Experimental report

11/06/2017

Proposal:	**1-04-108**	**Council:**	4/2016
Title:	Dynamics of super concentrated acetonitrile/LiTFSI electrolytes		
Research area:	Materials		

This proposal is a new proposal

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Samples: Acetonitrile/LiTFSI (C_2H_3N)/($CF_3SO_2NLiSO_2CF_3$)

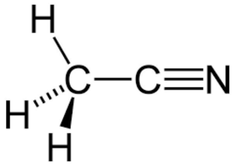
Instrument	Requested days	Allocated days	From	To
IN6	3	3	17/06/2016	20/06/2016

Abstract:

Acetonitrile (AN) is one of the most oxidation-tolerant organic solvents. In the particular case of lithium-ion batteries (LIB), this kind of electrolyte opens the possibility to use high voltage electrodes (∼5 V). Moreover,the electrochemical nature of organic solutions drastically improves over a certain threshold of Li-salt concentration (>3 mol dm-3). Our previous SAXS studied have demonstrated some higher degree of ordering a the high concentration range, but also reveal an unusual long range ordering in the dilute solutions. Here we propose to address the issue of molecular transport in in this kind of electrolytes by investigating the microscopic dynamics in the liquids by quasi-elastic neutron scattering as a function of momentum transfer. The interpretation of our current data together with the data obtained from the proposed experiment will help us to further increase the fundamental understanding of the system.

Dynamics of super concentrated acetonitrile/LiTFSI electrolytes

Since the initial commercialization in 1991 lithium-ion batteries (LIBs) have become standard in portable electronics and are currently expanding into the electric vehicle market. Several electrolyte concepts have been proposed in order to improve both the capacity and the safety aspects [1,2]. An interesting approach is based on the recent finding that highly concentrated solutions (e.g. 3 to 5 molar) of certain Li-salts in polar solvents behave completely different compared to standard electrolyte solutions where the Li-salt concentration is lower (~1 molar) [3-6]. In this work we address the issue of nanostructure and mesoscopic dynamics in highly concentrated electrolytes by means of small angle X-ray scattering (SAXS) and quasi-elastic neutron scattering (QENS). We have chosen to investigate highly concentrated solutions based on acetonitrile (AN), (see Figure 1), respectively, and the lithium salt LiTFSI. The flexible nature of TFSI allows for liquid electrolytes to be stable even at very high salt concentrations. We find that in both systems intermediate range ordering related to charge alternation is present and that the length scale of the intermediate range order is influenced by the symmetry of the solvent.



Acetonitrile (AN)

Figure 1. Chemical structure of acetonitrile. The acetonitrile molecule is symmetric around the C-C-N axis.

The SAXS diffraction patterns from the AN/TFSI solutions are shown in Figure 2. For neat AN only one broad peak around Q=1.7 Å^{-1} can be observed. This feature is typical for liquids and corresponds to correlations of first and second nearest neighbours, i.e. reflecting the short range order of the liquid [7,8]. As the Li-salt (LiTFSI) is introduced into the system we observe several changes in the diffraction pattern. Most striking is the appearance of a new peak at low Q-values, around 0.5 Å^{-1}, indicating the presence of ordering on intermediate length scales in the liquid. With increasing salt concentration the peak grows in intensity and shifts to higher Q. Also in the high Q region a new peak appears with the addition of LiTFSI. At low concentrations it is manifested as a shoulder/broadening of the acetonitrile peak but at higher concentrations (>10:1) a clear separate peak can be observed around 2.4 Å^{-1}.

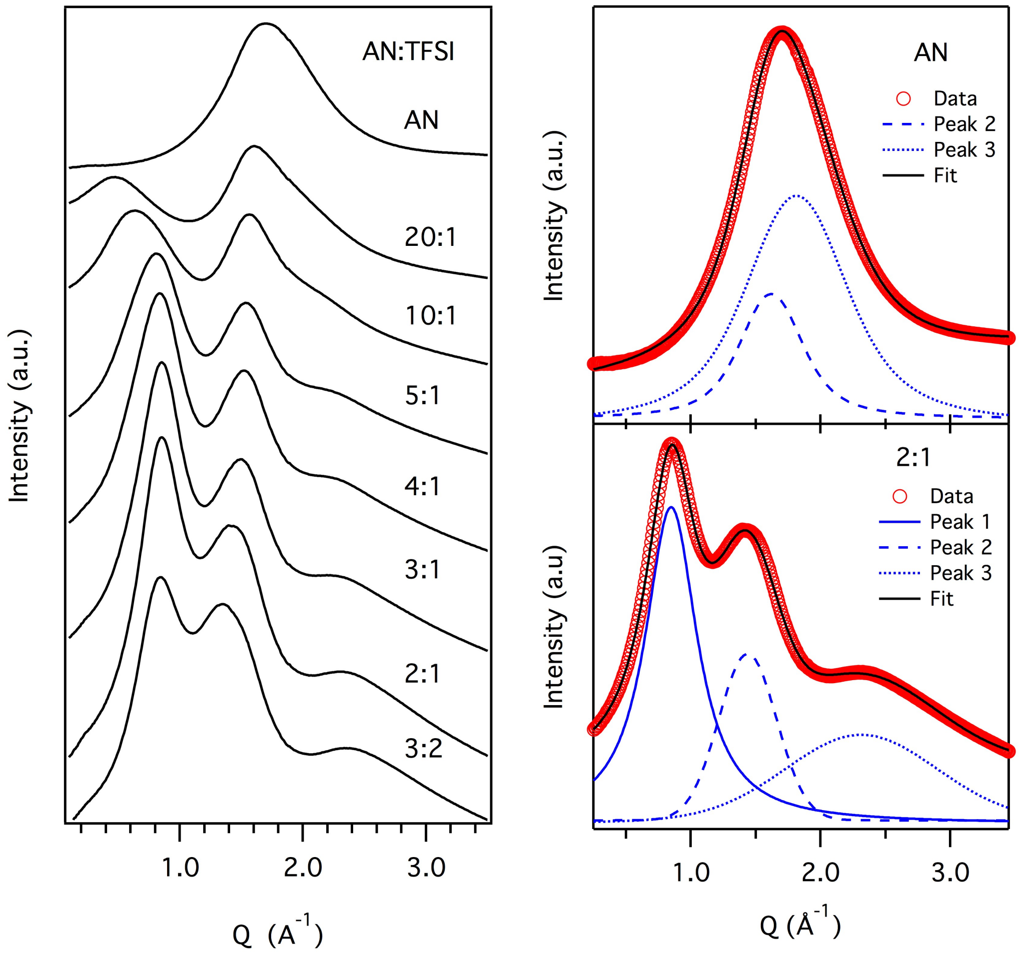


Figure 2. Left. SAXS diffraction patterns of AN/LiTFSI solutions at different concentration. Right: Examples of fitted SAXS diffraction patterns of neat AN (top) and of the 2:1 solutions (bottom). Linear baseline is not shown in the figure for clarity. At the higher salt concentration, 2:1.

The dynamics in the acetonitrile/LiTFSI solutions at dilute and high concentrations (i.e. from ratios 20 and 2 AN/Li) in the momentum transfer range 0.5-2 Å^{-1}, i.e. where we observe the low-q peaks in the SAXS data, were investigated using the time of flight spectrometer IN6, in the temperature range 250-350 K (10 temperature settings). The experiment was performed on fully deuterated acetonitrile to follow the coherent dynamics. The incident wavelength of 5.1 Å^{-1} in the IN6 was used to obtain the relevant momentum transfer and time range. e.g. at Q=0.75 Å^{-1} the accessible time range with this setting is 0.6-20 ps. The data is being analyzed in time domain, by performing a Fourier transform of the anti-Stokes side in the energy spectrum ($S(Q,w)$). However, at the moment the results are too premature to be presented. We expect that soon our results will address the issue of molecular transport in highly concentrated electrolytes properly analyzing our data from QENS. Hence, an updated version of this experimental report will be uploaded at a later stage.

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