



Poly(ethylene oxide carbonates) solid polymer electrolytes for lithium batteries

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ABSTRACT

Poly(ethylene oxide) (PEO) is the gold standard matrix for polymer electrolytes used in actual all-solid lithium batteries. However, PEO solid polymer electrolytes show some limitations; such as relatively low ionic conductivity and lithium transference number resulting in the actual polymer-lithium batteries operating at 70 °C. In the last years, polycarbonates (PC) have been presented as an alternative polymer matrix with superior ionic conductivity for solid batteries which may work at room temperature. In this article we systematically investigated the properties of new polymers which combine varying composition of both ethylene oxide and carbonate groups. A series of poly(ethylene oxide carbonates) (PEO-PCs) have been synthesized by polycondensation between different ethylene oxide diols and dimethyl carbonate. As a result, eight new PEO-PCs with number of ethylene oxide units ranging from 2 to 45 between carbonate groups were synthesized and characterized in terms of physico-chemical properties (T_m and T_g). These PEO₂₋₄₅-PC were formulated as solid polymer electrolytes (SPE) by adding different amounts of bis(trifluoromethane)sulfonimide lithium salt. The effect of the SPE composition (ethylene oxide/carbonate ratio, salt content) on the ionic conductivity and thermal properties (glass transition temperature and melting temperature) was investigated. The optimum SPEs showing the lowest glass transition temperature led to highest ionic conductivity value of $3.7 \cdot 10^{-5} \text{ S cm}^{-1}$ at room temperature. FTIR spectra revealed the coordination between the carbonate groups in the polymer chain and the lithium salt. ⁷Li-¹⁹F NMR analysis T_1 relaxation and diffusion coefficients measurements indicated local dynamics that correlates with the general conductivity behaviour.

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1. Introduction

Solid electrolytes are expected to play an important role in the growing demand of energy consumption. New all-solid battery technologies based on lithium, lithium-sulfur or sodium chemistries are interesting alternatives which contribute to the requirements in this area [1–3]. However, battery charge/discharge time, safety, weight and cost are some of the critical features that an all-solid battery needs to address [4]. The use of polymer electrolytes is emerging due to the improvements in battery safety and

flammability versus the current organic-liquid electrolytes. However, some limitations appear using polymer electrolytes [5] and the battery performance is affected by the slow ion movement, low lithium transference number, electrochemical window and the compatibility between the polymer electrolyte and the electrodes. Still, the possibility of tailoring the polymer chemical structure and morphology offers the possibility to overcome the limitations of solid polymer electrolytes (SPEs) [6].

Since the first report about ionic conductivity of salts in poly(ethylene oxide) (PEO) by Wright in 1973 [7], several generations of PEO SPEs for lithium batteries have been developed. However, low ionic conductivity and lithium transference number of PEO at room temperature, results in batteries usually operating at 70 °C. In the last decades, several attempts can be found in the literature in order to improve the PEO based SPEs properties; such as the

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incorporation of different types of salt [8], chemical functionalization [9], single-ion conducting polyelectrolytes [10,11], block copolymers [10,12], introduction of inorganic nanoparticles or nanofillers [13,14] or cross-linked PEO networks [15].

As an alternative to PEO, different families of polymers can be found as a SPE matrix in the literature [16,17]. Among them, aliphatic polycarbonates are becoming a popular family, due to the possibility of cycling the battery at room temperature [18,19]. Aliphatic polycarbonates' SPEs have shown excellent ionic conductivity values even at room temperature, good electrochemical stability and high lithium transference number. The improvements of the properties come from the plasticization effect of the lithium salt within the polycarbonate matrix which leads to very low glass transition values and high lithium mobility [20]. Moreover, the carbonate group shows a weak coordination with lithium ion as compared to the one of the ether groups which benefits the electrochemical properties [18,21]. Recently, two polycarbonates having 2–3 ethylene oxide links have been synthesized through polycondensation, showing promising properties, an ionic conductivities in the range of $10^{-5} \text{ S cm}^{-1}$ at room temperature after addition of cellulose nanofibers [23]. In another example, Tominaga et al. reported the copolymerization between CO_2 and different epoxies having ethylene oxide links in the final polymer [18]. In this particular case, the polycarbonates having few ethylene oxide units and carbonate showed an ionic conductivity in the range of $10^{-4} \text{ S cm}^{-1}$ at 60°C with high LiFSI content. Following this idea, in this work we further explored the combination of the two lithium friendly chemical groups, i.e., ethylene oxide and carbonate. We envision, on the one hand, that the ethylene oxide groups will be able to solvate different lithium salts through the chelating effect and, on the other hand, the lithium will have the beneficial effect of the carbonate group. Thus, we synthesized a series of eight different poly(ethylene oxide)/carbonate polymers PEO-PC with different content of ethylene oxide and carbonate groups by polycondensation between poly(ethylene oxide) end-capped diol and dimethyl carbonate. In these polymers the amount of ethylene oxide units was varied from 2 to 45 units between each carbonate group. The objective is to find the optimal composition and to investigate the factors such as glass transition temperature, crystallinity and lithium salt content that affect the ionic conductivity of these SPEs. In order to understand the chemical structure and the dynamics of these systems, the SPEs were analyzed by FTIR and ^7Li and ^{19}F NMR. The study was complemented by ^7Li and ^{19}F diffusion coefficients measurements.

2. Experimental

2.1. Materials

Dry dimethyl carbonate (99+ %) (DMC) and 4-dimethylaminopyridine (DMAP) (99%) were purchased from Across Organics. The diol diethylene glycol, hexaethylene glycol and poly(ethylene glycol) (M_n 1500 g mol^{-1}) were supplied by Fisher Scientific and the diol triethylene glycol, tetraethylene glycol, poly(ethylene glycol) (M_n 600 g mol^{-1}), poly(ethylene glycol) (M_n 1000 g mol^{-1}), and poly(ethylene glycol) (M_n 2000 g mol^{-1}) by Merck. All diols were dried by azeotropic distillation (60°C) in toluene for 8 h and DMAP was dried applying vacuum for 4 h at room temperature prior to use. Lithium bis(trifluoromethane)sulfonimide (LiTFSI) (99.9%) was supplied from Solvionic. Tetrahydrofuran (GPC grade) was obtained from Scharlab, acetonitrile (HPLC grade), diethyl ether (Extra Pure, SLR, Stabilised with BHT) and dichloromethane (DCM) (Certified AR for Analysis) from Fisher Scientific, toluene (HPLC grade) from Merck and deuterated chloroform (99.8%) from Deutero GmbH.

2.2. General synthetic route of poly(ethylene oxide carbonates) by polycondensation. $\text{PEO}_x\text{-PC}$

Poly(ethylene oxide) diols were polymerized by melt polycondensation with dimethyl carbonate as reported before [24–26]. In a typical experiment, a 2:1:0.01 mol ratio of DMC:diol:DMAP was used for the diols containing between 2 and 6 ethylene oxide units: diethylene glycol, triethylene glycol, tetraethylene glycol, hexaethylene glycol; $\text{PEO}_2\text{-PC}$, $\text{PEO}_3\text{-PC}$, $\text{PEO}_4\text{-PC}$, $\text{PEO}_6\text{-PC}$. On the other hand, for diols containing higher amount of ethylene oxide, PEG600, PEG1000, PEG1500, PEG2000, a mole ratio of 7:1:0.01 was required for a reasonable molecular weight, as it was studied by our group [26]; $\text{PEO}_{13}\text{-PC}$, $\text{PEO}_{22}\text{-PC}$, $\text{PEO}_{34}\text{-PC}$ and $\text{PEO}_{45}\text{-PC}$. All the polymers were dissolved in dichloromethane and purified by precipitation in cold diethyl ether. The complete disappearance of the monomers was determined by ^1H NMR, ^{13}C NMR and FTIR-ATR. The following example is given for $\text{PEO}_6\text{-PC}$: ^1H NMR (CDCl_3 , 500 MHz): δ = 4.28 (t, OCOOCH_2 , 4H), 3.72 (t, $\text{OCOOCH}_2\text{CH}_2$, 4H), 3.64 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 16H). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 155.14 (OCOO), 70.63 (OCH_2), 68.88 ($\text{OCOOCH}_2\text{CH}_2$), 67.05 ($\text{OCOCH}_2\text{CH}_2$).

2.3. Preparation of poly(ethylene oxide carbonates) based polymer electrolytes

Solid polymer electrolytes containing different amount of $\text{PEO}_x\text{-PC}$ polymer matrix and LiTFSI salt were prepared by solvent casting method from solution in acetonitrile (ACN) directly casted onto the stainless steel (SS) spacers. First, ACN was removed under vacuum at room temperature during 24 h, and then after, the evaporation was completed in an oven inside an argon filled glovebox, increasing the temperature up to 60°C and applying vacuum for 24 h.

2.4. Characterization methods

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker spectrometers at 500 MHz at room temperature, using deuterated chloroform. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy measurements (ATR-FTIR) were conducted on a Bruker ALPHA Spectrometer.

The absolute molar masses of poly(ethylene oxide carbonates) were analyzed by SEC/MALS/RI. The equipment was composed of a LC20 pump (Shimadzu) coupled to a DAWN Heleos multiangle (18 angles) light scattering laser photometer equipped with an He–Ne laser (λ = 658 nm) and an Optilab Rex differential refractometer (λ = 658 nm), (all from Wyatt Technology Corp., USA). Separation was carried out using three columns in series (Styragel HR2, HR4, and HR6; with pore sizes from 10^2 to 10^6 Å). Filtered toluene was used for the calibration of the 90° scattering intensity. The detectors at angles other than 90° in the MALS instrument were normalized to the 90° detector using a standard (PS 28,770 g mol^{-1} ; Polymer Labs), which is small enough to produce isotropic scattering, at a flow rate of THF through the detectors of 1 mL min^{-1} . In addition, the same standard and conditions were used to perform the alignment (interdetector delay volume) between concentration and light-scattering detectors and the band-broadening correction for the sample dilution between detectors. The analyses were performed at 35°C and THF was used as a mobile phase at a flow rate of 1 mL min^{-1} . $\partial n/\partial C$ was measured for $\text{PEO}_2\text{-PC}$, $\text{PEO}_3\text{-PC}$, $\text{PEO}_4\text{-PC}$ and $\text{PEO}_6\text{-PC}$ being around 0.06 mg mL^{-1} . On the other hand, for the materials containing higher amount of ethylene oxide units, the $\partial n/\partial C$ of PEO was used (0.136). The absolute molar mass was calculated from the RI/MALS data using the Debye plot (with first-order Zimm formalism) by using the ASTRA software version 6.0.3 (Wyatt Technology, USA).

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