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Additional Information

Novel poly(vinylidene fluoride-trifluoroethylene)/poly(ethylene oxide) blends for battery separators in lithium-ion applications

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Abstract:

Polymer blends based on poly(vinylidene fluoride-trifluoroethylene)/poly(ethylene oxide), P(VDF-TrFE)/PEO for Li-ion battery separators applications have been prepared through solvent casting technique. The microstructure, hidrophilicity and electrolyte uptake strongly depend on PEO content within the blend. The best value of ionic conductivity at room temperature was 0.25 mS.cm^{-1} for the 60/40 membrane. The membranes are electrochemically stable.

Keywords: P(VDF-TrFE)/PEO blends, Li-ion batteries, separator membranes, ionic conductivity

1. Introduction

Solid polymer electrolytes (SPE) can be used in solid state batteries [1] and other electrochemical devices [2] due to their high energy density, high ionic conductivity, and electrochemical stability [3, 4].

In solid state batteries, SPE are used as separators, the main parameters determining the performance of SPE being their thickness, permeability, porosity/pore size, wettability, electrolyte absorption and retention, chemical, dimensional and thermal stability [3].

Different host polymers have been used for SPE, among which stand out poly(ethylene) (PE) [5], poly(propylene) (PP) [6], poly(ethylene oxide (PEO) [7], poly(acrylonitrile) (PAN) [8], poly(vinylidene fluoride) and its copolymers [9]. One of the most used host polymer in SPE is PEO [10]. It shows high ionic conductivity of the order of 10^{-8} to 10^{-4} S.cm^{-1} at temperatures from 40 to 100ºC in some complexes systems, nevertheless presents poor flexibility [10]. Strategies for increasing the ionic conductivity of PEO include the incorporation of plasticizers and the production of polymer blends that reduce the crystalline fraction and increase the polymer segmental mobility [11].

An interesting polymer for battery applications are also PVDF and its copolymers such as poly(vinylidene fluoride-trifluoroethylene), P(VDF-TrFE), due to their high polarity, excellent thermal and mechanical properties, controllable porosity and wettability by organic solvents, being also chemically inert and stable in cathodic environment [12]. PVDF allows a favorable pore wetting in comparison to nonpolar commercial battery separators [13].

Polymer blends of the aforementioned polymers have been scarcely investigated and just for applications as electrochromic devices [14].

The main goal of this work consist in the evaluation of the performance of P(VDF-TrFE)/PEO polymer blends as potential battery separator membrane. Blends with and

without electrolyte solution (1M LiClO4.3H2O-PC) were prepared and their morphology and electrochemical properties and stability evaluated.

2. Material and Methods

2.1. Blend Preparation

P(VDF-TrFE) (M_w = 350 000) and PEO (M_w = 100 000) were acquired from Solvay and Polysciences, respectively. P(VDF-TrFE)/PEO blends were prepared by dissolving the appropriate amounts of each component in N,N-dimethylformamide (DMF) at 60ºC with the help of a magnetic stirrer until a homogeneous and transparent solution was obtained (after around 4 hours). The polymer/solvent volume ratio was 15/85.

P(VDF-TrFE)/PEO blends were prepared with compositions of 100/0, 80/20, 60/40, 50/50, 40/60 and 20/80 in weight ratio. P(VDF-TrFE)/PEO dissolutions were deposited on a clean glass substrates and the solvent was allowed to evaporate at 70ºC for 2 h. Complete removal of the solvent was achieved by placing the sample at 10^{-2} mm Hg for another 3 h at 70 ºC.

2.2. Electrolyte Solution and Uptake

The membranes were immersed in the liquid electrolyte, consisting of a 1 M solution of LiClO$_4$.3H$_2$O in propylene carbonate (PC), for 24 h. The uptake was evaluated after equation 1:

$$\varepsilon = \left(\frac{M - M_0}{M_0} \right) \times 100 \quad , \tag{1}$$

where ε is the uptake of the electrolyte solution, M_0 is the mass of the membrane and M is the mass of the membrane after immersion in the electrolyte solution.

2.3.   Characterization Methods

The microstructure of the membranes was examined by scanning electron microscopy (Leica Cambridge apparatus). Samples were cryofractured and the cross section was observed after deposition of a conductive layer of sputtered gold. Crystallinity of the PEO phase in the blend was calculated from the area of the melting peak appearing between 20 and 70ºC in a heating thermogram performed at 10ºC min^{-1} in a Pyris1 Perkin-Elmer DSC. Calculation of the crystalline fraction was based on the value of the melting enthalpy of 100% crystalline PEO: ΔH^{sl}= 203 J.g^{-1} [15]

Contact angle measurements (sessile drop in dynamic mode) were performed at room temperature in a Data Physics OCA20 device using ultrapure water (3 mL droplets) as the test liquid. At least 3 measurements on each sample were performed in different sample locations and the average contact angle was calculated.

The ionic conductivity was evaluated with an Autolab PGSTAT-12 (Eco Chemie) set-up for frequencies between 500 mHz and 65 kHz, using a constant volume support equipped with gold blocking electrodes located within a Buchi TO 50 oven. The sample temperature variation ranged from 20 to 140 ^{o}C and was measured by means of a type K thermocouple placed close to the films. The ionic conductivity was measured during the heating cycles. Then, the ionic conductivity was determined by

$$\sigma = \frac{t}{A \times R_b} \qquad (2)$$

where t is the thickness, A is the area of the samples and R_b is the bulk resistance obtained from the intercept of the imaginary impedance (minimum value of Z'') with the slanted line in the real impedance (Z') through the Randles circuit [16].

Evaluation of the electrochemical stability of the polymer blends was carried out within a dry argon-filled glovebox using a two-electrode cell configuration with a gold microelectrode as working electrode. The preparation of the 25 μm diameter gold microelectrode surface by a conventional polishing routine was completed outside the glovebox. The microelectrode was then washed with Tetrahydrofuran (THF), dried with a hot-air blower and transferred into the glovebox. Cell assembly was initiated by locating a freshly-cleaned lithium disk counter electrode (10 mm diameter, 1mm thick, Aldrich, 99.9% purity) on a stainless steel current collector. A thin-film sample of the electrolyte was centered over the counter electrode and the cell assembly completed by locating and supporting the microelectrode in the centre of the sample disk. The assembly was held together firmly with a clamp and electrical contacts were made to an Autolab PGSTAT-12 (Eco Chemie) apparatus used to record voltammograms at a scan rate of 100 mVs^{-1}. Measurements were conducted at room temperature within a Faraday cage located inside the glovebox.

3. Results and Discussion

P(VDF-TrFE) and PEO are semicrystalline polymers and the microstructure of the P(VDF-TrFE)/PEO blends is determined in large extent by the crystallization process during film formation. The conductivity of P(VDF-TrFE)/PEO based litium salt complexes is in large extent governed by the continuity and ionic mobility in the PEO phase. Since the melting temperature of PEO is around 60ºC, it was decided to prepare the films by solvent casting at 70ºC, temperature at which PEO is melted. Therefore, P(VDF-TrFE) crystallize from the solution and after solvent evaporation the film consists in semicrystalline P(VDF-TrFE) whose amorphous phase is blended with amorphous PEO chains. Subsequent cooling to room temperature produces PEO

crystallization in the confined spaces left by P(VDF-TrFE) crystals. As a consequence, the crystalline fraction of PEO rapidly decreases with decreasing PEO content (see Table 1). This feature is important for the behaviour of the blend as a solid polymer electrolyte. The microstructure of cross-sections of the blends can be observed in the SEM images of Figure 1.

Cross section of P(VDF-TrFE) (Figure 1a) does not reveal any texture. This copolymer crystallizes in the all trans β phase [17, 18] forming lamellar structures. On the contrary PEO forms large spherulites when crystallizes from the melt. The roughness of the cross-sections of cryo-fractured samples allows detecting the presence of PEO crystals for PEO contents above 40% by weight (Figure 1b); in addition SEM images reveal some porosity in these samples.

Electrolyte uptake (figure 1 d) is higher in blends containing 40 or 50% PEO than in pure PEO or pure P(VDF-TrFE) copolymer. A significant drop of electrolyte uptake is produced by increasing PEO content from 50 to 60%. Crystallization of P(VDF-TrFE) from the DMF solution segregates the solvent, in previous works [18] we have shown that a porous structure is produced by liquid-liquid or solid-liquid spinodal decomposition during solvent evaporation. It is not determined in what extent the same process is produced when PEO is present in the solution at 70ºC, i.e., in what extent after P(VDF-TrFE) crystallization the evaporation of the solvent remaining in the amorphous phase containing PEO leaves some porosity in what at the end of the process will be the PEO phase of the blend.

With respect to the electrolyte uptake (figure 1 d), the main results is the synergism in blend properties. Electrolyte uptake is higher in blends containing 40 or 50% PEO than in pure PEO or pure P(VDF-TrFE) copolymer. On the other hand a significant drop of electrolyte uptake is produced when going from 50 to 60% PEO in the blend.

Electrolyte uptake is the result of the influence of different factors. PEO is a water soluble polymer, in the blend with P(VDF-TrFE) its capacity of swelling in the liquid electrolyte is in large extent governed by the confinement produced by P(VDF-TrFE) whose shape is only slightly changed by swelling since electrolyte absorption in pure P(VDF-TrFE) is quite modest (Figure 1d). When the amount of PEO in the blend is small it is dispersed in small domains or blended with the amorphous P(VDF-TrFE). In this conditions the hydrophilic character of PEO only increases slightly electrolyte uptake. As the amount of PEO increases and PEO domains grow, uptake also does. Porosity is another important factor since micropores can store more liquid than the same volume of PEO. But the other factor controlling uptake is PEO crystallinity. From 50 to 60% PEO content in the blend, the crystallinity of PEO nearly doubles while electrolyte uptake suddenly drops. Confinement of PEO in the spaces allowed by P(VDF-TrFE) does not allow the dissolution of PEO crystals and the electrolyte must be absorbed by the amorphous PEO chains. The 20/80 blend do not disintegrade when immersed in the $LiClO_4.3H_2O$ in PC. This probes that just a 20% of P(VDF-TrFE) is enough to form a continuous phase in the blend. On the other hand, absorption of $LiClO_4.3H_2O$ in PC might produce changes in the microstructure of P(VDF-TrFE) [19] which can have an influence of the lithium salts uptake capacity of the blends.

The heterogeneous microstructure and different relative polymer contents lead to variations in the hydrophilic degree of the blends (figure 1 (e)). Pure P(VDF-TrFE) has a higher contact angle as compared to the other samples in the blend systems with the exception of the 80% PEO content membrane. The differences in contact angle are fully ascribed to the surface topography, the hydrophilic degree being lower for the compact samples and higher for the porous ones (figure 1).

The room temperature ionic conductivity of the blends (Table 1) increases with the inclusion of PEO due the higher d.c. conductivity contribution and the dipole-orientation relaxation process of PEO [20]. Without electrolyte uptake, the conductivity is larger for the blend samples with lower PEO contents due to the dispersion of ill-crystallized PEO within the PVDF-TrFE matrix. The conductivity of the blend containing 20% PEO is three orders of magnitude higher than that of P(VDF-TrFE). Increasing PEO content leads to a well formed phase separated microstructure of the two polymers, leading to a decrease of the conductivity. At low temperature the effect of PEO crystallinity is clear (figure 2a). Increasing temperature increases free volume and polymers segmental mobility and charge mobility, increasing ionic conductivity [3]. Around 60ºC ($1/T=0.003$ K^{-1}) the conductivity versus reciprocal temperature plot shows a change of slope due to melting of PEO crystals (Figure 3a), but at temperatures above melting the conductivity of the blends containing 40% or more PEO is still one order of magnitude lower than in the 80/20 blend. One can hypothesize that homogeneous mixing of amorphous PEO with amorphous P(VDF-TrFE) chains produce a continuous conductive phase improving ion conductivity of the blend.

After electrolyte uptake (Figure 2 b) and for PEO contents above 40%, polymer blends exhibits high conductivity $> 10^{-4}$ S.cm^{-1} at room temperature due to the larger concentration of ionic charge carriers and their mobility [21]. The conductivity is practically independent of blend composition. The ionic conductivity of the membrane depends strongly on the inclusion of PEO but not so much on its content. It is observed (figure 2 b) that inclusion of PEO increases thermal stability of the ionic conductivity of the samples with respect to the PVDF-TrFE and that the thermal stability is independent of the PEO content.

The electrochemical stability of for the membranes was measured by microelectrode cyclic voltammetry over the potential range -2V to 6V with electrolyte solution.

Figure 3 c shows the cycle voltammogram for the 50/50 membrane as it is one of the samples with the highest conductivity after electrolyte uptake separators. The sample shows good electrochemical stability independently of the scanning rate, with anodic potentials higher than 4V versus Li/Li+ and an oxidation peak around 1.0V. The anodic current onset is associated to the decomposition of the polymer electrolyte and increases with increasing the scanning rate.

Increasing potential sweeping rate shifts the cathodic peak potential in the negative direction. Several small peaks between 0.0V at 1.0 V can be observed, which are ascribed to reduction of the low levels of water present in polymer electrolyte or to oxygen impurities and this behavior has been observed for other systems based on PEO blends with lithium salt as well [22].

4. Conclusion:

Novel polymer blends based on poly(vinylidene fluoride-trifluoroethylene)/poly(ethylene oxide) has been produced by solvent casting for Li-ion battery separator applications. Solvent evaporation at 70ºC, a temperature higher than the melting point of PEO, confines melted PEO in the P(VDF-TrFE) semicrystalline phase. Then on cooling to room temperature only a limited fraction of PEO crystallizes. Ionic conductivity has a maximum in the sample containing 60% PEO reaching a value of 0.25 mS.cm^{-1}. The temperature behaviour of the conductivity and the cyclic voltammetry confirm that the polymeric blends have adequate stability for lithium-ion battery applications.

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Figure and Table Captions

Figure 1: Cross-section SEM images of P(VDF-TrFE)/PEO blends: a) 100/0, b) 50/50and c) 20/80. Inserts in the figure (a), (b) and (d) exhibits micrograph of the static contact angle. d) Uptake and e) contact angle as a function of PEO content for P(VDF-TrFE)/PEO blends.
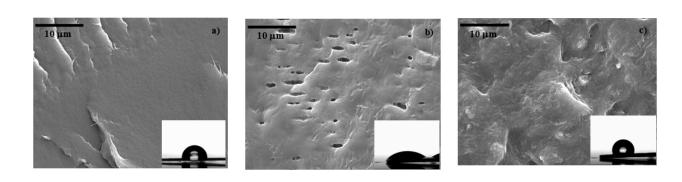
Figure 2: Log σ as function of 1000/T for P(VDF-TrFE)/PEO blend without electrolyte (a), after electrolyte solution uptake (b) and c) Cycle voltammogram of 50/50 P(VDF-TrFE)/PEO blend at different scanning rates
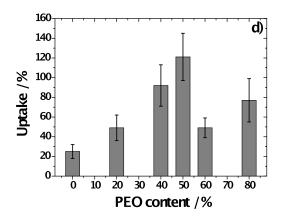
Table 1 – Effective conductivity of separator membrane with electrolyte solution and σ_0 (S/cm)=9.8mS cm^{-1} at 25ºC, conductivity of 1M LiClO$_4$.3H$_2$O-PC

Table 1 – Effective conductivity of separator membrane with electrolyte solution and σ_0 (S/cm)=9.8mS cm^{-1} at 25ºC, conductivity of 1M LiClO$_4$.3H$_2$O-PC

Sample	PEO crystalline fraction	σ_{eff} (mS.cm^{-1}), without uptake	σ_{eff} (mS.cm^{-1}), with uptake
100/0	-	$4.7*10^{-10}$	$8.7*10^{-5}$
80/20	10	$2.2*10^{-6}$	0.08
60/40	27.5	$3.2*10^{-7}$	0.25
50/50	34	$2.2*10^{-7}$	0.56
40/60	62.5	$2.8*10^{-8}$	0.68
20/80	56.3	$9*10^{-9}$	0.44

Figures

Figure 1

Figure 2