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## Insight on the conductivity mechanism in sodium 4,5-dicyano-2trifluoromethyl-imidazolide-poly (ethylene oxide) system

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#### ABSTRACT

Sodium polymer electrolytes, as much safer electrolytes, are expected to be applied in sodium batteries. Here we present a systematic analysis of the NaTDI-PEO electrolytes. Their relatively high conductivity is explained by means of detailed structural, thermal and spectroscopic studies. On the basis of these results and with help of the database obtained for NaTDI-glyme system, we propose the coordination modes for polymer-salt complex phases. Thanks to this, it is possible to simulate intramolecular interactions both in crystalline and amorphous phases and explain the influence of formed crystalline phases on the observed conductivity relationship.

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#### 1. Introduction

The studies on the application of lithium  $(Li^{+})$  and sodium  $(Na^{+})$ ions as charge carriers for electrochemical energy storage at ambient temperature began in late '60. Although the sodium conducting systems were successfully applied in batteries as early as in 1967 (Ford Motor Company, USA, Na/S 2.1 V systems), for the past two decades researchers focused on the lithium conducting systems. The fast development of Li-ion and Li-polymer batteries requires large amounts of lithium every year and is followed by an increase of the lithium price. The availability of lithium remains confined due to scarce amounts of this element in Earth's crust. Sodium appears to be the rational substitute, having only slightly lower than lithium electrochemical potential (-2.71 V vs. SHE). However sodium is much more abundant. Therefore, the difference in price between lithium and sodium will be increasing, as well as direct research to sodium batteries (electrolytes and electrodes) [1,2]. Worth to notice sodium technology showed tremendous potential as large-scale energy storage, for example from photovoltaics and wind farms [3-5].

PEO-based, sodium solid-polymer electrolytes for sodium

battery applications were reported for a few base salts as sodium bis(trisfluoromethanesulfonyl)imide (NaTFSI) [6-9], sodium trifluoromethane sulfonate (NaCF<sub>3</sub>SO<sub>3</sub>) [10–12], sodium thiocyanate (NaSCN) [10,13], sodium tetrafluoroborate (NaBF<sub>4</sub>) [11,14], sodium perchlorate (NaClO<sub>4</sub>) [15] and sodium hexafluorophosphate (NaPF<sub>6</sub>) [16]. One of the key factors affecting conductivities of the PEO based solid systems is the phase composition. Scientists generally agreed that an increase in the amount of crystalline phase significantly reduces the flexibility of the systems and results in a decrease of the conductivity. Generally, these membranes show ionic conductivities on the order of  $10^{-5} \,\mathrm{S \, cm^{-1}}$  or less at room temperature, which is not enough for general battery application. Most of the research is focused on diluted systems, with O/Na equal 10 or more. In such case the crystalline phase is mostly the pure polymer. In more concentrated electrolytes, salt molecules are also present in the crystalline phase with O/Na ratio ranging from 1:1 (PEO-NaI, PEO-NaCF<sub>3</sub>SO<sub>3</sub>) through 3:1 (PEO<sub>3</sub>-NaClO<sub>4</sub>) to 7:1 (PEO<sub>7</sub>-NaBPh<sub>4</sub>) and 8:1 (PEO<sub>8</sub>-NaAsF<sub>6</sub>) [12,17-19].

Properties of the electrolytes based on lithium Hückel-type salts were initiated by Polymer Ionics Research Group by studies of 4,5-dicyano-2-(trifluoromethyl) imidazole (LiTDI) and its analogues [20]. The explanation of the impact of LiTDI aggregation tendencies in aprotic solvents on the mechanism of the transport was also continued in systematic way [21–23]. Changing the topic to related sodium systems, the synthesis, structure and properties of its







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sodium alternative NaTDI initially in propylene carbonate solvates were published by Marczewska et al. [24]. This concept was intensively elaborated and broaden by works of Bitner-Michalska et al. showing the possibility of successful synthesis, high conductivity and cyclability of different sodium based anions in liquid and solid electrolytes [25–27]. The analysis of dissociation mechanism in NaTDI-oligo ether systems was recently given by Dranka et al. [28]. The idea of weekly coordinating salts was also successfully developed in the new family of fluorine-free solid-polymer electrolyte. Three novel sodium salts with diffuse negative charge, i.e. sodium pentacyanopropenide (NaPCPI), sodium 2345tetracyanopirolate (NaTCP) and sodium 2,4,5-tricyanoimidazolate (NaTIM), were designed and tested in a poly(ethylene oxide) (PEO) matrix as polymer electrolytes for all-solid sodium-ion batteries. Due to unique, non-covalent structural configurations of anions, improved ionic conductivity was observed. Electrochemical properties of Hückel type electrolytes in lithium and sodium systems have been published in various papers [20-27].

In this paper we provide a significant input and systematical research data focused on the explanation of the conduction mechanism of the PEO-NaTDI system.

#### 2. Experimental

### 2.1. Sample preparation

NaTDI was synthetized according to the procedure described elsewhere [24]. Poly(ethylene oxide) PEO ( $M_w = 5 \times 10^6$  g/mol, Aldrich) was dried under vacuum. NaTDI-PEO membranes were obtained as follows. NaTDI was dried under high vacuum (1 Torr) for 48 h and added to poly(ethylene oxide) in acetonitrile solution. The obtained solutions were poured onto PTFE dishes and thin foils of electrolytes were formed after vacuum drying. All operations were carried out inside an argon-filled glovebox.

#### 2.2. PXRD

Laboratory powder X-ray diffraction patterns were recorded at room temperature on a Bruker D8 Advance diffractometer equipped with a LYNXEYE position sensitive detector, using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). The data were collected in the Bragg–Brentano ( $\theta/\theta$ ) horizontal geometry (flat reflection mode) between 4° and 60° (2 $\theta$ ) in a continuous scan, using 0.03° steps, 384 s/step. The diffractometer incident beam path was equipped with a 2.5° Soller slit, and a 1.14° fixed divergence slit while the diffracted beam path was equipped with a programmable antiscatter slit (fixed at 2.20°), a Ni  $\beta$ -filter, and a 2.5° Soller slit, data were collected under standard laboratory conditions (temperature and relative humidity).

#### 2.3. Conductivity measurements

The electrochemical measurements were performed using a computer-interfaced multichannel potentiostat with frequency response analyzer option (Bio-Logic Science Instruments VMP3). Electrochemical impedance spectroscopy was carried out within the 500–0.5 kHz frequency range with 10 points per decade, 5 measurements per frequency, and 5 mV AC amplitude. Samples for all electrochemical measurements were prepared inside an argon-filled glovebox.

#### 2.4. Raman spectroscopy

The Raman spectra were collected on a Nicolet Almega Raman dispersive spectrometer and the diode laser with excitation line

532 nm was used. The spectral resolution for all experiments was about  $2 \text{ cm}^{-1}$ . Temperature-dependent spectra were obtained with the use of a Peltier cooled Linkam stage.

#### 2.5. FTir spectroscopy

The infrared spectra were recorded on a PerkinElmer 2000 FT-IR system with a wavenumber resolution of  $2 \text{ cm}^{-1}$ . Room temperature measurements were performed with use of the ATR Gladiator accessory with diamond crystal, the temperature dependent experiments were done with HATR accessory equipped with heated ZnSe crystal; the accuracy of the temperature was estimated to be 1 °C. The analysis of Raman and IR spectra was performed with the Omnic software.

### 2.6. DSC

The DSC studies were performed using a TA Instruments Q200DSC apparatus in nitrogen flow. The heating rate was equal to  $5 \degree C \min^{-1}$ .

#### 2.7. TGA-FTIR

The degradation products formed during the heating of the electrolytes were evaluated by thermogravimetry combined with infrared spectroscopy (TG–FTIR) measurements.

The sample mass was about 6–8 mg and the heating rate was 10 °C per minute. During the TG-FTIR experiments, spectra were repeatedly collected as interferograms and then processed to build up a Gram–Schmidt reconstruction. Each point of which corresponded to the total IR absorbance of the evolved components in the spectral range  $4000-750 \text{ cm}^{-1}$ . Consequently, the Gram–Schmidt plot was formed by averaging the intensities of all FTIR peaks over the entire spectral range. Thus, the total absorbance intensity of each mass loss is a function of the concentration of the evolved gases and their corresponding, infrared extinction coefficients. On the basis of FTIR data, the emission profiles of selected pyrolysis products were constructed.

#### 3. Results and discussion

Our recent structural studies on NaTDI complexes with oligoethers allowed to extract four structural motifs, shown in Fig. 1 [28]. We have synthesized PEO-NaTDI membranes in a wide O/ Na, spanning from 3 to 32. Structural studies have shown the presence of several complex phases, matching the structural motifs presented in Fig. 1.

Tables 1 and 2 summarize positions of selected bands in the Raman and FTir spectra of PEO-NaTDI membranes.

We have shown that the upshift or split of selected anion bands, i.e v<sub>CN</sub>, v<sub>CN Im</sub> and  $\delta_{NCN}$  is a clear indicator of ionic association, in the sense of the cation-donor center linkage. The behavior of these changes obeys the same rules, which have been discussed for LiTDI glyme solvates [21–23]. The main difference between the LiTDI and NaTDI glyme solvates representing the same coordination motif, i.e ionic pairs **II** or dimers **IV**, is a higher number of the ether oxygens in the cation coordination sphere of the NaTDI based ones. The observed shift in the position of the key bands in spectra of NaTDI solvates is weaker than in their LiTDI analogues. This effect is in agreement with higher ionic potential e/r for a smaller Li<sup>+</sup>cation.

Raman mapping is a particularly convenient tool to demonstrate the phase variability of solid samples. The Raman maps recorded for solid NaTDI-PEO electrolytes unveil their mosaic structure, typical for PEO based electrolytes. An exemplary map of PEO-NaTDI (O/Na = 20) is shown in Fig. 2. Download English Version:

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