Solid State Ionics 280 (2015) 1–9

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Effect of the degree of porosity on the performance of poly(vinylidene fluoride-trifluoroethylene)/poly(ethylene oxide) blend membranes for lithium-ion battery separators

A. Gören [a,b], C.M. Costa [a,*], M.N. Tamaño Machiavello [c], D. Cíntora-Juárez [d], J. Nunes-Pereira [a], J.L. Tirado [d], M.M. Silva [b], J.L. Gomez Ribelles [c,e], S. Lanceros-Méndez [a,*]

[a] Centro/Departamento de Física, Universidade do Minho, 4710-057 Braga, Portugal
[b] Centro/Departamento de Química, Universidade do Minho, 4710-057 Braga, Portugal
[c] Center for Biomaterials and Tissue Engineering, CBIT, Universitat Politècnica de València, 46022 Valencia, Spain
[d] Laboratorio de Química Inorgánica, Universidad de Córdoba, Edificio Marie Curie, Campus de Rabanales, 14071 Córdoba, Spain
[e] Networking Research Center on Bioengineering, Biomaterials and Nanomedicine, (CIBER-BBN), Valencia, Spain

ARTICLE INFO

Article history:
Received 17 April 2015
Received in revised form 29 July 2015
Accepted 6 August 2015
Available online 21 August 2015

Keywords:
PVDF-TrFE
PEO
Battery separator
Lithium-ion battery application

ABSTRACT

Porous polymer membranes based on poly(vinylidene fluoride-trifluoroethylene)/poly(ethylene oxide) copolymers, P(VDF-TrFE)/PEO, are prepared through elimination (from partial to total) of PEO, leading to interconnected micropores in the polymer blends.

Electrolyte uptake, thermal and mechanical properties depend on the amount of PEO present in the polymer blend. Further, the degree of crystallinity of PEO and the elastic modulus (E') of the polymer blend decrease with increasing PEO removal.

Electrical properties of the polymer blend membranes are influenced by the porosity and are dominated by diffusion. The temperature dependence of the ionic conductivity follows the Arrhenius behavior. The ionic conductivity is the highest for the membranes with a volume fraction of pores of 44% (i.e., 90% PEO removal), reaching a value of 0.54 mS cm^{-1} at room temperature.

Battery performance was determined by assembling Li/C-LiFePO$_4$ swagelok cells. The polymer blends with 90% PEO removal exhibit rate (124 mAhg^{-1} at C/5 and 47 mAhg^{-1} at 2C) and cycling capabilities suitable for lithium ion battery applications.

1. Introduction

Rechargeable Li-ion batteries are the most intensively studied energy storage systems for applications in computers, mobile phones and electric vehicles, among others, due to their outstanding properties: they are lighter and cheaper than other battery types, show high specific energy (100–265 Wh/Kg) and suitable power/weight relation (1800 W/Kg) [1,2].

The main goal of the different investigations is to maximize the energy and power per unit of weight or volume taking into account its safety [3–5].

One essential component in Li-ion batteries is the polymer electrolyte (PE). PE are defined as macromolecular systems (polymer blended or complexes with salts [6]) with high ionic conductivity ($>10^{-7}$ at 10^{-1} S/cm) [7,8]. Further, polymer electrolytes can be used in multiple applications, including electrochromic devices [9–11], fuel cells [12,13] and sensors/actuators [14], supercapacitors/ultracapacitors [15], together with Li-ion batteries [4,16].

Solid polymer electrolytes (SPE) [8], gel polymer electrolytes (GPE) [17] and composite polymer electrolytes (CPE) [18] are different types of polymer electrolytes (PEs).

The SPE are the ones with the simplest fabrication. For Li-ion battery applications, different lithium salts are dissolved in a polymeric matrix. CPE are very similar to SPE but differ in the inclusion of different nanofillers (inert oxide ceramic, molecular sieves, metallic, carbonaceous fillers, ferroelectric materials) dispersed in the polymer matrix to improve the mechanical, thermal and electrochemical properties. The GPE are obtained in two steps, first the salts are dissolved in a polar or ionic liquid and then added to a host polymer to provide an adequate mechanical stability [19,20].

For battery applications, the separator/electrolyte is extremely important as it separates both electrodes (anode and cathode), controls the number of ions and allows the movement of the ions between the electrodes during the charge and discharge process of the battery [21].

The main parameters of a separator/electrolyte are permeability, porosity/pore size, electrolyte absorption and retention, low ionic

---

* Corresponding authors.
E-mail addresses: cmscosta@fisica.uminho.pt (C.M. Costa), lanceros@fisica.uminho.pt (S. Lanceros-Méndez).

http://dx.doi.org/10.1016/j.ssi.2015.08.003
0167-2738/

strength, mechanical and thermal stability, resistance to chemical degradation by electrolyte impurities and uniform thickness [16,21].

Different polymers such as poly(ethylene oxide) (PEO) [22–24] and poly(acrylonitrile) (PAN) [25] can be used as battery separators. Among the most interesting polymers for this application are the highly polar and piezoelectric fluorinated polymers: poly(vinylidene fluoride) (PVDF) and their copolymers poly(vinylidene fluoride-*co*-trifluoroethylene), P(VDF-TrFE); poly(vinylidene fluoride-*co*-hexafluoropropene), P(VDF-HFP) and poly(vinylidene fluoride-*co*-chlorotrifluoroethylene), P(VDF-CTFE) [16].

For battery separators, these fluorinated polymers show strong advantages in comparison to other polymers (such as polyolefins) as they show high dipolar moment and dielectric constant which are important to increase lithium salts dissolution, semi-crystallinity, chemical resistance, suitable mechanical strength, possibility of porosity control through binary and ternary polymer/solvent systems and high anodic stability due to the presence of strong electron-withdrawing groups (—C—F—) [16,26,27].

In particular, poly(vinylidene fluoride-*co*-trifluoroethylene), P(VDF-TrFE) has excellent properties to be used as battery separator in lithium ion battery applications, as sample preparation varying polymer/solvent ratio allows tailoring the degree of porosity, which is correlated to electrolyte uptake and ionic conductivity [27].

Polymer blend materials are often used as battery separators in lithium ion battery applications for obtaining improved thermal, mechanical and electrical properties when two or more polymers that compose the blend show complementary properties that allow tuning separator performance. For example, it is typical to combine one polymer with excellent mechanical properties and another polymer with high affinity with the electrolyte solution [6].

Poly(ethylene oxide) PEO polymer is most used as polymer electrolyte and P(VDF-TrFE)/PEO blends have been produced with a room temperature ionic conductivity of 0.25 mS cm^{-1} for 1 M $LiClO_4 \cdot 3H_2O$ electrolyte solution, despite the blends do not showing any porous microstructure [28].

Previously P(VDF-TrFE)/PEO polymer blends have been tested for lithium-ion battery applications with an 1 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate/dimethyl carbonate (EC-DMC, 1/1 in weight) electrolyte solution. The reported rate capability of Li/Sn–C half-cells indicated lower values for the blend membrane with PEO compared to the P(VDF-TrFE) copolymer, due to the lower ion conductivity of the blends [29].

The objective of this work is to evaluate the physicochemical characteristics and battery performance of P(VDF-TrFE)/PEO polymer blends as a function of the porosity, by partially or totally removing PEO from the membranes.

2. Experimental details

2.1. Materials

P(VDF-TrFE) ($M_w = 350{,}000$ g/mol) and PEO ($M_w = 100{,}000$ g/mol) were acquired from Solvay and Polysciences, respectively. The solvent *N,N*-dimethylformamide (DMF, 99.5%), propylene carbonate (PC, anhydrous 99.0%) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99,95%) were purchased from Aldrich.

2.2. Polymer blend preparation

The P(VDF-TrFE)/PEO blends were prepared with a composition of 50/50 weight ratio by dissolving the adequate amounts of both polymers in DMF at a 15/85 *w*/*v* polymer/solvent ratio. The choice of this composition is due to the fact that larger PEO contents in the polymer blend lead to fragile membranes and removing PEO yields a discontinuous material [30,31]. The polymers were dissolved at 60 °C during 4 h by stirring until a homogeneous and transparent solution was obtained. The solutions were deposited in Petri dishes and the solvent evaporated at 70 °C for 2 h. Finally, complete removal of the solvent was achieved in vacuum for another 3 h at 70 °C. Samples with average thickness of 300 μm were obtained.

2.3. Removal of PEO and measurement of the degree of porosity

Porosity was obtained by removing PEO from the samples. Due to its hydrophilic nature, PEO was removed just by fully immersing the samples in distilled water for different times.

The percentage of PEO removal was calculated after different immersion times using the following equation:

$$\%PEO\ removal = \left(\frac{W_0 - W_i}{W_0}\right) \times 100 \qquad (1)$$

where W_0 and W_i denote the weight of dried membrane and weight of membrane after soaked in water, respectively. After removing from water, the membrane was dried in the oven at 60 °C during 1 h.

The porosity of the P(VDF-TrFE)/PEO blend membrane is the initial percentage of PEO minus the percentage of PEO that remains after PEO removal at a given time.

2.4. Electrolyte solution and uptake

The electrolyte uptake was determined, after immersing the membranes in a solution of 1 M LiTFSI in PC for 24 h, by Eq. (2):

$$\varepsilon = \left(\frac{M - M_0}{M_0}\right) \times 10\% \qquad (2)$$

where $\boldsymbol{\varepsilon}$ 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. This electrolyte solution exhibits similar viscosity as the 1 M $LiPF_6$-EC-DMC electrolyte commonly employed in lithium-ion batteries [32]. The electrical conductivity of the 1 M LiTFSI in PC electrolyte is $\sigma_0 = 6.5$ mS cm^{-1} at 25 °C. After uptake, the excess of the electrolyte solution at the surface of the membrane was removed through absorbent paper.

2.5. Characterization techniques

The microstructure of the membranes was examined in a scanning electron microscope, Jeol JSM-5410 after sputter deposition of a gold conductive layer.

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 were carried out in each sample in different sample locations and the average contact angle was calculated.

The crystalline phase of each polymer within the blend was determined by Fourier transform infrared spectroscopy (FTIR) using a Thermo Nicolet Nexus equipment in ATR mode over a range of 650–1750 cm^{-1} with 64 scans at resolution of 4 cm^{-1}.

Differential scanning calorimetry analysis (DSC) was carried out with a Perkin-Elmer Pyris 1 DSC instrument under a flowing nitrogen atmosphere between 25 and 200 °C at a heating rate of 10 °C min^{-1}. All samples were measured in 30 μL aluminum pans with perforated lids to allow the release and removal of decomposition products. The degree of crystallinity (ΔX_{cryst}) for each polymer was calculated using Eq. (3):

$$\Delta X_c = \frac{\Delta H_f}{\Delta H_{100}}, \qquad (3)$$

where ΔH_f is the melting enthalpy of the sample and ΔH_{100} is the melting enthalpy for a 100% crystalline sample, being 103.4 J g^{-1} for P(VDF-TrFE) [33] and 203 J g^{-1} for PEO [34].