkable electrochemical stability. The increased electrochemical stability is not yet well understood, and insight into the changes in structure and dynamics will help in the development of better performing electrolytes. The proposed experiment on IN16B will investigate how Li-salt concentration affects the dynamic properties of the electrolytes by combining data from IN16B with previous data from IN6, Raman spectroscopy to determine the average local coordination around the Li-ions, and by comparing with predictions from molecular dynamics simulations. The aim is to elucidate what drives the conduction mechanism in these new super-concentrated electrolytes

Beamtime report from IN16B, experiment 6-02-589 17-21 September 2018

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Power: 51 MW
Wavelength: 6.27 Å, Si(111)

Sample: Acetonitrile (AN), fully deuterated d3-AN, d3-20AN:1LiTFSI, d3-5AN:1LiTFSI, d3-2AN:1LiTFS.

Normal cylindrical aluminium cells of 0.25 to 0.3 mm thickness for the deuterated samples.

The protonated AN was measured during the first-scheduled beamtime on 5 July, however, as the neutron reactor was stopped during the first day, the experiment was rescheduled to September. For H3-AN we did one temperature EFWS/IFWS scan in temperature. For the other four samples (D3-AN, D3-20AN, D3-5AN and D3-2AN) measured in September, we measured both a full EFWS/IFWS (30 s and 2 min, respectively) temperature scan on cooling and spectra, roughly 24 h for each sample, counting 3 h per spectrum.

Temperature scans on the samples

The elastic and inelastic ($E_{\text{offset}} = 2\,\mu\text{eV}$) fixed energy window intensities on temperature scans are plotted for the five samples in Fig. 1. From both the EFWS and IFWS, it is clear that adding salt slows down the dynamics, in particular, for D3-5AN:LiTFSI and D3-2AN:LiTFSI that both supercool and enter a glassy state, avoiding crystallisation completely on cooling.

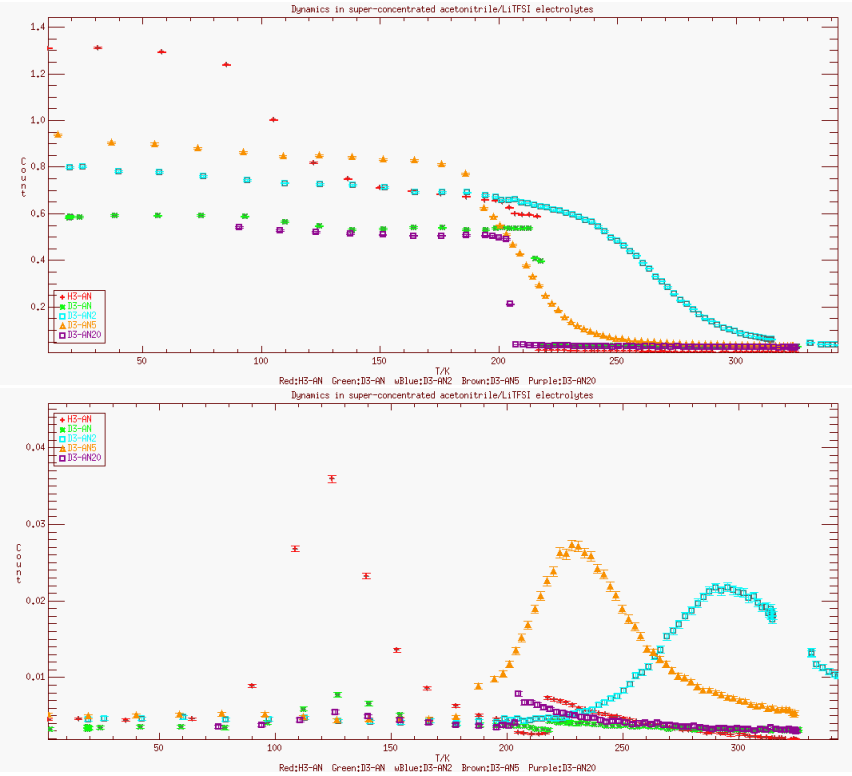

Figure 1: Elastic and inelastic fixed window scans with $\Delta E = 0$ and 2 μeV, respectively, for the five samples. Here shown summed over Q.

Dynamic structure factor

Spectra were measured at 2, 225, 235, 250, 275 and 300 K for all four samlpes with deuterated acetonitrile. And in addition at 325 K for D3-AN and D3-AN2, and at at 350 K for D3-AN2. A comparison of the four different samples at 250 and 300 K are shown in Fig. 2 and 3, respectively, for $Q = 0.56,\ 1.28$ and $1.79\,\text{Å}^{-1}$. There are no signs in the Q-dependence of a prepeak in the samples with salt, which is observed structure data from x-ray. All four samples behave like liquids with no mesoscopic lengthscale. The same samples (in same sample cells and so on), were measured at IN5 a week later during the beamtime TEST-2969 at $\lambda = 5\,\text{Å}$.

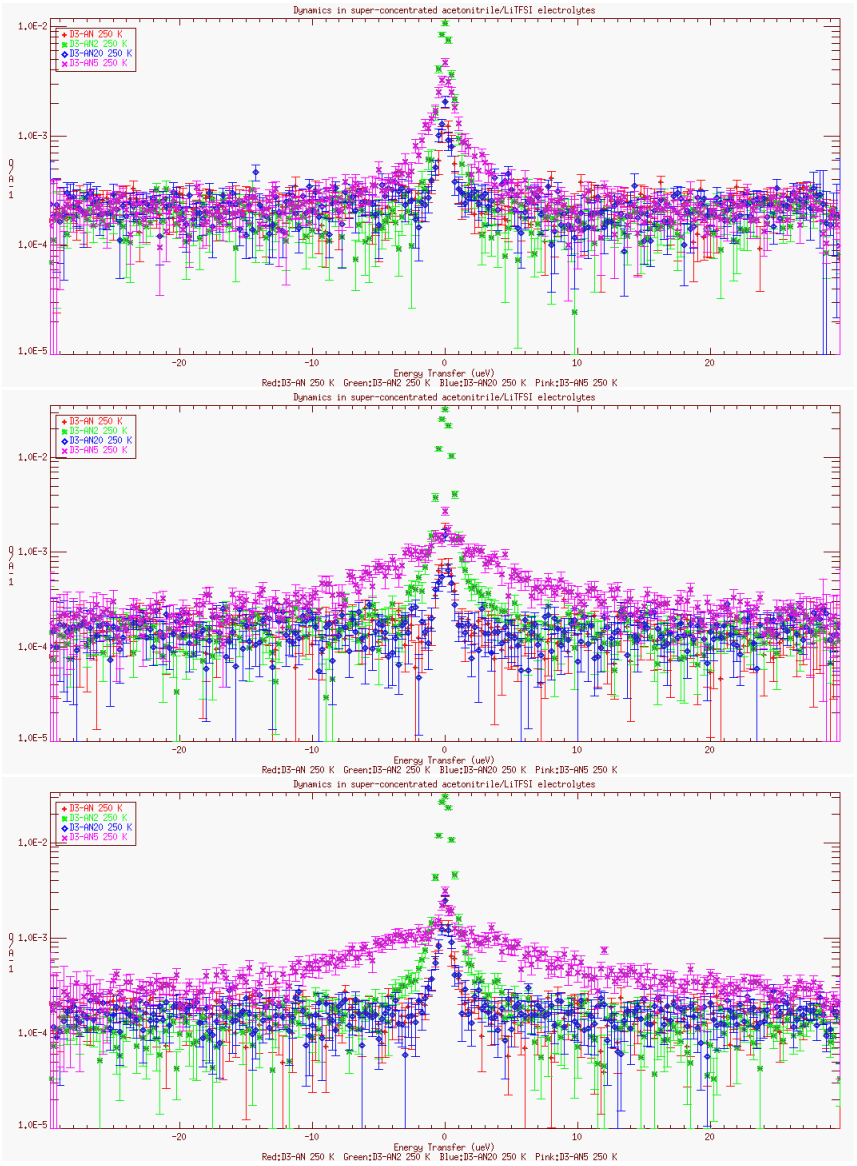

Figure 2: $S(Q,\omega)$ of the four samples at 250 K. Here shown for $Q = 0.56$ (top), 1.28 (middle) and $1.79\,\text{Å}^{-1}$ (bottom).

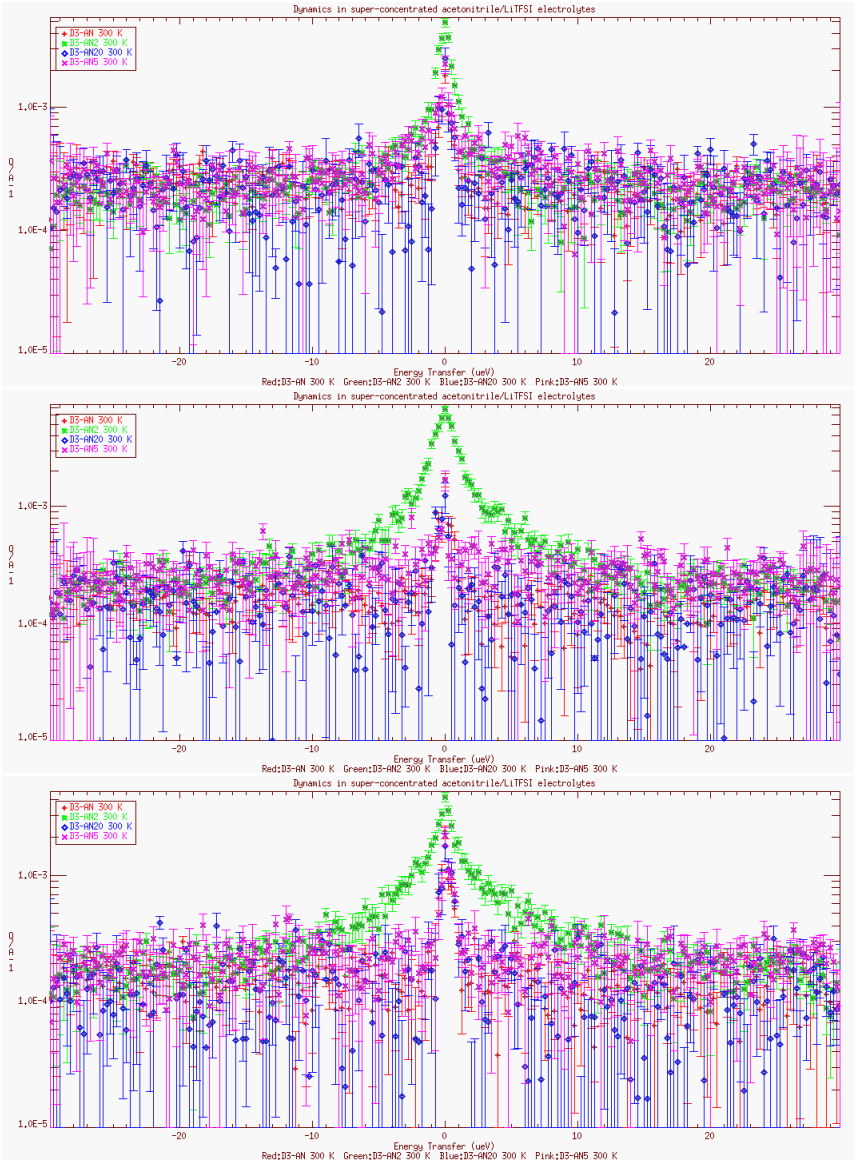

Figure 3: $S(Q, \omega)$ of the four samples at 300 K. Here shown for $Q = 0.56$ (top), 1.28 (middle) and 1.79 Å^{-1} (bottom).