Development of sodium-conducting polymer electrolytes: comparison between film-casting and films obtained via green processes

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ABSTRACT

Sodium-conducting solvent-free polymer electrolytes based on commercially available and inexpensive materials poly(oxyethylene), POE, and three different sodium salts (NaI, $NaCF_3SO_3$ and $NaClO_4$) were prepared and exhaustively characterized. In order to minimize the environmental impact related to conventional film processing based on casting, a combination of lyophilization and hot-pressing was successfully applied. Contrary to film-casting, this new approach led to very homogeneous and pore-free films. This study suggests the obtained polymer electrolyte films as a promising route to enhance not only ionic conductivity but also mechanical properties. Furthermore, a preliminary work on salt blends hosted by POE shows that they strongly decrease melting point and crystallinity of the polymer electrolytes and paves the way for enhanced sodium-conducting materials.

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1. Introduction

Nowadays, electrochemical energy storage extensively relies on Lithium-Ion Batteries (LIB). Stimulated by the demand of portable electronics, the trend has been tremendously accelerated by delocalized energy management needs (smart grids) and electric vehicles [1,2] and it is expected to explode in the future. Such expected increase of LIB production has put back on stage the current and unsolved debate about lithium resources. They are actually very limited, since lithium is only the 33rd most abundant element on Earth and its heterogeneous distribution is mainly concentrated in South America [3]. Therefore, the lithium cost has significantly increased during the last 30 years and will continue with the expected growth of LIB markets. Hence, not only regarding economic reasons, but also preservation of Earth resources, it is necessary to anticipate its substitution by more abundant elements and to start focusing on post LIB. Given their high availability and low cost, alkaline elements such as Na and K, and alkaline-earth ones such as Mg and Ca, emerge as promising candidates. With a redox potential of − 2.71 V vs SHE and theoretical capacities of 1.2 Ah/g and 1.1 Ah/cm^3, Na presents physical and chemical properties close to Li

(3.8 Ah/g and 2.1 Ah/cm^3) [4], and therefore, a similar behavior. Thus, the search for new electrodes and electrolytes for sodium batteries (SB) should benefit from previous learning of Li ones. Despite the 1st proof of concept was demonstrated more than 30 years ago [5,6], SB technology has recently attracted a growing interest [7–9]. Indeed, developments were performed on both Na/S [10,11] and Na/NiCl₂ (ZEBRA) [12,13] batteries 25 years ago. These batteries, operating at high temperature, are mainly dedicated to stationary applications and use β-Alumina as electrolyte. In order to move successfully from LIB to SB, low and medium temperature operating batteries should be attainable to cover the LIB markets, including portable electronics, electric vehicles and smart grids. Therefore, the achievement of high performance SB calls for reliable electrolytes for both Na-ion and Na-polymer batteries. The formers require liquid electrolytes in combination with porous or dense separators (gelled or plasticized polymer electrolytes). Following this approach, Stallworth et al. investigated PAN gelled electrolytes by ^{23}Na NMR and Impedance spectroscopies [14], Egashira et al. characterized Na tertiary liquid electrolytes incorporating a tetrafluoroborate ionic liquid, PEGDME and NaBF₄ [15]. Furthermore, Bhide et al. [16] reported EC-DMC Na electrolytes, claiming that $NaPF_6$/EC-DMC leads to a stable surface film on $Na_{0.7}CoO_2$, enabling reversible cycling. Kumar et al. used Na-triflate in EMI-Tf to swell PVDf-HFP [17] and Ding et al. evaluated the effect of temperature and Na⁺ concentration on liquid electrolytes [18]. Cao et al. [19] reported the development of polymer electrolytes

based on perfluorinated sulfonic membranes in their Na-form, which were swelled in ethylene carbonate − propylene carbonate (EC-PC; v:v, 1:1) to produce ion-exchange membranes also acting as separators in Na-ion batteries. To improve mechanical properties of ambient-temperature Na-ion batteries, composite polymer electrolytes made of PVdF-HFP copolymer reinforced by glass-fiber were also proposed [20]. Recently, the potentiality of UV-induced photopolymerization of an oligoether precursor was claimed as a feasible and scalable solvent-free process to prepare amorphous cross-linked polymers to be swelled by Na-ion liquid electrolytes [21]. Regarding polymer electrolytes, Na indeed preceded Li with the pioneering works of P.V. Wright et al. on NaI, NaSCN and poly (oxyethylene) POE complexes [22–25]. In more recent contributions, Na salts hosted in PVA (polyvinyl alcohol) or in PAN (polyacrylonitrile) have been reported [26,27]. Nevertheless, both PVA and PAN are questionable for SB, the former because of its hydroxyl groups (OH), and the latter because of the acidity of its tertiary proton [28,29]. Additionally, the high conductivity reported for such polymer electrolytes could be probably due to traces of water or remaining solvents. A publication from J. Serra-Moreno et al. [30] on POE/NaTFSI/SiO_2 nanocomposite electrolytes shows interesting conductivity. However, at the typical salt concentration range of polymer batteries, *i.e.* $30 \leq O/M \leq 20$, these POE/NaTFSI composite electrolytes are semi-crystalline, melting between 64 °C and 61 °C with crystallinity degrees of 55% and 42%, respectively, whereas amorphous cross-linked NaTFSI electrolytes exhibited, at O/Na = 20, conductivities reaching 0.02 and 0.8 mS·cm^{-1} at 25 °C and 80 °C, respectively, without any hysteresis [31]. Boschin et al. [32] presented a fundamental study regarding the influence of morphology and ion association (NaFSI and NaTFSI) on the performance of POE-based polymer electrolytes. In order to favor the electrode/electrolyte interface, Na-CMC, the sodium form of carboxymethyl cellulose used as additive in the electrode formulation, was found to reinforce the POE electrolyte when blended with POE/$NaClO_4$ [33]. Ni'mah et al. [34] introduced TiO_2 nanoparticles to decrease crystallinity in POE-$NaClO_4$ polymer electrolytes, reporting only a discrete increase in conductivity from 1.35×10^{-4} S cm^{-1} to 2.62×10^{-4} S cm^{-1} at 60 °C for the composition O/Na = 20. Several approaches dealing with lithium-polymer electrolytes could be revisited for sodium ones as e.g. fully organic cross-linked host polymers [31,35–37] or hybrid organic-inorganic ones made, by sol-gel, from trialkoxysilanes [38].

Mainly due to the relative scarcity of data regarding Na-conducting POE electrolytes, it was decided, in this study to focus on commercial POE as host polymer and on well-known commercial Na salts. Although POE $5 \cdot 10^6$ g/mole is often used as host, it was recently demonstrated that even a mild shearing of POE solutions produces a dramatic decrease of chain lengths [39]. Hence, in this work, POE $3 \cdot 10^5$ g/mole and three fairly inexpensive Na salts (NaI, $NaCF_3SO_3$ and $NaClO_4$) were selected for Na polymer electrolytes preparation. Furthermore, special attention was also paid to the impact of the film elaboration process on the polymer electrolyte performance. In consequence, the assessment of reliable, economic and environmental friendly organic solvent-free processes regarding conventional film-casting was performed. In this sense, films prepared from organic solutions were compared with those prepared by a combination of lyophilization and hot-pressing (LHP). Additionally, the effect of Na salt blends was also investigated.

2. Experimental

2.1. Materials and polymer films preparation

All reagents were supplied by Sigma-Aldrich in analytical grade. Sodium iodide (NaI), sodium trifluoromethane sulfonate ($NaCF_3SO_3$) and sodium perchlorate ($NaClO_4$) were used with POE host (M_w 3×10^5 g/mol). As a first approach, all solutions were prepared with an intermediate O/Na ratio of 20. In this sense, specific amounts of polymer and salts were dissolved by stirring during six hours in acetonitrile (ACN) and deionized water for film-casting and LHP, respectively. For film-casting films, solutions were degassed to remove air bubbles and later poured into glass petri dishes covered by a PTFE film (Bytac® surface protection laminate, Sigma-Aldrich). The solvent was slowly evaporated at room temperature during 48 hours. Using this methodology, films with thickness in a range from 120 μm to 165 μm were obtained. For LHP films, solutions were frozen at −20 °C and later lyophilized (FreeZone^1, LABCONCO, USA) during 48 hours. Afterwards, the material so obtained was hot pressed between two stainless steel plates ($100 \times 100 \times 5$ mm^3) applying pressure and temperature (50 kN; 100 °C). The films so obtained had a thickness ranging from 75 μm to 100 μm. Films obtained by both approaches were subsequently dried under vacuum at 50 °C during 12 hours to eliminate residual traces of solvents and later stored in vacuum to avoid moisture absorption.

2.2. Scanning electron microscopy

The structural/morphological characterization of the films was performed using a Philips XL-30 scanning electron microscope (SEM) operating at 10 kV. For avoiding surface charge effects, before imaging, samples were gold coated using the sputter coater Polaron SC7610 (Fision Instruments, UK) at 18 mA under 1×10^{-2} mbar vacuum for 2 minutes.

2.3. X-Ray diffraction

X-Ray diffraction (XRD) measurements were carried out using a Philips X'PERT MPD diffractometer (Cu Kα radiation) operating at 40 kV and 40 mA. The XRD patterns were recorded over a 2θ range of 5−80° using a step scan of 0.02° and a counting time of 1 sec per step.

2.4. Thermal and thermomechanical analyses

The thermogravimetric analysis (TGA) of the samples was performed using a Pyris^1 TGA (Perkin Elmer, USA) thermogravimetric analyzer. Samples were heated in a platinum crucible from 30 °C to 400 °C at a heating rate of 10 °C/min under air atmosphere. Onset temperature (T_{onset}) was determined as the point of intersection of the tangent drawn at the point of greatest slope with the extrapolated base line. For differential scanning calorimetry (DSC) studies, we used a DSC822e (Mettler Toledo, Switzerland) under a 50 mL/min constant N_2 (g) flow. A first scan to eliminate any residual solvent was applied from 30 °C to 150 °C (10 °C/min). At the same rate, samples were then cooled down and heated up from −100 °C to 250 °C to determine melting temperature (T_m), enthalpy of fusion (ΔH_m) and glass transition temperature (T_g). The relative percentage of crystallinity (X_c) was directly related to the area under the 1st melting peak by using the equation [40]:

$$X_c = \Delta H_m / \Delta H_m^0 \times 100\%$$

where ΔH_m is the melting enthalpy estimated experimentally and $\Delta H°_m$ is the melting enthalpy for POE 100% crystalline (213.7 J·g^{-1} [41]). T_g was estimated as the intersection of the tangent drawn through the heat capacity jump with the base line recorded before the transition. The uncertainty of the measurements was estimated to be ±1 °C.

Dynamic Mechanical Thermal Analyses (DMTA) on samples 2.5×4 mm^2 were conducted using a DMA Q800 (TA Instruments,