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Two routes for N-rich solid polymer electrolyte for all-solid-state lithium-ion batteries

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Abstract

Very few works have been realized on Li-ion all-solid-state batteries using solid polymer electrolytes (SPE) based on nitrogen-rich polymers (NRP)s, especially poly(ethyleneimine) (PEI) and poly(oxazoline) (POx). Synergizing the advantages of the two polymers, two complementary routes with blends of polymers (POx:BPEI) and the synthesis of copolymers POx-co-PEI by partial hydrolysis of POx were highlighted in this work. Free-standing membranes with low glass transition temperature exhibited valuable compromise between mechanical properties, thermal stability and effective Li⁺ (LiTFSI) transport. Comparable ionic conductivity to the PEO (structural counterpart of PEI) ($2,7 \cdot 10^{-5} \text{ S cm}^{-1}$ at 60 °C) was reached and explained by complexation and interactions between lithium salt and several electro-donor sites of NRPs during a FTIR spectroscopy investigation.

Key words: Polyoxazoline, branched polyethyleneimine, blend of polymers, copolymers

Introduction

Solid Polymer Electrolytes (SPE) have attracted a lot of interest since Wright proved, in 1970[1], that solid state matrix could dissociate salts and transporting charged species. Using solid electrolytes, without any solvent could overcome some concerns found in conventional Li-ion batteries as decrease the formation of Solid Electrolyte Interphase (SEI) or improve the energy density by using lithium metal. The golden star candidate is poly(ethylene oxide) (PEO), studied for the first time as an electrolyte by Armand et al. in 1983[2]. PEO possesses numerous properties such as a good ability of dissociate salts thanks to its sufficient dielectric constant, high degradation temperature and low glass transition temperature (T_g). Nevertheless, low ionic conductivity at room temperature is observed due to its semi-crystalline nature below 60 °C. Furthermore, poor mechanical strength is reported. Various strategies have been investigated to improve these two major aspects such as the crosslinking[3] of the polymer chains, the blending[4], or the copolymerization[5].

Numerous alternative polymers to PEO have been studied[6] including polycarbonates (poly(trimethylene carbonate) (PTMC)[7], poly(ethylene carbonate (PEC)[8]) or fluoropolymers like poly(vinylidene fluoride) (PVdF)[9]. Among them, the class of Nitrogen Rich Polymers (NRP)s was little studied whereas they possess interesting properties for SPE application. Especially, the N-rich analogous polymer to PEO, where a secondary amine substitutes the oxygen atom resulting in the polymer called poly(ethylenimine) (PEI)[10]–[12]. The PEI was chosen due to closely spaced polar groups, established solvating ability of metal salts[13], [14], high chemical versatility (polymer backbone can be chemically modified), and low cohesive energy density. The higher donor number of –N– (i.e., 60) than –O– (i.e., 22) makes it a better candidate for dissolving lithium salts[15]–[17]. PEI exists under two macromolecular structures: the branched PEI (BPEI) and linear PEI (LPEI). LPEI has the same drawback than PEO with a high crystallinity[18]. BPEI consists in highly branched structure where 3 amine types can be found: tertiary (N), secondary (NH) and primary (NH₂). It presents very poor mechanical properties at RT, looking like viscous honey but possesses a low T_g , allowing easy ion transport through the matrix.

Concerning BPEI, Paul et al. associated it to trifluoromethanesulfonate (LiTf, CF₃SO₃Li) reaching a ionic conductivity of $1 \cdot 10^{-6} \text{ S cm}^{-1}$ at 20 °C for N:Li = 20[19]. Pehlivan et al., studied BPEI with another lithium salt: lithium bis(trifluoromethyl sulfonyl)imide (LiTFSI) [20]–[22]. At room temperature, the conductivity attained was $2 \cdot 10^{-6} \text{ S cm}^{-1}$ at a molar ratio of

50:1[21] but in these conditions, the resulting SPE isn't a free-standing membrane. By addition of small amount (8 wt%) of SiO₂ nanoparticles, improved ionic conductivities can be reached up to $3,8 \cdot 10^{-5} \text{ S cm}^{-1}$ at room temperature [23], [24]. BPEI was also used in more complex systems like a crosslinked polymer electrolyte membranes consisting of BPEI and PEO in presence of 20 wt% plasticizer and exhibits excellent ionic conductivity $1,2 \cdot 10^{-3} \text{ S cm}^{-1}$ at 80 °C[25]. Zhang et al. used BPEI as the core of a SPE matrix, with polyester segments as the arms. The N-rich core can promote the dissociation of lithium salts, while the polyester segments can effectively dissolve lithium salts and transport ions[26].

LPEI doped with different lithium salts has already been reported in the literature, and presents a low conductivity at room temperature, $1 \cdot 10^{-8} \text{ S cm}^{-1}$, to reach $1 \cdot 10^{-3} \text{ S cm}^{-1}$ at 150 °C[27]. A higher conductivity value at room temperature of $1 \cdot 10^{-4} \text{ S cm}^{-1}$ was announced by Tanaka et al.[28], [29] using PEI-PEO poly-blends with LiClO₄. Other systems such as a triblock copolymer PEI-*b*-PEO-*b*-PEI used as a “dual” matrix for polymer electrolytes is selective for hard cations (Li⁺/PEO) in one phase and for soft cations (Cu²⁺/PEI) in the other. Best conductivities, $1 \cdot 10^{-6} \text{ S cm}^{-1}$ at 20 °C and $1 \cdot 10^{-4} \text{ S cm}^{-1}$ 80 °C[30], were obtained in presence of PEI-Cu(TFSI)₂. Finally, Doyle et al. generated a single-ion conducting polymer electrolyte (SICPE) by grafting PEO chains in PEI backbone, LPEI-*graft*-PEG, mixed to LPEI bearing lithium *N*-propylsulfonate groups. The resulting SICPE showed electrochemical stability in the ±5 V range, and ionic conductivities of $4 \cdot 10^{-4} \text{ S.cm}^{-1}$ at room temperature and $5 \cdot 10^{-3} \text{ S cm}^{-1}$ at 80 °C[31] For comparison, PEO in presence of LiTFSI (molar ratio of 30) owns an ionic conductivity of $3 \cdot 10^{-7} \text{ S cm}^{-1}$ at 25 °C and $1 \cdot 10^{-4} \text{ S cm}^{-1}$ at 80 °C[32].

To overcome the crystallinity of LPEI [18], copolymers containing LPEI repetitive units were investigated with other NRP including poly(2-R-2-oxazoline)s (POx)s. POxs received an increasing attention due to their biomedical properties[33] and their tunable physical properties (glass transition temperature from 20 to 90 °C, amorphous or semi-crystalline character, various solubilities). Moreover, the POx backbone is easily functionalized using appropriate initiator, terminating agent and/or oxazoline monomer[34]. Poly(2-ethyl-2-oxazoline) is the most widespread of this class of polymers because FDA approved, amorphous, filmogenic with a medium Tg about 40 °C. This polymer was used in this work in POx:BPEI blends to improve mechanical properties of BPEI.

The literature dealing with POx as solid polymer electrolyte is rare. Chien et al. reported PEO-*b*-PEtOx with various block lengths in lithium-sulfur (Li-S) batteries and explored this

copolymer as cathode binder improving the integrity of the as-cast electrodes thus playing a key role for power capability[35]. Yang et al. recently reported POx as a gel additive in Li-S batteries in order to reduce the loss of cathodic active material[36]. Aziz et al. focused on the ionic transport of chitosan:PEtOx blends in presence of the conductive salt magnesium trifluoromethanesulfonate[37]. Very recently, Drews et al. studied a gel polymer electrolyte (GPE) made by UV curing of cationic vinylimidazolium-terminated PEtOx macromonomers with polyfunctional acrylic comonomers dissolved in an organic electrolyte (LP30), affording electrolyte-swollen polymeric ionic liquid (PIL) networks with PEtOx side chains. The resulting GPE outperforms LP30-soaked commercial Celgard separator in terms of thermal stability, ionic conductivity and electrochemical stability window[38]. To our knowledge, POx has not yet been reported as solid-state polymer electrolyte for lithium-ion batteries.

In this study, we report the preparation of solid polymer electrolytes for all-solid-state lithium-ion batteries based on NRP especially POx and PEI. A first route consists in a blend of polymers looking for increase the mechanical properties of BPEI by adding of POx in presence of LiTFSI (Figure 1). An alternative pathway is the synthesis of copolymers by partial hydrolysis of POx into POx-co-PEI to overcome the crystallinity of LPEI. These transparent films are thermally and electrochemically characterized.

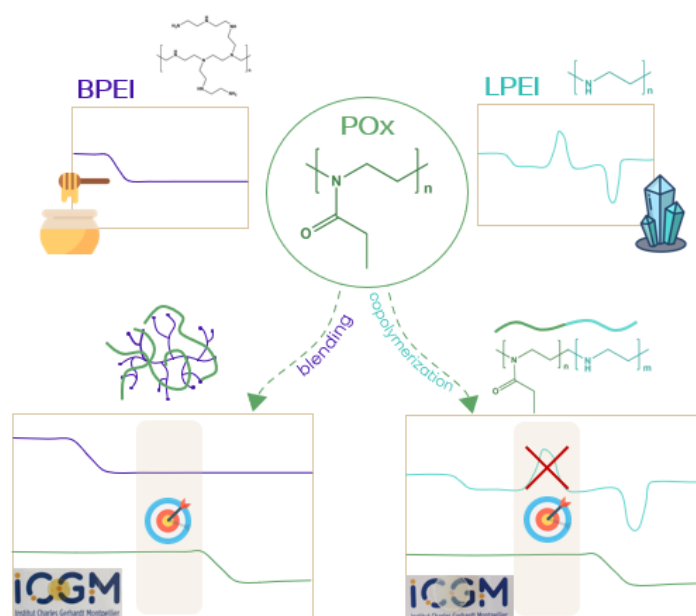


Figure 1. Illustration of NRP-based electrolytes strategies.

Experimental section

1. Materials and solid polymer electrolytes preparation

1.1 Used materials

Poly(2-ethyl-2-oxazoline) (POx, $M_w = 50\,000\text{ g mol}^{-1}$, $\bar{D} = 3-4$), branched poly(ethylenimine) (BPEI, $M_w = 25\,000\text{ g mol}^{-1}$), LiTFSI (purity >99%), hydrochloric acid (HCl, 37%), pellets of potassium hydroxide (KOH) and ethanol absolute ($\geq 99.8\%$) were purchased at Sigma-Aldrich and used as received.

1.2 Typical procedure for the synthesis of poly(2-ethyl-2-oxazoline)-co-poly(ethylene imine) (POx-co-PEI) by hydrolysis of POx moiety

10 g of POx were dissolved in distilled water (100 mL) and acidified using 37% hydrochloric acid solution (150 mL) until reach an HCl concentration of 6 mol L^{-1} . The flask was placed in an oil bath under reflux conditions. Various hydrolysis degrees of POx units into PEI units were obtained in function of the reaction time. The mixture was cooled down to room temperature, and a 2.5 mol L^{-1} sodium hydroxide solution was added until a pH of 7. Dialysis against water during 48 hours was carried out using 1 kDa Spectra/Por® 6 membrane. Finally, water was removed by freeze-drying and the resulting POx-co-PEI was produced as a white powder (i.e., 8.5 g for 22% of PEI molar ratio, yield = 85 %).

1.3 Typical preparation of solid polymer electrolytes (SPE)s

The solid polymer electrolytes were prepared by the standard solution cast technic. Initially, BPEI and POx or POx-co-PEI were added in the suitable solvent: ethanol. The solutions were stirred at room temperature until a homogenous solution. The lithium salt, LiTFSI, was added to the polymer solution, respecting the stoichiometric ratio (N:Li = 50, calculating by dividing the number of moles of polymer repeated units to the number of moles of LiTFSI), followed by stirring until a transparent solution. Finally, the polymer salt solution was cast in a Teflon mold. Two steps of drying were required to ensure a total evaporation of solvents: at $70\text{ }^\circ\text{C}$,

15 h in a ventilate oven and 15 h in vacuum. The resulting SPEs were directly placed in glove box to further analysis.

2. Structural, thermal and electrochemical characterizations of SPEs

^1H NMR spectra were recorded using a Bruker Advance DRX 400 (400 MHz). External reference was tetramethylsilane (TMS) with chemical shifts given in ppm. Samples were diluted in 0.5 mL of deuterated solvents, deuterium oxide (D_2O) or chloroform-d (CDCl_3) depending on their solubility. The chemical shifts were referenced to the peak of residual non-deuterated solvent at 4.79 ppm for D_2O and 7.26 ppm for CDCl_3 .

Differential scanning calorimetry (DSC) characterizations were performed to investigate the glass transition temperature of each pure sample or doped with LiTFSI. Analyses were carried out using a NETZSCH DSC200F3 calorimeter. The calibration was performed using adamantane, biphenyl, indium, tin, bismuth and zinc standards. Nitrogen was used as purge gas. Samples were prepared in glove box to avoid any air contact and water contamination. Approximately 10 mg of sample were placed in perforated aluminium pans and the thermal properties were recorded between $-100\text{ }^\circ\text{C}$ and $80\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C min}^{-1}$. The reported values are the values measured during the second heating ramp.

The thermal stability was tested by thermogravimetric analysis (TGA) on a TA TGA G50 instrument using a 40 mL min^{-1} flux of nitrogen as purge gas. Samples were prepared in glove box to avoid any air contact and water contamination. Approximately 10 mg of sample were used for each analysis. Ramps from room temperature to $500\text{ }^\circ\text{C}$ were applied at a rate of $20\text{ }^\circ\text{C min}^{-1}$.

The **identification of interactions** between polymer and salt was monitored by Fourier transform infrared (FTIR) spectroscopy regarding the shift of characteristic bands of typical groups. The analysis was realized on a Perkin Elmer Spectrum 100 equipped with a ZnSe crystal using the ATR technique. Spectra were recorded in transmittance mode over the wavenumber region $4000\text{-}650\text{ cm}^{-1}$.

Electrochemical Impedance Spectroscopy (EIS) measurements were employed to determine the ionic conductivity of polymer membranes in the frequency range from 1 MHz to 1 Hz with an amplitude of 20 mV using a BioLogic VSP potentiostat. The EIS measurement was carried out by a two-electrode cell configuration where the membrane was sandwiched

between two stainless steel electrodes (SS) as ion-blocking electrode (SS | SPE | SS). The temperature dependence of the Li-ion conductivity of each membrane was collected (30, 40, 60 and 80 °C).

To investigate the electrochemical stability window of SPEs, the measurement was assessed using Linear Sweep Voltammetry (LSV) technique from Open-Circuit Voltage (OCV) to 6 V at a scan rate of 0.1 mV s⁻¹ at 60 °C. Then, as SS electrode played a part of a working electrode and Li metal was utilized as a reference and counter electrode (Li | SPE | SS).

Results and discussion

The first strategy for polymer electrolyte film was a simple blending of complementary polymers: POx as filmogenic polymer with medium Tg value and BPEI for its low Tg and intrinsic conductivity. Ethanol was chosen to favor the miscibility both polymers. After evaporation step, transparent films were shaped without apparent defects. The limit of this process was the possible incompatibility between the polymers for some mass ratio even if POx and PEI possess similar chemical structures.

The second strategy needs a preliminary step of chemical modification with the partial hydrolysis of POx into POx-co-PEI under acidic condition[39]. The synthesis of the copolymers POx-co-PEI was monitored by ¹H NMR spectroscopy following the conversion of the characteristic signal of POx units into those of PEI units (Figure 2). The reaction corresponds to the appearance of the -CH₂-NH signal at 2.70-2.90 ppm attributed to the PEI backbone and the disappearance of the starting POx peaks (i) at 1-1.3 ppm related to CH₃ of the side chain of POx, (ii) at 2.25-2.55 ppm related to CH₂ of the side chain of POx and (iii) and at 3.15-3.62 ppm related to CH₂ of the backbone of POx. The composition of POx-co-PEI copolymers was deduced from the calculation of hydrolysis rate based on the equation 1:

$$\text{Hydrolysis degree (H\%)} = \frac{I[\text{PEI backbone}]}{I[\text{PEI backbone}] + I[\text{POx backbone}]} \times 100 \quad (1)$$

where I[PEI backbone] corresponds to the (CH₂-CH₂-NH) integration at 2.70-2.90 ppm and I[POx backbone] to the (CH₂-CH₂-N(COCH₂CH₃)) integration at 3.15-3.62 ppm.

As illustrated in Figure 2, the intensity of PEI peak increases with the reaction time. The linear relationship between the hydrolysis degree and the time of reaction (Figure 2c) allows the control of the composition of statistic copolymer POx-co-PEI and its prediction before synthesising. Low hydrolysis ratios were reached after only few minutes of reaction while high ratios were reached after 5 hours. We noted that very high ratio of PEI wasn't targeted to avoid any crystallization issue.

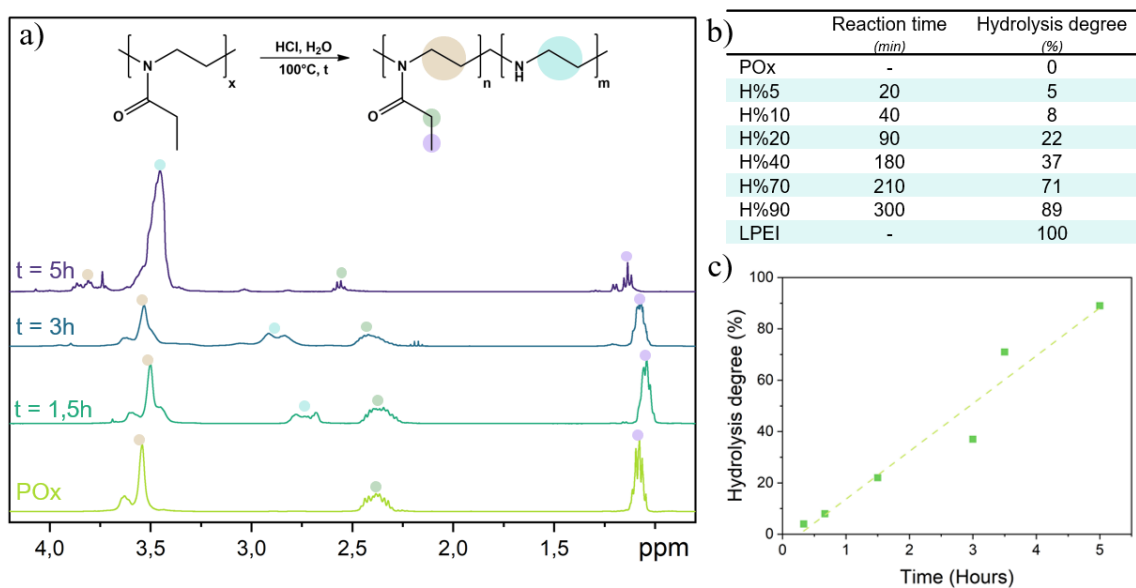


Figure 2. a) ^1H NMR spectra of POx and POx-co-PEI after different reaction times of hydrolysis b), and c) hydrolysis degree versus reaction time.

The thermal behaviour of POx-co-PEI copolymers and POx:BPEI polymer blends has been investigated by DSC. Preliminary thermal studies on bulk materials POx and BPEI showed a stiffening of SPE with addition of salt, with progressive increase of T_g. For the polymer blends one or two T_g are observed, demonstrating the homogenous or heterogenous character of the resulting materials, respectively. The starting polymers, BPEI and POx, have a distinct T_g at -42 and 43 °C, respectively (Figure 3a). Miscible blends are only produced for small amounts of BPEI (5 and 10 wt.%) and larger amount of BPEI (90 wt.%) with a unique T_g close to the T_g of POx and that of BPEI, respectively. Between the extreme zones, from 20 to 80 wt.% of BPEI, immiscible blends were produced with two intermediate T_g. The resulting blend was heterogeneous with two domains: one predominated by POx with high T_g about 40 °C and another one by BPEI with very low T_g about -30 °C. The impact of the addition of LiTFSI salt on the T_g of POx:BPEI blend was also investigated. A remarkable effect was observed with the homogenization by Li salt of the blends whatever the rate of BPEI. LiTFSI acts as a binder/mixing agent. For doped blends composed of 0 to 20 wt.% of BPEI, only the POx contribution was predominant, high T_g from 20 to 60 °C were reached. From 40 wt.% of BPEI, all the samples show a low T_g between -30 and -40 °C, suitable for self-supported films and solid polymer electrolyte application.

The same investigation was conducted on PO_x-co-PEI copolymers bearing different hydrolysis degree. By comparison, PO_x is an amorphous polymer with a T_g about 43°C while LPEI is semi-crystalline polymer with a T_g about -20 °C and a melting temperature about 50 °C (Figure 3b). As expected, no exothermic neither endothermic peak appeared on thermograms, corresponding to crystallisation and melting phenomena respectively, meaning that all the resulting PO_x-co-PEI copolymers were amorphous. Each sample presents a single T_g confirming the formation of a statistical and homogeneous copolymer. Partially hydrolysed copolymers show a T_g between 57 and 10 °C, decreasing with the addition of LPEI units in the copolymer structure. From 70 to 90%, copolymers show very high and unexpected T_g, about 100 °C. In fact the highly hydrolysed copolymers should tend to a T_g close to -20 °C which is that of LPEI (corresponding to copolymer with a hydrolysis ratio of 100%). The reason of this behaviour was not fully understood, that was why they don't appear in this study. The lithium salt LiTFSI has less effect on copolymer T_g than on polymer blend T_g with a maximum of only a few degrees increase (7 °C) for PO_{x90}-co-PEI₁₀.

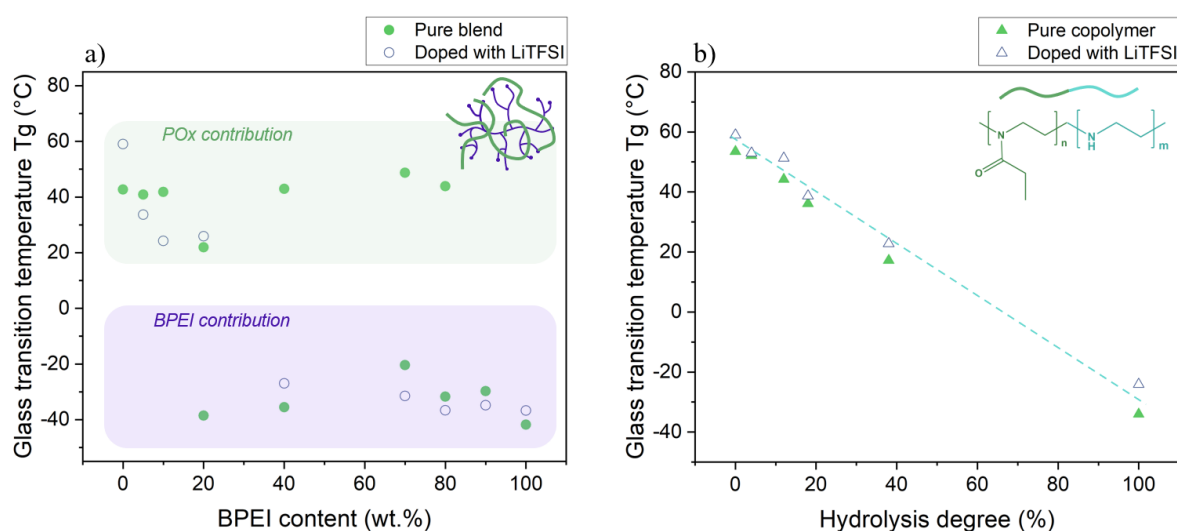


Figure 3. a) Glass transition temperature versus BPEI content with or without Li salt (PO_x:BPEI polymer blend route) and b) Glass transition temperature versus hydrolysis degree with or without Li salt (PO_x-co-PEI copolymer route).

The thermal stability is an important property for solid polymer electrolyte as it will endure some change in temperature into the battery pack of electric vehicles. Further climate and seasons variation, the repetitive charge and discharge of the cell will produce a thermal

activity, increasing the temperature within the electrochemical system. Liquid electrolytes found in conventional Li-ion batteries are the origin of limited thermal stability. For example, the system composed of LiPF_6 in a carbonate solution (1 M in 1:1:1 EC:DMC:EMC) suffers of a mass loss by 25% during the first 26 h of storage at 85 °C[40]. At these temperatures, LiPF_6 degradation or carbonate solvents evaporation were demonstrated by DSC, GC-MS and NMR spectroscopy. To overcome such problem, SPE must feature better thermal stability.

First, thermal stability of bulk materials (i.e., BPEI, Pox and LiTFSI) was investigated to ensure participation of each of them in the stability of blends and copolymers. As shown in Figure 4b, for both blends and copolymers, no weight loss was observed below 150 °C validating our protocol and attesting that solid-state polymer electrolyte were fabricated without any traces of solvent or water. When BPEI chains or LPEI units were introduced in blend and copolymer respectively, the thermal stability decreased (Figure 4a) since POx was more stable than PEI. The decomposition phase happens between 340 and 420 °C for all samples. However, slight drop occurs about 150 °C for blends, explained by the intrinsic weight loss of BPEI at this temperature. Nevertheless, blends seem to possess a better stability than copolymers. When salt was added, the stability was reduced most of the time. In our case, LiTFSI exhibits high thermal stability, above 400 °C but **its addition might influence and lower the stability of the polymer.**

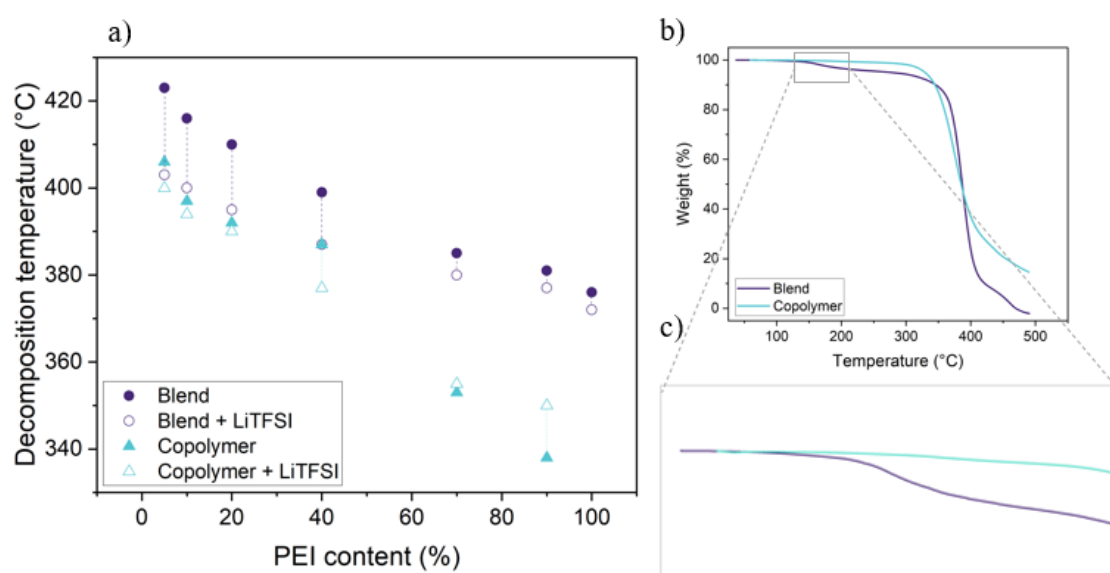


Figure 4. a) Decomposition temperature for PO_x:BPEI blends and PO_{x-co}-PEI copolymers versus PEI content with or without Li salt by using ATG technic, b) ATG curve of PO_{x60}:BPEI₄₀ and PO_{x60-co}-PEI₄₀ with a c) zoom on the region of 100-200 °C.

Electrochemical Impedance Spectroscopy (EIS) is commonly employed to investigate the internal resistance of best candidates at different temperature (here 25, 40, 60 and 80 °C). From the above Tg analyse, two samples stand out from the crowd. The blend composed of PO_{x10}:BPEI₉₀ and LiTFSI (N:Li = 50) shows very low Tg (-35 °C) while being a self-standing film, transparent and handleable (Figure 5). The addition of only a minimal amount of PO_x chains enhances mechanical properties, cancelling the viscous honey behaviour of pure BPEI. Towards copolymer samples, we chose the one with highest hydrolysis ratio H% = 40, PO_{x60-co}-PEI₄₀, to carry on electrochemical characterization, by adding same amount of LiTFSI than previously. This copolymer presents the lowest Tg for such systems, below room temperature, making it the most suitable to obtain self-standing film and correct chain



mobility.

Figure 5. Illustration of handleable films of both blend of PO_{x10}:BPEI₉₀ and PO_{x60-co}-PEI₄₀ in presence of LiTFSI as polymer electrolyte.

Ionic conductivity (σ) was calculated according to the thickness of the membrane (d), the simulated resistance of the electrolyte membrane using equivalent electrical circuit (R) and effective contact area between electrolyte and stainless-steel electrodes (S) using equation 2:

$$\sigma = \frac{d}{RS} \quad (2)$$

As expected [41], the ionic conductivity increases with temperature reaching $1.10^{-4} \text{ S cm}^{-1}$ for the blend $\text{POx}_{10}:\text{BPEI}_{90}$ and $5.10^{-6} \text{ S cm}^{-1}$ for the copolymer $\text{POx}_{60}\text{-co-PEI}_{40}$ at 80°C (Figure 6). This significant difference, about 2 orders of magnitude, can be explained by the thermal properties of samples. Indeed, the copolymer presents a glass transition temperature about 20°C , which was very high compared to blend T_g at -35°C . In this case, polymer chains were less mobile, limiting the segmental motion within the polymer matrix thus minimizing the ionic conductivity. Furthermore, no ionic conductivity could be measured below 40°C , illustrating the motionless structure at such temperatures. Serious drop was observed for the blend sample, when temperature cools down to 25°C . **The system should need some thermal energy to achieve full motion of both BPEI and POx polymer chains resulting in an** optimal ion transport and ultimate ionic conductivity. In terms of ionic conductivity, the obtained values are comparable to PEO-based SPEs [32].

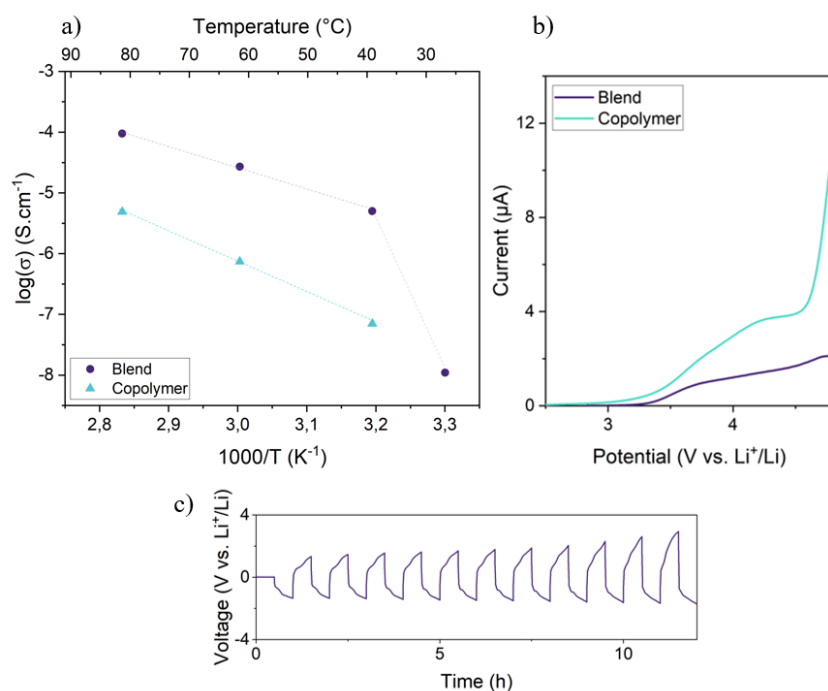


Figure 6. a) Conductivity related to the temperature of $\text{POx}_{10}:\text{BPEI}_{90}$ and $\text{POx}_{60}\text{-co-PEI}_{40}$, b) Stability window in potential of $\text{POx}_{10}:\text{BPEI}_{90}$ and $\text{POx}_{60}\text{-co-PEI}_{40}$ and c) voltage in function of time for $\text{POx}_{10}:\text{BPEI}_{90}$ in lithium symmetric cell.

Electrochemical stability window is an important parameter of electrolyte and needs to be examined before using in batteries. Figure 6b shows the voltage stability window measurement analysed using linear sweep voltammetry in the $\text{SS}/\text{SPE}/\text{Li}^0$ cell configuration

between OCV and 6 V (at scan rate 10 mV s^{-1}) at $60 \text{ }^\circ\text{C}$. It may be noted that the blend $\text{POx}_{10}:\text{BPEI}_{90}$ has a wider voltage stability window than the copolymer $\text{POx}_{60}\text{-co-PEI}_{40}$. If the limit of stability of $1 \text{ } \mu\text{A.cm}^{-2}$ was applied, the highest voltage handled by SPE was about $\sim 4 \text{ V}$ for the blend and 3.5 V for the copolymer. It may be concluded that this blend polymer salt complex can be a potential candidate for the application in lithium-ion battery even though high potential cathode could not be used (for instance NMC).

As preliminary tests, we introduced the best candidate of our study, the blend $\text{POx}_{10}:\text{BPEI}_{90}$ and LiTFSI (N:Li = 50), in a parallel cell configuration, between two pellets of lithium metal (Figure 6c). We used quite gentle conditions with low current ($20 \text{ } \mu\text{A.cm}^{-2}$) and charge and discharge occurring during 30 min at $60 \text{ }^\circ\text{C}$. From the shape of voltage curve, we can deduce the Li^+ cations pass through the studied membrane. Lithium can strip and plate on lithium electrode. After 10 hours however a rapid increase in polarization is observed likely due to the high resistivity of the prepared SPE correlated to a concentration gradient of Li^+ cations within the membrane, thus inhibiting easy and fast transport of charged species.

Lithium transport usually occurs thanks to complexation along the polymer backbone. Heteroatoms act as complexing sites allowing the migration of lithium cations site by site, **migrating** intra- and inter-chains. In PEO case, molecular dynamics simulations suggest that Li^+ are complexed through approximately five etheroxygens of a PEO chain[42].

For N-rich polymers, many types of interactions may exist between Li^+ ions and electron-rich sites (nitrogen atoms) meaning primary, secondary and tertiary amines of (B)PEI and N-atom of POx amide (Figure 7). The supplementary carbonyl bond of POx amide can also be engaged in the complexation process.

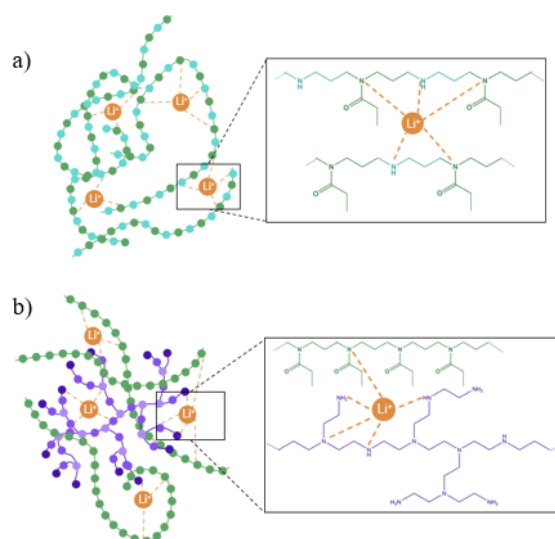


Figure 7. Potential interactions between Li cations and polymer chains in the solid polymer electrolyte based on a) POx-co-PEI copolymer and b) POx:BPEI blend.

The occurrence of polymer-ion interactions in the all-solid polymer electrolyte was examined by FTIR spectroscopy regarding the eventual shift of characteristic peaks of polymer with and without the presence of salt. It may be noted that LiTFSI concentration used was quite low resulting in small shifts in position. This shift corresponds to a modification of environment of the considered bond demonstrating an interaction between the lithium salt and the polymer. The spectra of POx-co-PEI and POx:BPEI $650\text{--}4000\text{ cm}^{-1}$ have been normalized related to the C=O peak at 1630 cm^{-1} . The present work examines, for the first time, the complexation of LiTFSI salt by POx using relevant characteristic peaks of POx located at 1629 and 1191 cm^{-1} associated to C=O and C–N stretching, respectively.

In a first study on pure POx, a shift of 10 cm^{-1} of C=O stretching bond, was observed with addition of LiTFSI (N:Li=8) (Figure 8 a) illustrating the implication of POx in complexation of Li salt. For POx-co-PEI and POx:BPEI in presence of LiTFSI, a little shift of the same band was detected for the copolymer whereas no change happens for the blend (Figure 8 b). This effect of salt on POx was accentuated for C-N bond stretching at 1191 cm^{-1} with a shift of 12 cm^{-1} for N:Li of 8 (Figure 8 d). As observed for C=O, higher shift was detected for copolymer in comparison to polymers blend. Figure 8 c) and f) illustrate interactions involving both oxygen and nitrogen atoms along POx polymer chains and Li species.

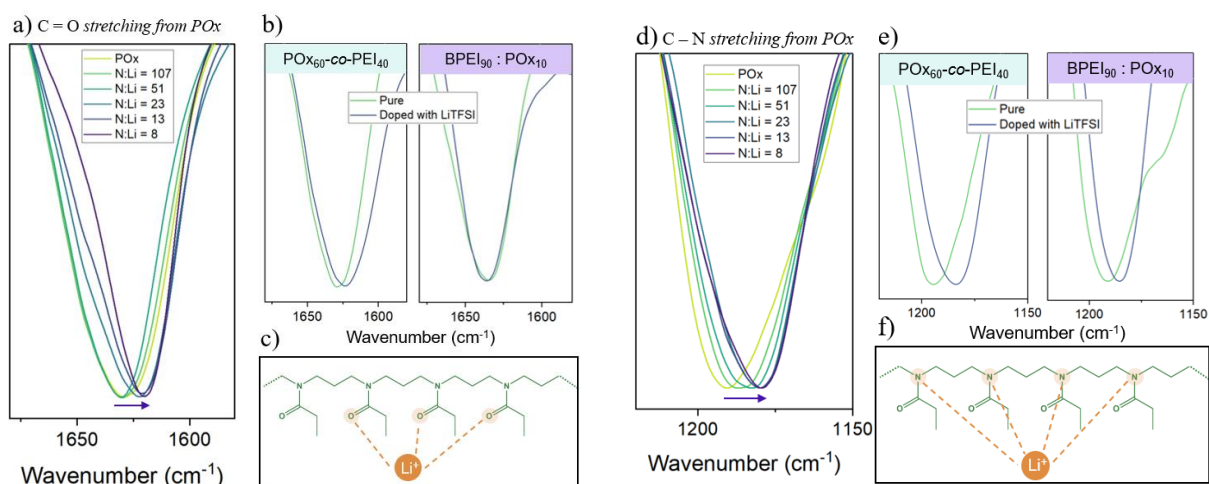


Figure 8. Shifting of a) C=O stretching of POx with addition of LiTFSI and b) C=O stretching vibration in blend and copolymer SPEs, c) Schematic illustration of C=O---Li⁺ interaction in SPEs. Shifting of d) C–O stretching of POx with addition of LiTFSI, e) C–N stretching in blend and copolymer SPEs, and f) Schematic illustration of C–N---Li⁺ interaction in SPEs.

Complexation between BPEI and LiTFSI has already been studied in literature[19]. It has been shown that dissolving salt leads to the substitution of N–H---N hydrogen bonding (3282 and 3352 cm⁻¹) found in pure BPEI by Li⁺---NH---TFSI⁻ interactions. In accordance to the literature, Figure 9a illustrates Li⁺---N and N–H---TFSI⁻ interactions resulting in weakening N–H bond and shifting to higher wavenumber, 3309 and 3367 cm⁻¹ and Figure 9b demonstrates the same modification in our systems where shifts were observed in the region of 3500-3200 cm⁻¹ associated with N – H stretching vibration mode of BPEI.

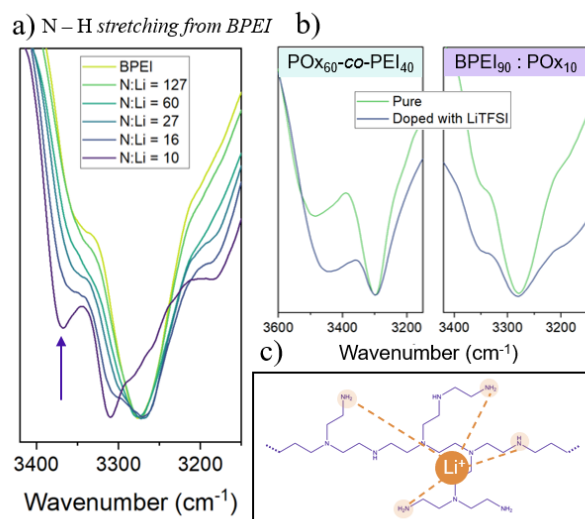


Figure 9. a) Shifting of N–H stretching of BPEI in presence of LiTFSI, b) N–H stretching in blend and copolymer SPEs, and c) schematic illustration of N–H---Li⁺ interaction in SPEs.

To conclude, the shift of amine and amide bonds peaks in presence of Li salt was sharper with copolymer PO_x-co-PEI than blend of polymers PO_x:BPEI, indicating a greater complexation of Li cation in copolymers. Knowing that the lower ionic conductivity was obtained for copolymers, the high complexation seems to prevent mobility of Li-ion. FTIR analysis suggests Li⁺ interactions with both oxygen and nitrogen atoms of PO_x and PEI.

Conclusion

Two SPE for Li-ion batteries based on Nitrogen Rich Polymers (PEI) were achieved and demonstrated their potential use in electrochemical systems. The PO_x-*co*-PEI copolymer synthesis route allows getting homogeneous materials but required a synthetic step of hydrolysis of PO_x into PO_x-*co*-PEI which takes place under controlled manner. For the blend route, the best candidate corresponds to the minimal amount of PO_x in the blend to reach a compromise between mechanical, thermal stability and chain mobility. By both routes, handleable films were shaped, characterized by a low T_g comprised between those of PO_x and BPEI without any problem of crystallization phenomena. The best ionic conductivity was reached for blend route with $2,7 \cdot 10^{-5} \text{ S cm}^{-1}$ at 60 °C – similar value to the oxygen rich polymers homologue of PEI with PEO[32]. We demonstrated by FTIR spectroscopy various interactions between LiTFSI and NRPs especially between Li⁺ and i) the carbonyl group and N atom of PO_x and ii) different types of amines in BPEI. Too much complexation, especially in copolymers, might limit the transport of Li⁺. Regarding the electrochemical performance, the stability was reached until 4 V vs Li/Li⁺. The overall electrochemical stability window shows that an application as SPE in Li-ion batteries could be envisioned. Future research will focus on the description of transport mechanism using solid-state NMR for instance. Also, some tests with minimal addition of solvent will be electrochemically studied.

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