Polymer electrolytes based on POE and Na-TFS salt for all-solid-state batteries

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ABSTRACT

Purpose: Currently, electrochemical energy storage systems mostly focus on lithium-ion batteries; especially in the field of portable electronics and electric transportation. Nevertheless, it is expected that the exponential growth of these markets and limited lithium resources will increase the price of lithium-based energy storage systems. To meet growing demands in terms of green and sustainable electric power storage, alternative electrochemical technologies towards post lithium-ion batteries are required.

Design/methodology/approach: In the present study, polymer electrolytes based on poly(oxyethylene) (POE) and Na-TFS ($NaCF_3SO_3$) were developed to be used in solvent-free batteries. Electrolytes were prepared using two methodologies: (i) a green-chemistry approach based on lyophilization combined with hot-pressing and (ii) the film-casting method.

Findings: Advantages and limitations of both approaches were investigated by several characterization techniques (morphology, thermal and conductivity studies). Using lyophilization/hot-pressing, waste and chemical derivatives production is prevented (Green Chemistry approach) and uniform and porous-free films with controllable thickness and improved mechanical properties are achievable.

Research limitations/implications: Further work regarding the development and application of novel polymer backbones is necessary to reach performances comparable to lithium-based polymer electrolytes in terms of electrical properties (conductivity).

Originality/value: This work is in total agreement with the current need of developing alternative materials towards sustainable and environmental friendly post lithium-ion batteries. This global aspiration is supported by the recent re-emerging focus on sodium-ion batteries.

Keywords: Engineering polymers; Sodium ion battery; Solvent-free electrolyte; Energy storage

MATERIALS

1. Introduction

The growing energy demand, significant increase of price in refined fossil fuels and environmental consequences associated to their use, has promoted a rising global concern regarding alternative materials and technologies for energy storage and generation. The use of polymer materials in the fabrication of electrolytes has lately gained more attention. This mainly responds to the advantages associated to the production of all-solid-state batteries, which include no leakage, volumetric stability, solvent-free conditions, easy handling and improved electrochemical performance [1]. Moreover, due to their mouldability, mechanical strength and flexibility of design, solid polymer electrolytes (SPEs) allow obtaining almost any desirable shape, enabling miniaturization of final devices [2]. Most SPEs consist of a host polymer or backbone, to provide dielectric strength and mechanical stability, and an inorganic salt, which supplies ionic carriers to produce conductivity [3]. Film-casting is the preferred technique for preparing polymer electrolytes [4]. This approach consists on solvating a host polymer and a salt in an auxiliary solvent [5,6]. Once the solvent is evaporated, a film with a thickness in a range from some micrometers to a few millimeters can be peeled-off from the surface of the host container. An alternative to film-casting proposed in this work is based on lyophilization (freeze-drying/dehydration technique typically used for materials long-term storage and shipping) [7,8], followed by hot-pressing. The process consists on freezing an aqueous solution and sublimating it from solid to gas phase in vacuum conditions. The material so obtained is later hot-pressed to produce a uniform film.

Poly(oxyethylene) (POE), polyvinyl chloride (PVC) and polyvinyl alcohol (PVA) [9,10] are the polymers most frequently used for electrolytes preparation. POE is a semi-crystalline polymer able to dissolve a wide variety of inorganic salts to form polymer electrolytes that exhibit ionic conductivity and considerable chemical and thermal stability [11]. Although most POE electrolytes reported are based on lithium [12], other inorganic salts (magnesium, calcium, ammonium, potassium and sodium [13, 14]) have been also explored. Among them, sodium-based electrolyte films have recently re-emerged as possible candidates to replace lithium ones [15, 16], since sodium besides being cheaper and more available than lithium, allows obtaining solid electrolytes with considerable conductivity. Most works related to sodium-based electrolytes reported focus on the use of film-casting [17,18]. Nevertheless, lyophilization followed by hot-pressing has not received

the same diffusion [19]. Only a few works related to the preparation of lithium-based electrolytes by hot-pressing of bulk materials are found in the literature [20].

In this experimental work, we have prepared and characterized sodium based polymer electrolytes based on freeze-drying/lyophilization followed by hot-pressing towards solvent-free post lithium-ion batteries. For comparison purposes, conventional film-casting was also applied. Both approaches were investigated through several characterization techniques to determine strengths and weakness of each methodology regarding solvent-free and environmental friendly battery applications. In particular, we have paid attention on electrical (complex impedance spectroscopy) and thermal (DMA, TGA and DSC) properties. In all cases, polymer electrolytes consisted of POE as backbone filled with $NaCF_3SO_3$ salt.

2. Experimental

2.1. Materials and electrolyte preparation

Sodium trifluoromethanesulfonate ($NaCF_3SO_3$) was used for filling the POE polymer host (M_w 3 x 10^5). To prepare different compositions, specific amounts of the polymer and salt were dissolved by stirring in acetonitrile (ACN) and deionized water for film-casting and lyophilization/hot-pressing, respectively. For film-casting electrolytes, solutions were degassed to remove air bubbles and then casted into Teflon petri dishes. Solvent was evaporated at room temperature during 48 hours to produce 120-165μm thickness films measured using a digital micrometer (Mitutoyo). Regarding lyophilization/hot-pressing electrolytes, solutions were frozen at -20°C, lyophilized during 48 hours and hot-pressed (50 kN at 100°C) between two stainless steel plates to provide 75-100μm thickness films. In both cases, films were dried under vacuum at 50°C during 12 hours and later stored in a desiccator to avoid later moisture absorption.

2.2. Characterization techniques

Scanning electron microscopy (SEM) was used for morphological characterization. For this purpose, samples were gold coated using the sputter coater Polaron SC7610 (Fision Instruments, UK) at 18mA current under 1 x 10^{-2} mbar vacuum for 2 minutes. Thermogravimetric analysis (TGA) was carried out using a Pyris[1] thermogravimetric

analyzer (Perkin Elmer, USA) by heating samples from 30°C to 400°C (10°C/min) under air atmosphere. For differential scanning calorimetry (DSC), we used a DSC822e (Mettler Toledo, Switzerland). Thermal scans at 10°C/min were performed under a 50 mL/min constant $N_2(g)$ flow on 8.5 mg samples. A first scan to eliminate thermal history was applied from 30°C to 150°C. Afterwards, samples were cooled down to -100°C and heated up to 250°C to determine melting temperature (T_m), enthalpy (ΔH_m) and glass transition temperature (T_g). Dynamic mechanical thermal analyses (DMTA) were conducted using a DMA Q800 (TA Instruments, USA) working in tensile mode at 1 Hz, 15µm as oscillation amplitude and heating samples from -100°C to 60°C (5°C/min) under N_2 atmosphere. Conductivity measurements were carried out at different temperatures (20-100°C) using stainless steel blocking electrodes and an Impedance/Gain-Phase Analyzer SI1260 (Solartron, UK) by applying a 100 mV amplitude signal (frequency: 1Hz-10MHz).

3. Results and Discussion

3.1. Microstructural analysis

According to SEM images, a remarkable difference in roughness and texture of casted and hot-pressed polymer films is clearly noticed (Figure 1).
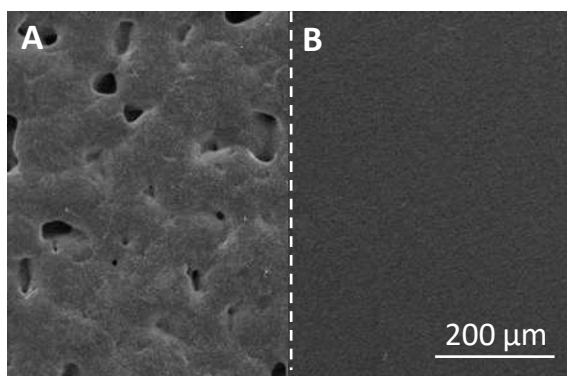

Fig. 1. SEM micrographs of POE-NaCF$_3$SO$_3$ electrolytes: prepared by film-casting (A) and lyophilization/hot-pressing (B)

Films prepared by film-casting presented a highly porous surface (pores ranging from 11 to 65µm), which might be caused by uncontrolled solvent evaporation. On the other hand, a compact, flat and porous-free surface was observed on those films prepared by hot-pressing of previously lyophilized material. This is an indisputable asset, since the presence of pores in solvent-free electrolytes is critical for battery applications concerning mechanical performance, critical to ensure cell safety during operation. Besides providing ion transport, the polymer electrolyte must be able to prevent any physical contact between the electrodes, for avoiding short circuits and thermal runaway.

3.2. Thermal and thermomechanical behavior

Thermogravimetric analysis (TGA)

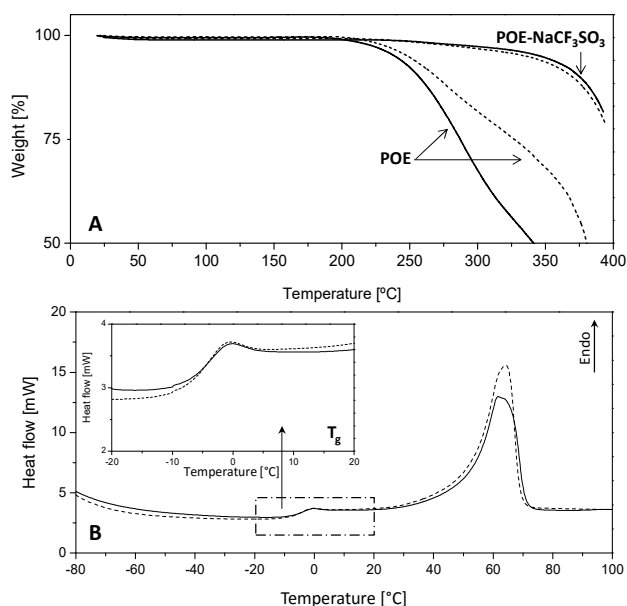TGA studies showed no significant difference between casted and hot-pressed electrolytes (see figure 2A).

Fig. 2. A: TGA patterns of POE and POE-NaCF$_3$SO$_3$. B: DSC curves obtained for POE-NaCF$_3$SO$_3$ electrolytes. Continuous line: lyophilization/hot-pressing; dashed line: film-casting

An initial small weight loss below 100°C, probably related to humidification of samples during handling, was observed in all cases. Degradation of POE was detected at an onset temperature of 213.4°C and 204.9°C for casted and hot-pressed samples, respectively. On the other hand, degradation of polymer electrolytes started later (240°C

and 254°C for casted and hot-pressed, respectively). Such delay could be attributed to a strong interaction between salt molecules and chain fragments originated from thermal degradation of POE, as previously described by Cameron et al [21].

Differential scanning calorimetry (DSC)

Traces regarding T_m and T_g for POE-NaCF$_3$SO$_3$ electrolytes are shown in figure 2B. T_m values were read directly from the maximum of the predominant endothermic peaks. The relative percentage of crystallinity (X_c), related to the area under the melting peak, was estimated as the ratio between experimental melting enthalpy (ΔH_m) and melting enthalpy for POE 100% crystalline (ΔH_m^0), expressed in percentage [22]. T_g was determined as the intersection of the tangent drawn through the heat capacity jump with the base line recorded before the transition (inset figure 2B). Table 1 summarizes T_m, T_g and X_c for POE and sodium electrolytes.

Table 1.
T_m, X_c and T_g for POE and electrolytes (C: film-casting; H: lyophilization/hot-pressing)

Film	T_m [°C]	X_c [%]	T_g [°C]
POE	66.7	91.8	-55.5
POE-NaCF$_3$SO$_3$ (C)	62.2	58.5	-15.2
POE-NaCF$_3$SO$_3$ (H)	61.6	56.9	-15.7

POE free of salt presented a T_m at 66.7°C, which corresponds to a 91.8% of completely crystalline POE (213.7 J·g^{-1}), according to the bibliography [23]. However, the interaction between the host polymer matrix and the salt leads a polymer complex more asymmetric with respect to the original POE matrix with lower T_m in both cases. Regarding crystallinity (X_c), it significantly decreased, reaching values under 60% in both electrolytes, which indicates that amorphosity increases and it is related to the interaction of the salt with the backbone polymer. A slightly lower crystallinity value was estimated for the electrolyte prepared by lyophilization/hot-pressing, reduced about 1.6°C. This indicates a higher amorphosity degree in such sample, and anticipates enhanced electrical properties, since ionic mobility is expected to be improved. Concerning T_g, in both polymer electrolytes, it shifted to more positive values when compared to POE free of salt (-55.5°C). Since T_g reflects the segmental mobility of the polymer chains, and therefore, ionic mobility in fully amorphous polymer electrolytes, the higher this value, the higher the expected conductivity [24].

Dynamic mechanical thermal analysis (DMTA)

Figure 3 presents storage modulus (E') and tan δ for POE free of salt and electrolytes. The temperature dependency of mechanical properties is related to the cross-link density, where E' initially slowly decreases as a function of temperature. As temperature approaches Tg, E' starts to decrease rapidly. At this point, the amorphous component of the polymer achieves an increased degree of freedom and, at the end of Tg, E' declines by about 50% from the starting value.
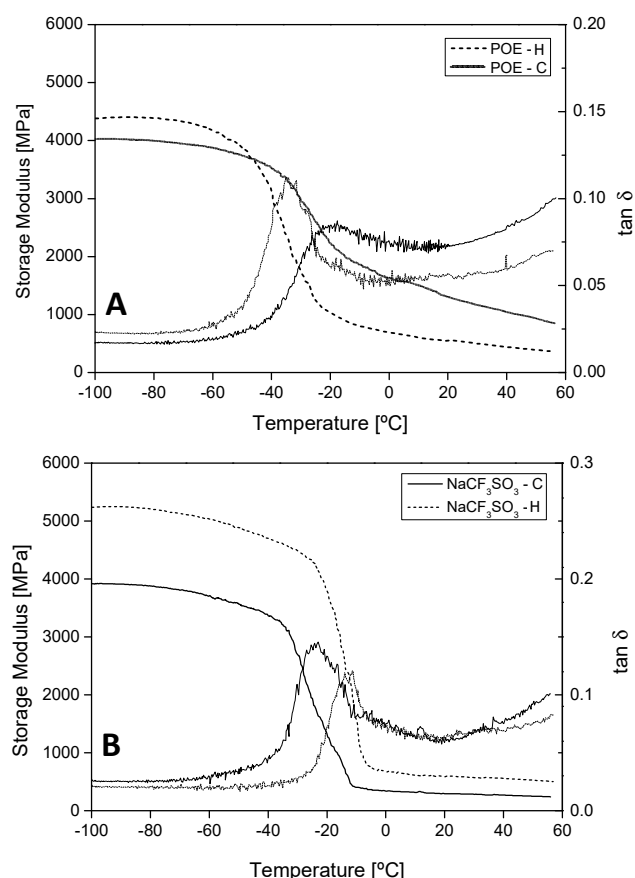

Fig. 3. DMTA curves obtained for POE (A) and electrolytes (B; O/Na = 20), including storage modulus (E') and tan δ (continuous line: film-casting; dashed line: lyophilization/hot-pressing)

Once Tg is exceeded, the modulus exhibits a region of relative stability because of the crystalline component of the material, which only remains under Tm, and once exceeded, mechanical properties are suddenly lost, leading to sample creeping. In agreement to SEM images, higher E' values were estimated for electrolytes prepared by

lyophilization/hot-pressing. An improvement of about 500 MPa was calculated for POE free of salt and about 1.5GP regarding electrolytes. Below Tg, tan δ curves increased as temperature increased, leading to a peak that suggests dispersion of a large amount of energy. The dispersion would be originated from the interfacial friction occurred in the polymer-salt complex.

3.3. Design of drop forging formed on TSFP

Figure 4 A shows the complex impedance plots obtained at different temperatures for casted films. The semicircle at the high frequency region is related to the bulk conductivity of the polymer electrolyte, while the spike at the low frequency zone is associated to the blocking electrodes conductivity. As temperature increases, the semicircle becomes smaller, consequence of its shifting to the high frequency region promoted by the conductivity increase. The frequency dependent conductivity at different temperatures is depicted in Figure 4 B. Conductivity is lower at the low frequency region, since charge accumulation effects at the electrode-electrolyte interface reduce ions mobility. As temperature increases, conductivity increases, and the plateau shifts to higher frequencies. At the high frequency region, the mobility of the ionic charges increases, leading to higher conductivities. The logarithmic DC conductivity (Log σ_{DC}) vs the inverse absolute temperature comparing both procedures is at the inset in Figure 4 B. Values were obtained by extrapolation of the plateau region to ω=0. Slightly higher conductivities were observed at the high temperature region for hot-pressed electrolytes, in accordance to a higher amorphosity degree (DSC measurements). The conductivity patterns obey the Vogel-Tamman-Fulcher (VTF) expression [19], being the best fitting parameters and their corresponding conductivities, at room temperature (20°C) and 95°C, those summarized in Table 2. The lowest E_a, was obtained for samples processed by lyophilization followed by hot-pressing, suggesting easier ionic transport.

In general terms, the ionic conductivity increases while temperature increases, since flexibility of the polymeric chain is favored by a decreased in viscosity [25].

Nevertheless, when temperature approaches T_m, a singular behavior is observed, not only a right shift and narrowing of the plateau region (frequency vs conductivity), but also a considerable decrease in conductivity. Such behavior was also observed when samples at different concentrations were investigated, as it will be exposed later.
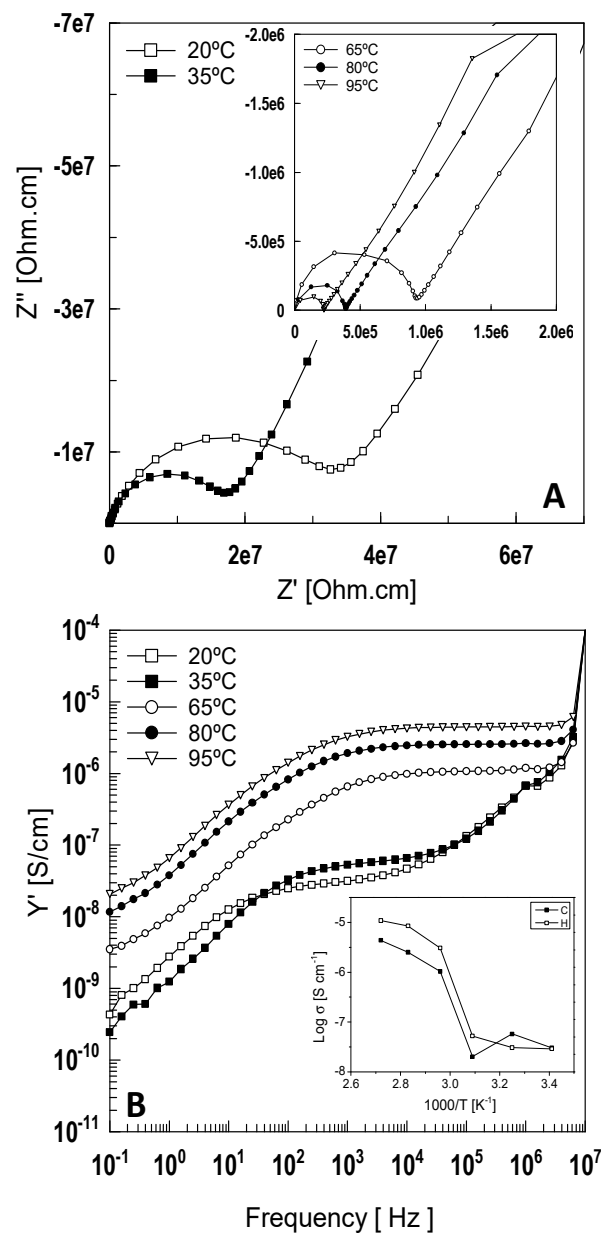

Fig. 4. Complex impedance plots: A) and frequency dependent conductivity: B) for $NaCF_3SO_3$ based electrolytes prepared by film-casting. Inset in B: logarithmic σ_{DC} vs inverse absolute temperature (C: film-casting; H: lyophilization/hot-pressing)

To determine the effect of salt concentration at different temperatures, additional POE-$NaCF_3SO_3$ electrolytes were prepared by lyophilization/hot-pressing (O/Na= 8, 12, 16, 20 and 25). Log σ_{DC} vs the inverse absolute temperature for all O/Na ratios is depicted in Figure 5A.

Table 2.
Conductivity and fitting parameters at 20°C and 95°C (C:film-casting; H: lyophilization/hot-pressing)

Conductivity (S·cm⁻¹)		VTF fitting			
@20°C	@95°C	A $S \cdot cm^{-1}$	E_a eV	T_0 K	R^2
C	3.03×10^{-8}	4.38×10^{-6}	0.10	0.103	197	0.997
H	2.89×10^{-8}	1.09×10^{-5}	0.13	0.092	198	0.934

A: pre-exponential factor; E_a: activation energy; T_0: ideal glass transition temperature ($T_g-60K \leq T_0 \leq T_g-40K$).
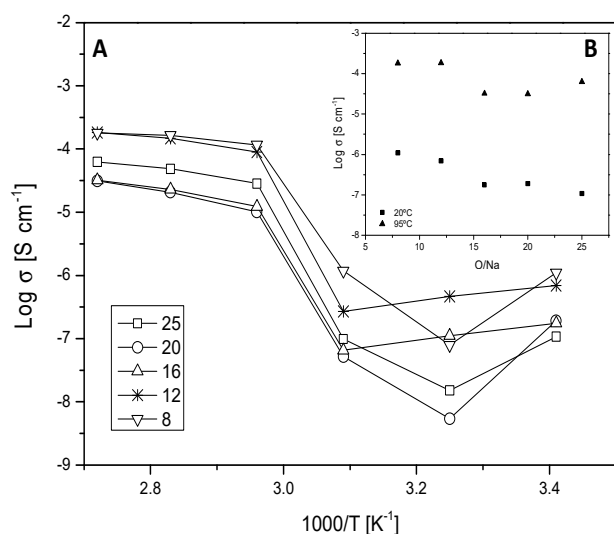

Fig. 5. A: logarithmic σ_{DC} vs inverse absolute temperature at different O/Na ratios. B: conductivity against sodium concentration at 20°C and 95°C

As seen there, a similar behavior than that previously exhibited for O/Na = 20 when temperature approaches T_m was observed at all concentrations. Further studies are currently undergoing to determine the reason of such a change in the electrolyte behavior under these conditions. Figure 5 B shows conductivity values for 20°C and 95°C at different O/Na ratios. In both cases, a non-linear behavior of conductivity when salt concentration increases was observed. J. Serra et al.[19], explain this effect as a result of the compromise established between the amorphization effect of the salt and the charge carrier number. Tough the fraction of the amorphous phase of the complex is increased by the salt concentration, the ionic motion in the polymeric backbone is restricted by the ion pair formation and their interactions [25]. Hence, conductivity decreases when concentration increases from O/Na = 25 to 20. Nevertheless, beyond that region, for an O/Na ratio of 12 and 8, conductivity increases again probably due to the triple ion formation or re-dissociation effect. The highest conductivity value was observed for O/Na = 12 at 95°C.

4. Conclusions

Sodium polymer electrolytes based on POE and $NaCF_3SO_3$ were prepared using the lyophilization followed by hot-pressing. For comparison purposes, analog electrolytes were prepared by conventional film-casting. Their thermal, morphological, electrical and mechanical properties were compared to determine advantages and limitations of each methodology. Using the proposed approach, more uniform and porous-free surfaces with controllable thickness were obtained, providing films with enhanced mechanical behavior, as demonstrated by DMTA assays. Furthermore, using this preparation procedure, chemical derivatives production is prevented, promoting green chemistry practices in the batteries field. Further studies are currently undergoing to determine the effect of this processing technique on the performance of electrolytes based on different sodium salts and polymer backbones.

Acknowledgements

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