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Characterization of NaX (X: TFSI, FSI) – PEO based solid polymer electrolytes for sodium batteries

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ABSTRACT

Solid polymers electrolytes (SPEs) based on sodium bis(fluorosulfonyl) imide (NaFSI) and poly(ethylene oxide) (PEO) with different ether oxygen to sodium (O:Na) molar ratios (n), resulting in NaFSI(PEO)$_n$ materials are here presented for the first time. These SPEs are extensively compared with the corresponding NaTFSI(PEO)$_n$ system in terms of ionic conductivities, thermal properties, and charge carriers – to in detail outline both the role of the different anions used and the salt concentrations employed. While for the most dilute systems (n = 20) the two SPE families show similar ionic conductivities in the entire temperature range investigated (273-343 K), for n = 6 and n = 9 they differ significantly; at room temperature, the NaFSI based SPEs show lower ionic conductivities than the NaTFSI based analogues. This difference is mainly ascribed to differences in the morphology; while the NaTFSI salt, possibly by virtue of its large TFSI anion, acts to inhibit crystallization, NaFSI rather seems to favor crystallization. Furthermore, careful Raman spectroscopy analysis of the charge carrier speciation reveal higher aggregates to be present in the most concentrated SPE, NaFSI(PEO)$_6$, and the NaFSI based SPEs in general to result in less "free" anions than the NaTFSI based SPEs. Moreover, as both NaTFSI(PEO)$_n$ and NaFSI(PEO)$_n$ for n = 20 and n = 9 exhibit very similar glass transition temperatures, the FSI ion seem to be equally plasticizing as the TFSI ion, but for n = 6 the different speciation in terms of charge carriers also affects the relative dynamics of the polymer chains.

1. Introduction

The lithium ion battery (LIB) technology has played an important role in promoting the portable electronic devices revolution ever since the early 1990's [1]. Now when extending from portable applications to also large stationary applications such as energy storage for the "smart" grid – to accommodate renewable sources and allowing for peak-shaving *etc*, the availability and cost of lithium, [2,3] are key issues necessary to deal with. Amongst the accessible battery chemistries, sodium based batteries represent a realistic alternative. Research on close to room-temperature operating sodium batteries basically started in the 1980-90's [4–6], and recently received new momentum [7–10]. Within the various electrolytes available for sodium batteries, solid polymer electrolytes (SPEs) are fundamentally interesting as they avoid the use of organic liquids and thereby enable fabrication of flexible, safe, and compact solid-state structures.

SPEs for sodium based batteries simply consist of a sodium salt dissolved in a polymer matrix, the latter usually being poly (ethylene oxide) (PEO) due to its effectiveness in dissolving alkali metal salts. Following the trend of sodium battery research, studies on sodium SPEs were performed mainly during the 90's [11,12] and have re-gained attention quite recently [13,14]. Up to now, different combinations of Na-salts and PEO have been considered – mostly mimicking the much more researched lithium based SPEs.

Indeed, for example the ionic conductivities of sodium and lithium PEO-based SPEs are very comparable [15,16] and both rather modest; 10^{-5}-10^{-6} Scm^{-1} at room temperature. To reach the often quoted target value for battery application of 10^{-3} Scm^{-1}, SPE based batteries should be made to operate at temperatures in the range 333–353 K. Furthermore, to maximize the conductivity, the amorphous and ion conducting phase of these often semi-crystalline materials [17,18], should be promoted. The counter-anions to the Li and Na cations that have been investigated for both lithium and sodium SPEs are: perchlorate, ClO_4^- [19,20], triflate, $CF_3SO_3^-$ [21,22], iodide, I^- [23,24], thiocyanate, SCN^- [25],

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tetrafluoroborate, BF_4^- [26], bis(trifluoromethanesulfonylimide) (TFSI), $[(CF_3SO_2)_2N]^-$ [11,12,27,28], bis(pentafluoroethanesulfonylimide) (BETI), $[(C_2F_5SO_2)_2N]^-$ [29] and more recently also bis (fluorosulfonyl) imide (FSI), $[(FSO_2)_2N]^-$ [30]. The anion applied is crucial; *e.g.* triflate based SPEs usually show ionic conductivities lower than 10^{-7} Scm^{-1} at room temperature [21] and the use of the ClO_4^- anion has severe safety concerns. Among the above mentioned SPEs, the BETI and TFSI based SPEs have shown the highest ionic conductivities so far.

TFSI has been the most studied anion for SPEs ever since its introduction [27,31] and LiTFSI is *e.g.* used in the SPE based lithium metal battery operating in the Bolloré/Bluecar [32]. This large and flexible anion has a combination of size and high degree of charge delocalization that result in plasticizing properties [15,27,33,34]. Furthermore, the low lattice energy of TFSI based salts favors their dissociation in a polymeric matrix and once solvated the formation of ion pairs and high order aggregates is reduced, due to much weaker ion-ion interactions as compared to for example triflate based SPEs [21,35,36]. The FSI anion has many similar basic characteristics to the TFSI anion. In general, the DFT computed ion-ion interactions between Na^+ as well as Li^+ with TFSI and FSI are similar; 490.5 and 485.6 kJmol^{-1} for Na^+ and 591.7 and 580.4 kJmol^{-1} for Li^+ [37]. These values, and the differences between Li^+ and Na^+, are somewhat comparable to the interactions between Na^+ and a PEO oligomer – albeit obtained at a much lower computational level [38]. Based solely on DFT, PEO based SPEs using NaFSI (or LiFSI) can arguably be similarly or even more promising as compared to those employing NaTFSI (or LiTFSI) from a total conductivity point of view. Yet the slightly smaller size of the FSI anion might be a significant factor enough to alter the properties of PEO based SPEs in a rather unpredictable fashion.

The phase diagram for the NaTFSI-PEO system [15] shows the formation of crystalline complexes with stoichiometries of NaTFSI $(PEO)_7$ (T_m = 323 K) and NaTFSI$(PEO)_3$ (T_m = 341 K), and possibly an amorphous phase of *ca.* NaTFSI$(PEO)_{10}$. NaTFSI$(PEO)_n$ with $n < 7$ appears to be completely crystalline, while for n>7 an amorphous phase appears – rendering the SPEs semi-crystalline. The glass transition temperature (T_g) of the amorphous phase is 237 K and constant for all compositions [15]. In the very first LiTFSI-PEO phase diagram reported by Vallée et al. [33] no crystallization was detected, for $12 > n > 6$. In contrast to NaTFSI $(PEO)_n$, LiTFSI$(PEO)_n$ has three crystalline complexes with n: 6, 3, and 2. The former feature, later confirmed by Lascaud et al. [39], seems to be unique since it was not found for NaTFSI-PEO nor KTFSI-PEO [15]. This composition range was coined "the crystallinity gap" [39], and initially attributed to a crystallization failure of the LiTFSI$(PEO)_6$ complex in the presence of excess PEO [39]. Later, Labrèche et al. [40] published a revised LiTFSI-PEO phase diagram void of this crystallinity gap. Moreover, Edman et al. reported on slow re-crystallization kinetics from the melt for SPEs of salt rich stoichiometries ($12 \geq n \geq 5$) [28]. Thus, while perhaps these SPEs are not thermodynamically stable, the TFSI anion still seems very suitable for obtaining kinetically stable totally amorphous SPEs [27,28].

For LiFSI$(PEO)_n$ as well as NaFSI$(PEO)_n$ no phase diagrams are available in the literature. Nevertheless, LiFSI$(PEO)_{20}$ has recently been proposed as a promising SPE [30]. Despite displaying an ionic conductivity one order of magnitude lower than for LiTFSI$(PEO)_{20}$ at room temperature, a cell using this SPE showed excellent electrochemical cycling performance at 353 K [30]. There are no reports on how/if FSI is comparable to TFSI in terms of power of creating amorphous SPEs and there are also no reports on the analogous NaFSI$(PEO)_n$ system.

Here we study the basic properties of both NaFSI$(PEO)_n$ and NaTFSI$(PEO)_n$ SPEs, with focus on the materials characterization in terms of thermal properties, ionic conductivities, and the nature of the charge carriers. As no previous studies have been carried out for NaFSI$(PEO)_n$ and also no spectroscopic studies for any FSI based SPEs have been reported, we here for the first time connect the gathered data on morphology and ion association both to the influence of the different anions, FSI and TFSI, and to the different O:Na molar ratios, and furthermore also are able to compare with the corresponding Li based SPEs.

2. Experimental

High molecular weight PEO (Polysciences 4031, Mw: 5×10^6 g/mol) was dried at 323 K under high vacuum conditions ($<10^{-3}$ Pa) for 48 h. Anhydrous acetonitrile (99.8%, Sigma Aldrich) was dried over 3 Å molecular sieves (Fluka). NaTFSI (99.5%, Solvionic) was dried at 393 K and NaFSI (99.7%, Solvionic) at 348 K, both under medium vacuum conditions (< 7 Pa) for 48 h.

Samples of NaTFSI$(PEO)_n$ and NaFSI$(PEO)_n$ were prepared by dissolving appropriate amounts of polymer and salt in acetonitrile, in order to obtain O: Na^+ molar ratios (n) of 6, 9 and 20. After stirring for at least 4 days at 200 rpm, which arguably may reduce the PEO Mw somewhat – but still remains far beyond the entanglement limit, the solutions were poured in PTFE molds. After solvent evaporation, the cast films were dried under medium vacuum conditions (<7 Pa) at 323 K for 24 h, in order to eliminate any solvent residuals.

All sample preparation was performed in a glove box, under argon atmosphere ($O_2 < 5$ ppm, $H_2O < 1$ ppm). While the presence of polymerization residuals and additives in the PEO[1] can interfere with the Karl-Fischer measurements, we still estimate the water content in all the SPEs to be <100 ppm.

Differential scanning calorimetry (DSC) traces were registered on a TA Instrument Q1000. For each measurement, 10–15 mg of sample was sealed in an aluminum pan inside the glove box. The samples were first cooled from 313 K to 193 K at 10 K/min and subsequently heated, at the same rate, to 423 K. During the measurements, a flow of helium gas guaranteed a dry sample chamber. To simplify a direct comparison with the conductivity measurements, additional 2 K/min traces were registered. These samples were heated from 313 to 343 K, cooled to 243 K, and thereafter heated to 343 K – all to mimic the conductivity measurements. For each sample composition at least four separate runs were made. The melting temperature (T_m) was obtained as the peak maximum of the heat capacity change, while the glass transition temperature (T_g) was obtained as the midpoint of the heat capacity change during the heating scan.

Ionic conductivity measurements were performed using a Novocontrol broadband dielectric spectrometer, in the range (10^{-2}–10^7) Hz. The SPE films were cut to disc shaped samples and sandwiched between two blocking stainless steel electrodes. The cell was kept under pure and dry nitrogen atmosphere. Initially, the samples were brought to 343 K in order to melt them and guarantee a good electrolyte-electrode contact. Thereafter, a cooling/heating cycle was made: 343-243-343 K, using a step of 10 K and an equilibration time of 30 min. A nitrogen gas cryostat with a temperature stabilization of 0.2 K was employed to control the temperature of the cell. The DC conductivity (σ) was obtained using the formula:

$$\sigma = \frac{4t1}{d^2 \pi R}$$

[1] The following residuals and additives are listed: ammonia (200 ppm), ethylene oxide (40 ppm), monoethylamine (200 ppm), BHT (1000 ppm), and untreated fumed silica (3 %).