



Optimizing ionic conduction of poly(oxyethylene) electrolytes through controlling the cross-link density



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ABSTRACT

Combining polycondensation/hydrogenation allowed varying crosslink density in a controlled way. The obtained solvent-free and oligomer-free polymer electrolytes exhibit outstanding conductivities in a wide temperature range. In comparison with poly(oxyethylene) (PEO) based electrolytes, the conductivities of the new crosslinked polymer electrolytes are much higher at ambient temperatures. Furthermore, their conductivity maxima exceed the PEO ones and, to the best of our knowledge, are the highest known. Moreover, contrary to PEO electrolytes, they don't creep after melting. The unsophisticated architecture and chemistry make easy the scale up of these promising polymer electrolytes.

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1. Introduction

Due to safety concerns, related to the use in electric transportation of several hundred kg of batteries, all solid-state and lithium polymer batteries, LPB, are once again in the forefront of alternatives to lithium-ion batteries. Regarding LPB, proofs of concept were early established [1] on 10 Wh Li/VO_x prototypes, with electrolytes consisting of LiTFSI/poly(oxyethylene), PEO, copolymers. LPB concept was later validated in Li/LiFePO₄ configuration by Scrosati et al. [2], the technology being presently used in urban electric rent car fleets as Paris (Blue Solution) [3]. From countless reports, PEO the reference host polymer, combines indisputable assets e.g. ability to dissolve a variety of salts, ionic conductivity maxima exceeding 1 mS/cm, acceptable stability vs Li metal and electrochemical oxidative stability up to roughly 3.9 V vs Li/Li⁺. Fairly cheap, PEO is commercialized in a wide range of molecular weights, with M_w up to millions. High molecular weights undergoing dramatic chain breakings [4], even under mild magnetic stirring in solution, make therefore useless $M_w > 300,000$ g/mole. Additionally, mechanical instabilities of very long chains

allow neither preparing reproducible POE electrolytes nor expecting stability during the battery life. If PEO has indisputable assets, its electrolytes suffer however from (i) poor conductivities from room temperature up to their melting and (ii) poor mechanical strength beyond i.e. in the operating temperature range of LPB. Attempts to lower both crystallinity and melting temperatures through the use of bulky anions as imide, (CF₃SO₂)₂N[−] [5,6], and methide (CF₃SO₂)₃C[−] [7], were partly successful. Indeed crystallinity temporary vanishes, but for salt concentrations, $8 \leq O/Li \leq 10$ exceeding those, $20 < O/Li < 30$, used in practical batteries. These so-called plasticizing salts don't prevent the polymer electrolyte creeping that roughly starts from 70 °C. Cheradame et al. early demonstrated that polyether-urethane networks could both suppress crystallinity and prevent electrolyte creeping [8]. The one-step easy preparation of these networks, from oligo(oxyethylene) end-capped by hydroxyl groups i.e. PEG, tri-isocyanates and polyurethane catalysts, requires however the removal of electrochemically unstable isocyanates and dihydroxy oligomers. Several PEO architectures were proposed to enhance ionic conductivities [9] in particular comb-like poly(macromonomers) based on polymethacrylate [10], polyacrylate [11], polysiloxane [12] or polystyrene [13] skeletons and oligo(oxyethylene) groups.

Our strategy was a 2-steps synthesis involving 1) the synthesis of film-forming prepolymers having high enough molecular weights and crosslinkable groups 2) the UV or thermal cross-linking. The prepolymers were either prepared by

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polycondensation of Jeffamines[®] (with terephthalic acid) [14], or polyethylene glycol [15] or by ring-opening copolymerization of oxiranes [16]. The whole of the syntheses protocols were selected in view of possible industrial scale up. Conductivity comparison between electrolytes based on PEO and on cross-linked amorphous hosts shows a tremendous conductivity increase of the latter below the melting temperature of PEO electrolytes. Beyond, the PEO melting temperature the crosslinked electrolytes exhibit lower conductivity, this being generally ascribed to the decrease in segmental motion induced by cross-linking. Despite the decrease in conductivity maxima these electrolytes are very attractive thanks to (i) significant conductivity increase below the PEO melting temperature and (ii) mechanical reinforcement avoiding electrolyte creeping and allowing film thickness to be significantly decreased. The storage modulus, E' , of cross-linked polymer electrolytes generally range between 1 and 3 MPa on the rubbery plateau while PEO electrolytes generally starts to creep after melting. Reaching higher modulus, i.e. > 10 MPa supposes a neat increase in cross-link density, which results in dramatic conductivity drop and, in terms of ionic conductance, thinner film doesn't compensate the conductivity losses. An approach, which allows tremendously increasing E' while having a very limited impact on the conductivity, deals with nanocomposite electrolytes, i.e. based on NanoCrystallineCellulose, NCC [17]. Once reinforced by NCC, linear PEO electrolytes exhibit storage modulus much higher than 10 MPa, on the rubbery plateau, but have the same drawback than unreinforced PEO electrolytes, i.e. low conductivity below the melting temperature.

This research was focused on the design of solvent-free network electrolytes with high conductivity and good mechanical properties on a large range of temperatures. The objective was to obtain 3D polymer electrolytes, with much higher conductivities at room temperature than PEO ones and close conductivity maxima. Therefore PEO networks with controlled cross-link density were synthesized. The impact of cross-linking density on conductivity and physicochemical properties of polymer electrolytes were thoroughly investigated.

2. EXPERIMENTAL

2.1. Materials

Acetonitrile (ACN), p-xylene, N,N-Diisopropylethylamine (DIEA), diethylether, 3-chloro-2-chloromethyl-1-propene, acetic acid, p-toluenesulfonylhydrazine (pTSH), NaOH and LiTFSI from Aldrich and IRGACURE[®] 2959 from CIBA were used without further purification. Amberlyst A21 (Acros) was immersed in an aqueous solution of 1 M sodium hydroxide overnight. After water removal by filtration, Amberlyst A21 was dried under vacuum at 90 °C for 24 h.

2.2. Polycondensate-1,000 (PC-1,000) synthesis

PC-1000 (Scheme 1) was synthesized according to previous report [15] and washed by ultrafiltration (cut-off 3 kDa). After complete dissolution of the reaction medium in water (12 g/200 ml), acetic acid was added until neutral pH to preserve the ultrafiltration membrane. After removal of salts i.e. sodium acetate, sodium chloride, and oligomers ($M_n < 3,000$ g/mol), water was removed by lyophilization.

2.3. Hydrogenation of PC1,000 (PC1,000-XH)

PC1,000 was dissolved in p-xylene (30–40 ml) and stirred at 50 °C until complete dissolution. According to the targeted rate of hydrogenation adequate amounts of pTSH were added (Table 1) to

the solution, as well as Amberlyst A21 or DIEA (to trap the sulfinic acid), and the reaction medium was refluxed. Conversion was followed by ¹H NMR. When the targeted hydrogenation rate was reached (1–2 hours) the reaction medium was cooled down at room temperature. Then, the reaction medium was filtered and the resulted solution was precipitated in diethyl ether, DEE to recover the PC1,000-XH (where X is the % of hydrogenation) powder. After several washings with DEE, to remove residual pTSH, white powders were obtained.

When DIEA was used instead of Amberlyst A21 (A21) (Table 1), 2 mol of DIEA per mole of pTSH were added. The purification protocol was the same than the previous one.

2.4. Film manufacturing

The polymer electrolyte films of PC1,000-XH were cast from ACN solutions containing LiTFSI, PC1,000-XH and IRGACURE[®] 2959 photoinitiator. Two salt concentrations were prepared i.e. O/Li = 20 and 30. For example for O/Li = 20, 0.6 g of PC1000-XH were dissolved in 8 ml of ACN and then 0.1852 g of LiTFSI and 2.6 mg IRGACURE[®] 2959 were added. After overnight stirring in darkness, the solution was cast onto a Teflon plate. After solvent removal at 30 °C, the films were irradiated, for 1 min, using a UV light generator of 15 mW/cm² (0.25 mJ/cm²) and a P300 MT Power supply, Fusion UV system Inc. to cure the film. Then the crosslinked films NPC1,000-XH were dried under vacuum at 70 °C for 72 h and stored in a glove box. For comparison, two films of composition O/Li = 20 and 30 based on POE 300,000 g/mole were cast.

2.5. Characterization methods

¹H NMR (400.15 MHz) and ¹³C NMR (100.62 MHz) spectra were performed on a Bruker Advance 400 spectrometer in D₂O as solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 v FT-IR spectrometer using KBr pellets.

SEC analyses were performed at ambient temperature using a Waters 590 GPC equipped with a Waters 410 differential refractometer and a Waters 745 Data Module. The 20 µl of PC solution (solution of 4 mg of polymer/1 ml THF) filtered through a 0.45 µm PTFE filter was injected in the device. The eluent has a flow rate of 1 ml/min and 3 ultrastaygel columns of 500, 10³, and 10⁴ Å were used; the set being calibrated with polystyrene standards. Each sample was analyzed twice, the values being calculated only if the elution volumes were found identical.

Glass transition temperatures (T_g), melting temperature (T_m), and melting enthalpy (ΔH_m) were measured in N₂ flow using a DSC- Mettler – Toledo. Around 10 mg of sample were placed in a DSC aluminum crucible in glove box. In a typical procedure, the samples, kept in glove box for at least 2 days, were submitted to two heating cycles from –100 °C up to 100 °C at a scanning rate of 5 °C/min. The samples were cooled down at 30 °C/min, T_g , T_m and ΔH_m were measured during the 2nd heating scan. T_g were taken as the inflection point of specific heat increment at the glass-rubber transition while T_m was taken at the beginning of the peak.

Thermomechanical analyses were performed with a TA Instruments DMA2980. Measurements were performed in isochronal conditions at 1 Hz frequency. Strain magnitude was fixed at 0.05% of the sample length and 150% force track. The temperature was varied from –100 °C to +100 °C at 2 °C/min heating rate.

The molecular weight between cross-links was calculated with the next equation [17]:

$$M_c = \frac{3\rho RT}{E}$$

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