

Formulating PEO-Polycarbonate Blends As Solid Polymer Electrolytes By Solvent-Free Extrusion

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ABSTRACT

Liquid electrolytes are currently state-of-the-art for commercialized lithium-ion batteries. However, their use implicates inherent challenges, including safety concerns associated with flammability, limited thermal stability, and susceptibility to dendrite formation on the lithium metal anode, that can compromise the battery's lifespan. Solid-state polymeric electrolytes offer an alternative to conventional liquid electrolytes, aiming to mitigate the safety, stability, and performance drawbacks. Polymer blends play a central role in developing advanced materials with tailored properties, particularly in polymeric electrolytes. This study investigates the preparation and the comprehensive characterization of polyethylene oxide (PEO) and polycarbonate (PC) blends obtained through an easily scalable and solvent-free extrusion process. This process granted the efficient dispersion and mixing of PEO and PC, ensuring the resulting blends' homogeneity through a solvent-free and industrially scalable process. The blends, consisting of PEO, PC, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were prepared using different ratios of the two polymers. In addition, two molecular weight PEO (M_w of $4 \cdot 10^5$ g/mol and $4 \cdot 10^6$ g/mol) were blended with two types of PCs, polyethylene carbonate (PEC) and polypropylene carbonate (PPC). This work aimed to demonstrate the feasible application of a solvent-free extrusion procedure, easy to scale up for industrial application. At the same time, an optimization and an investigation of the relative effects between the application of different PCs and the variable ratios of PEO/PCs on the

mechanical, morphologic and electrochemical properties of the final polymeric membranes was carried out for future applications of these systems, as efficient electrolytes in all-solid-state lithium batteries.

Keywords: polymer blend, polyethylene oxide, polycarbonate, solid polymer electrolytes, solid-state batteries, lithium battery, solvent-free extrusion.

1. Introduction

The undeniable impacts of climate change are becoming increasingly apparent in our daily lives, with a surge in extreme events surpassing earlier predictions. Concurrently, the incessant progress of society and technology demands substantial power, underscoring the urgent need for reliable and sustainable energy generation and storage. The ever-increasing demand for high-performance, safe, and sustainable energy storage solutions has fueled extensive research into advanced lithium battery technologies [1,2]. Typically, Li batteries employ organic liquid electrolytes, characterized by low ionic resistance, leading to drawbacks such as limited lifespan, high costs, diminished power densities, and the growth of lithium dendrites [3–5]. Furthermore, traditional electrolytes include low molecular weight compounds, such as ethers or carbonates used as solvents, which are highly flammable, with obvious safety concerns for battery explosion in the event of exposure to a fire or as a consequence of battery overheating [6]. Replacing traditional liquid electrolytes with solid-state electrolytes (SSEs) has been regarded as a way to limit or overcome these problems [7–9]. SSEs can be classified into two main categories: inorganic solid electrolytes (ISEs) and solid polymeric electrolytes (SPEs). ISEs have been widely investigated due to their high ionic conductivities ($> 0.1 \text{ mS cm}^{-1}$ at RT), high moduli, enhanced electrochemical stability window, and excellent thermal stability [7,10,11]. Nevertheless, the effective utilization of ISEs has been constrained by various considerations. These challenges encompass poor contact with the electrodes, high costs, manufacturing complexities as well as their inherent brittleness. Compared to ISEs, SPEs, which are made of a polymeric matrix and lithium salts, have emerged as a promising candidate due to their intrinsic advantages, including improved safety, ease of synthesis, low cost, flexibility, electrochemical stability, and suitability for extensive manufacturing process [12,13]. Regrettably, many of these features are optimal in hydrocarbon polymers characterized by low dielectric constant, resulting in the inability to promote the dissociation of ion pairs within the electrolyte. Thus, polymers such as polyethylene oxide (PEO), have gained significant attention as a polymer matrix since the 1970s, thanks to the oxygen in the polymeric chain, being able to coordinate Li^+ , thus allowing the hopping mechanism to let the cation move through the system, while enhancing the solubility of the lithium salts, reducing the crystallinity [14,15]. Despite offering good ionic conductivity and compatibility with lithium ions, PEO-based SPEs suffer from challenges such as inadequate mechanical strength and electrochemical stability, hindering their widespread adoption in practical applications [16]. In addition, PEO-based electrolytes display a high degree of crystallinity, causing low ionic conductivities for application at lower temperatures ($T < 60 \text{ }^\circ\text{C}$) [17,18]. Reducing PEO crystallinity is a key strategy to overcome these limitations and to advance the development of robust SPEs for lithium batteries [19]. Luckily, there are various physical approaches, such as the

addition of plasticizers [20], inorganic fillers [21], polymer blending [22] chemical modification like copolymerization [23], crosslinking [24] and the introduction of single-ion polymers [25,26], to develop SPEs displaying improved ionic conductivity or better lithium transport number [27]. PEO's high ionic conductivity arises from its ability to coordinate with lithium ions and transport them through the polymer matrix. However, its low glass transition temperature and limited mechanical strength have represented the primary drawback. On the other hand, PCs are renowned for their excellent mechanical properties, including high tensile strength, yet their ionic conductivity is relatively low.

This paper explores an efficient, economical, and solvent-free approach for blending PEO with polycarbonates (PC). This class of polymers has received significant attention due to its similar structure to organic-based solvents employed in traditional gel electrolytes [28]. PC-based SPEs possess high lithium ion transference numbers, wide electrochemical stability windows, and compatibility with the lithium metal anode [29]. Some examples of PC-based SPEs, such as poly(trimethylene carbonate) (PTMC) [30], poly(ethylene carbonate) (PEC) [31] and poly(propylene carbonate) (PPC) [32], are already reported in the literature with applications solid-state batteries but, to the best of the authors' knowledge, an investigation of the better PEO/PCs ratio and the most promising PCs was not reported before. This study aims to leverage the characteristics of PEO and PC to produce polymeric blends exhibiting an optimal trade-off among ionic conductivity, mechanical strength and thermal stability, making them suitable for their further possible uses as solid polymer electrolytes. The integration of PEO with PCs in a polymeric blend seeks to capitalize on the strengths of both polymers, addressing the challenges inherent to PEO-based SPEs. Moreover, the electrolyte blends have been prepared by exploiting a solvent-free extrusion process, eliminating the risks associated with flammable solvents, making it an ideal method for preparing polymer electrolytes in Li-ion batteries. This simplifies the manufacturing process, reducing production costs and environmental impact compared to the solvent-based methods obtaining at the same time better homogenized and uniform samples even if with ceramic or inorganic fillers [33,34] This research aims to comprehensively investigate the manufacturing, characterization, and performance evaluation of PEO/PC blends for further possible uses as electrolytes in lithium batteries. These polymeric blends will exhibit a superior combination of ionic conductivity and electrochemical stability, which is essential for developing next-generation lithium batteries with improved safety and performance characteristics. As the global transition toward sustainable energy solutions intensifies, the outcomes of the present study may impact the development of lithium battery technologies, offering a path to safer, more efficient and environmentally sustainable energy storage solutions.

2. Experimental

2.1 Materials

Polyethylene oxide (M_w of $4 \cdot 10^5$ g mol⁻¹ and $4 \cdot 10^6$ g mol⁻¹, CAS: 25322-68-3) was purchased from Sigma Aldrich. Polyethylene carbonate (CAS: 25608-11-1) and polypropylene carbonate (CAS: 25511-85-7) were received from Specific Polymers. Bis(trifluoromethane) sulfonamide lithium salt (LiTFSI) was purchased from Sigma-Aldrich (CAS: 90076-65-6). All polymers were dried for 3 days

under vacuum at 60 °C. The LiTFSI was dried under vacuum for one day at room temperature, two days at 70 °C, and finally two hours at 110 °C. Anhydrous *N*-methyl pyrrolidone (NMP, CAS: 872-50-4) was obtained from Merck and used as received. Conductive carbon C65 (Imerys) and polyvinylidene fluoride (PVdF, Solef 6020, Solvay) were used as received.

2.2 Preparation of PEO/PC blends

A mini-compounder (Haake MiniLab II – Thermo Fischer Scientific) was used to prepare the formulations. The extruder is designed to produce small quantities (approximately 7 cm³) of polymeric, composite, or nanocomposite materials. The tool consists of two co-rotational twin screws whose rotation speed can be controlled. The compounder allowed the proper mixing of the polymeric components without using solvents, melting the polymer into the compounder's chamber and recirculating it many times. The PEO, PCs, and LiTFSI were weighted in an M-Braun glove box (H₂O < 0.5 ppm and O₂ < 0.5 ppm). All components were loaded in the mini-extruder with a continuous flow of N₂ to avoid moisture contamination, as the extrusion process was carried out outside the glovebox. Firstly, half of the PEO/PC was introduced in the extruder, then LiTFSI was added little by little, and then the last part of the polymer blend was added. The mixtures were left for 15 minutes of mixing into the compounder chamber to reach a good homogeneity. The operating conditions during the extrusion were 140 °C and 130 rpm. After mixing, the blended polymer was extracted from the extruder, sealed under vacuum, and transferred into the glovebox. The final membrane was obtained by hot-pressing the blended polymer at 70 °C and 10 bar. Before use, the membranes were dried under vacuum at 40 °C for 12 h in the B-585 oven (Buchi Glass Drying Oven, Switzerland) and then transferred under vacuum inside the argon-filled M-Braun dry glovebox to minimize the presence of residual moisture/humidity. The extrusion process and an example of the resulting membrane are reported in Figure S1.

2.3 Characterization

The following tests were carried out to characterize the physical, morphological, and electrochemical properties of the polymeric membrane. The thermal stability was measured by thermogravimetric analysis (TGA, Netzsch TG 209 F3). The analysis was conducted between 25 °C and 600 °C under a nitrogen atmosphere, using a heating ramp of 10 °C min⁻¹. The temperature at which the degradation process starts was fixed when 5 % of loss in weight is reached. Differential scanning calorimetry (DSC, Netzsch 214 Polyma Equipment) was carried out to evaluate the degree of crystallinity. The measurements were conducted in a temperature range between -50 and 100 °C with a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere (40 mL min⁻¹). The crystallinity degree was calculated as described in Equation 1, using the value of 205 J/g as melting enthalpy (ΔH_m^0) for 100% crystalline PEO [35,36].

$$\text{Crystallinity (\%)} = \frac{\Delta H_m}{\Delta H_m^0} * 100 \quad (\text{Eq. 1})$$

The dynamo-mechanical and viscoelastic properties and the relaxation temperatures of the polymer blends were evaluated by dynamic mechanical thermal analysis (DMTA, Q800 by TA Instruments). All measures were carried out applying an isofrequency of 1 Hz with a ramp of temperature from -60°C to 60°C at 3°C min⁻¹ using bar specimens obtained from the above described membranes. From DMTA, storage modulus, loss modulus, and relaxation temperatures (taken as peaks temperature in the loss modulus curves) were obtained. Scanning electron microscopy (SEM,

Solaris X, Tescan) was used to characterize the surface and cross-section morphology of the prepared membrane, using a beam energy of 5 keV. The cross-section was obtained by breaking the membranes after having soaked them in liquid nitrogen for 1 minute.

The ionic conductivity of the PEO/PC samples was determined by electrochemical impedance spectroscopy (EIS), using a VMP3 potentiostat/galvanostat (Biologic). A membrane disk of 16 mm in diameter, with a thickness of about 150 μm , was sandwiched between two stainless-steel (SS) blocking electrodes in an SS||electrolyte||SS configuration using an EL-Cell Std (EL-CELL, Germany) electrochemical test cell. For each membrane, the thickness was accurately measured before and after the measurement using a micrometer (Mitutoyo) to evaluate the cell constant properly. The EIS data were recorded on a Biologic (VMP-300) electrochemical workstation in a frequency range of 0.1 Hz – 1 MHz and applying a sinusoidal voltage of 20 mV at various temperatures (0 – 80 $^{\circ}\text{C}$) using an environmentally controlled climate chamber (MK 53 E2 from BINDER, Germany). The cells were kept for 100 min at each temperature with intervals of 10 $^{\circ}\text{C}$ for proper equilibration. The Nyquist plots were analyzed using Ec-Lab software. The ionic conductivity was determined according to Equation 2:

$$\sigma_i = \frac{D}{AR} \quad (\text{Eq. 2})$$

where D represents the thickness of the membrane (cm), A denotes the area of the membrane (cm^2), and R (Ω) is the total resistance. The electrochemical stability window (ESW) of the PEO/PC blends was measured from the electrochemical linear sweep voltammetry (LSV), considering 5 $\mu\text{A cm}^{-2}$ as the threshold and reporting the corresponding E value. The cells were assembled by sandwiching the components in a Li||electrolyte||carbon-coated Al (CC-Al) configuration with a lithium metal (Albemarle) counter and CC-Al working electrode disks. Carbon-coated electrodes were prepared from a slurry containing NMP, conductive carbon C65 (80% wt.), and PVdF (20% wt.). The slurry was deposited onto an Al foil, dried overnight at ambient temperature, cut into disks, and vacuum dried at 120 $^{\circ}\text{C}$ for 1 day before use to remove water and residual NMP solvent. The measures were conducted at a scan rate of 1 mV s^{-1} in the range from OCV to 7 V, at the temperature of 40 $^{\circ}\text{C}$.

2.4 Design of Experiment

The production of polymeric blends involves interplay among various parameters. In this case, we selected three experimental variables (polycarbonate type, polyethylene oxide molecular weight, and blend composition) that are relevant to the production of the blend. Each of these factors can significantly impact the final properties of the polymeric membrane, such as the conductivity, the electrochemical stability (in the following paragraph is indicated as voltage), as well as the crystallinity. The objective of our study is to systematically investigate the influence of these key factors on the production of a PEO/PC polymeric blend. About the type of PEO, we explored the effects induced by the variation of molecular weight using two distinct PEOs with M_w of $4 \cdot 10^5 \text{ g mol}^{-1}$ (400k) and $4 \cdot 10^6 \text{ g mol}^{-1}$ (4M) respectively, which can influence the blend's viscosity and chain entanglement. At the same time, we examined the influence of employing two different types of polycarbonates, namely polyethylene carbonate (PEC) and polypropylene carbonate (PPC). The blend composition ratio and the relative effects on the final properties were also investigated, varying the percentage of PEO (0, 30, 50, 70, and 100%) in the formulation with PC. To evaluate the influence

of these factors and their correlations, we used a Design of Experiment (DoE) approach, which offers several advantages over traditional one-factor-at-a-time experimentation[37]. A full factorial design was used to investigate the combination of experimental factors leading to the production of 20 different membranes ($2 \cdot 2 \cdot 5$ combinations) with four membranes prepared in replicate, to evaluate the experimental variability (The set of experiments is reported in Table S1). A multivariate analysis based on multiple linear regression (MLR) has been performed to quantify the effects of the experimental variables on the blend properties [38]. For each property (conductivity, voltage, and crystallinity), a regression model has been calculated (at a 90 % confidence level) which is able to describe their variation over the investigated experimental domain.

3. Results and Discussion

3.1 Thermal and mechanical properties

Thermal analyses were performed to evaluate the thermal stability of the prepared membrane. TGA thermograms (Figure S2) pointed out that PEO shows a start in decomposition around 370 – 375 °C for both M_{ws} while PCs start decomposing at lower temperatures, namely 218 °C for PEC and 240 °C for PPC. The addition of LiTFSI influences the thermal stability of PEO and PCs differently. For PEO, the thermogram evidences an increase in thermal stability, up to 380 – 390 °C, most likely associated with the strong interaction between Li^+ and EO units of the polymeric chains [39]. On the contrary, a reduction to 200 °C was observed for PCs, generally associated with the use of PCs and the catalytic activity of LiTFSI in triggering the depolymerization process at high temperatures [40,41]. The overall effect of the PC addition is a slight reduction in the thermal stability of about 20 °C. However, the TGA thermal stability of all the compositions remains up to 190 °C, which is considered sufficiently since the operative temperature of cells is not expected to exceed 100 °C, assuring high safety levels in normal conditions as well as in case of thermal runaways [42,43]. As expected, the thermograms of the PEO-PC mixtures evidence two main degradation steps, the first associated with PCs degradation and the second related to PEO and LiTFSI degradation. The mass loss relative to the two polymer degradations agrees with the PEO:PCs formulations ratio introduced in the extruder. The residual mass at 600 °C is associated with the LiTFSI residue, and the differences among samples are related to the slightly different quantities of salt used to maintain the same [EO]:[Li] ratio at 20:1. DSC analyses were carried out to evaluate the effects of LiTFSI salt and the influence of PCs on the crystallinity degree (Figure S3). Both types of neat PEO showed a crystallinity degree of 70 %, and the addition of LiTFSI salt halved the crystallinity, thanks to the high solubility and interaction of Li^+ with the polymeric chains and the plasticizing effect of TFSI⁻ anion [44]. Moreover, as highlighted in Figure 1, the melting peaks' intensity decreases and shifts to lower temperatures when the polycarbonate ratio increases [45]. The multivariate analysis of the crystallinity values measured for the different blend compositions (Table 1) evidences that the amount of PEO is the sole relevant variable influencing this parameter (Figure S4). In particular, the crystallinity degree decreases proportionally with the percentage of PEO in the blend. The predicted variation of crystallinity shows that the blend becomes completely amorphous at values equal to or lower than 40 % (Figure 1) of PEO. On the contrary, the molecular weight of PEO and the structural unit of PC did not seem to affect the resulting crystallinity. Moving toward the use of these polymeric membranes as electrolytes, a reduced crystallinity is expected to increase the lithium-ion conductivity,

particularly at room temperature. Among the two types of polycarbonate tested, the formulations containing PEC showed a higher reduction in crystallinity values, most likely associated with the lower T_g of the PEC polymer. Instead, no significant changes in the T_a values (obtained from DMA analysis) were observed in all formulations, as reported in Table 1. The presence of both relaxation peaks of PEO and PCs pointed out that the polymers are slightly soluble.

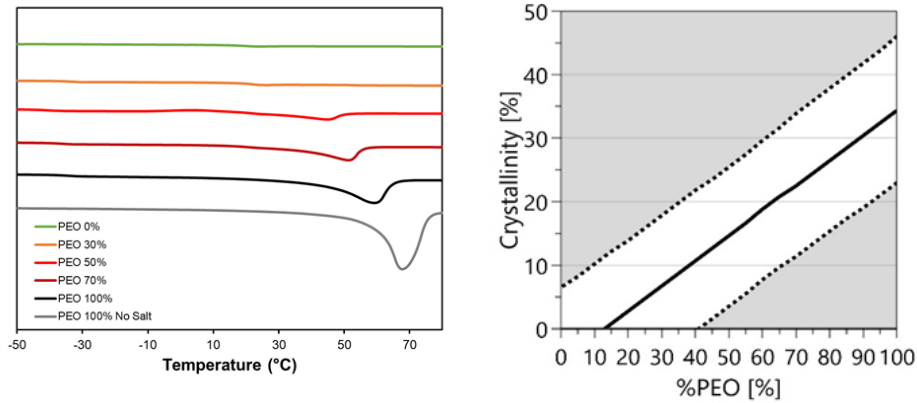


Figure 1. DSC measures of PEO/PEC blend under N_2 from $-50\text{ }^\circ\text{C}$ to $100\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ (left). Effect of the % of PEO on the crystallinity calculated from DoE analysis (right). In this case, the mathematical fitting can go below 0 % of crystallinity, which has no physical sense due to the impossibility of setting a lower limit, so the lower limit was set at 0% of crystallinity for completely amorphous samples.

Table 1. T_a values (obtained from DMA) and percentage of crystallinity (obtained from DSC) for all samples.

| PC (%) | PEO 4M/PEC formulations | | | PEO 4M/PPC formulations | | | PEO 400k/PEC formulations | | | PEO 400k/PPC formulations | | |
|--------|--------------------------------|--------------------------------|-------------------|--------------------------------|--------------------------------|-------------------|--------------------------------|--------------------------------|-------------------|--------------------------------|--------------------------------|-------------------|
| | T_a PEO ($^\circ\text{C}$) | T_a PEC ($^\circ\text{C}$) | Crystallinity (%) | T_a PEO ($^\circ\text{C}$) | T_a PPC ($^\circ\text{C}$) | Crystallinity (%) | T_a PEO ($^\circ\text{C}$) | T_a PEC ($^\circ\text{C}$) | Crystallinity (%) | T_a PEO ($^\circ\text{C}$) | T_a PPC ($^\circ\text{C}$) | Crystallinity (%) |
| 0 | -30 | - | 35 | -30 | - | 35 | -32 | - | 33 | -32 | - | 33 |
| 30 | -33 | 22 | 33 | -34 | 37 | 19 | -33 | 25 | 24 | -34 | 36 | 22 |
| 50 | -36 | - | 1 | -31 | 40 | 9 | -33 | 23 | 8 | -31 | 39 | 11 |
| 70 | -36 | 23 | 0 | -33 | 40 | 0 | -33 | 21 | 0 | -32 | 40 | 0 |
| 100 | - | 21 | 0 | - | 26 | 0 | - | 21 | 0 | - | 26 | 0 |

Relevant information about the T_g values of the tested formulations can be obtained from DSC measurements, even if, in most cases, the melting peak overlaps the signal related to PC's T_g . Firstly, the addition of LiTFSI increased the T_g of PEO from $-50\text{ }^\circ\text{C}$ to $-35\text{ }^\circ\text{C}$, as reported in the literature [46], whereas the T_g of PCs was less affected by the salt addition, changing from $14\text{ }^\circ\text{C}$ to $20\text{ }^\circ\text{C}$ for PEC and from $27\text{ }^\circ\text{C}$ to $25\text{ }^\circ\text{C}$ for PPC. The presence of two different T_g s is in agreement with the DMA analysis, confirming that the PEO and PEC/PPC are not miscible, suggesting phase separation within the blend. Finally, the addition of PCs to the LiTFSI-PEO system allows it to reach lower crystallinity values.

DMA thermograms were performed in a range of temperature from $-60\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$ for the formulation containing 50 wt.% of PEC and PEO 400k, which can be compared to the pure PEO 400k formulation. Due to the quite similar storage and loss modulus values, resulting in limited significance in evaluating the best formulation, the DMA thermograms are considered only to assess the T_{α} of the materials (whose values are reported in Table 1). In this case, two different T_{α} can be pointed out for the two-component formulation, indicating a phase separation.

3.2 Morphological characterization

The films obtained after hot-pressing were flexible, self-standing, and homogeneous by naked eye. The morphologies of the three polymeric blends composed of PEO and PEC at varying weight ratios (30 wt.%, 50 wt.%, and 70 wt.% of PEC) were investigated by SEM analysis. SEM images of the surface morphology of the polymeric blends revealed that all three compositions exhibited a homogeneous surface. No distinct domains or phase boundaries attributable to PEO or PEC can be observed, irrespective of the weight ratios, at the reported magnification (Figure 2).

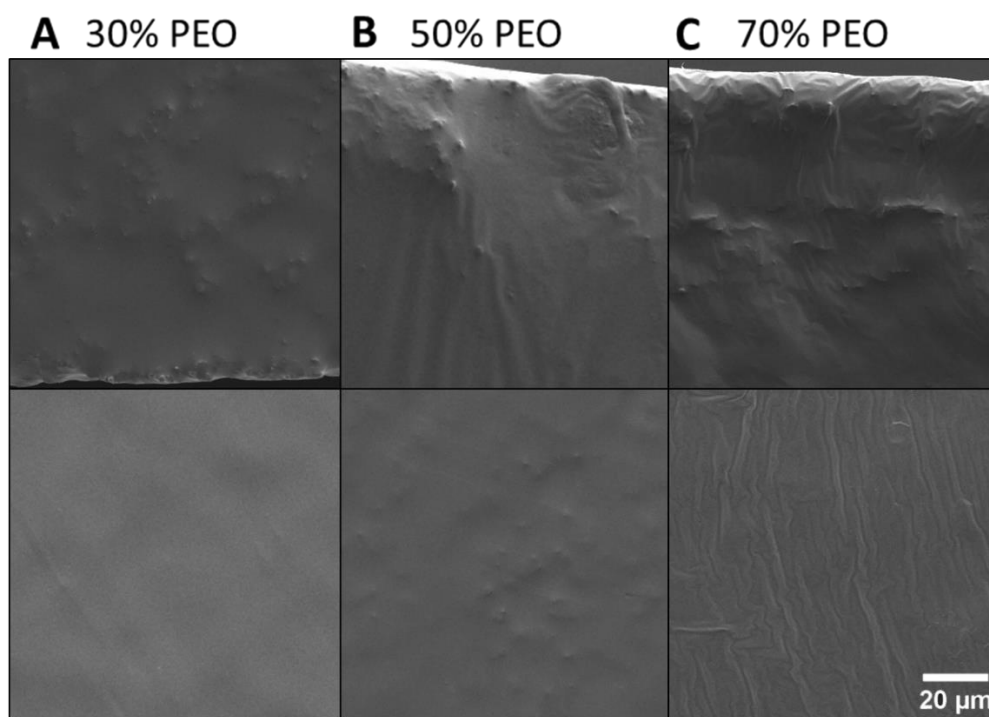


Figure 2. SEM micrographs of the cross-section (top) and the surface (bottom) of the PEO/PEC blend with 30 % (A), 50 % (B), and 70 % (C) of PEO.

The micrographs obtained from the surface analysis displayed a uniform and continuous appearance, suggesting that the PEO and PEC components should be well-homogenised on a microscale level. The cross-sectional study of the polymeric blends yielded results similar to the surface analysis. These statements seem to contradict the separation phase pointed out by the presence of two different T_{α} in the DMA thermograms, probably connected with the limited magnification and resolution of the SEM images ($20\text{ }\mu\text{m}$ was the maximum magnification without causing damage to the polymeric samples). By obtaining better quality images, phase separations might be pointed out, but this is out of the scope

of the present work, which is related to optimising the thermal and electrochemical properties of the polymeric blends.

3.3 Electrochemical properties

The practical utility of solid polymer electrolytes is influenced by their ionic conductivity, which can be determined by electrochemical impedance spectroscopy (EIS) analysis. All Arrhenius plots of PEO/PC membranes with different contents of PEO in a temperature range of 0 – 80 °C are reported in Figure S5, while in Figure 3, the conductivities of PEO 400k/PEC formulations are reported.

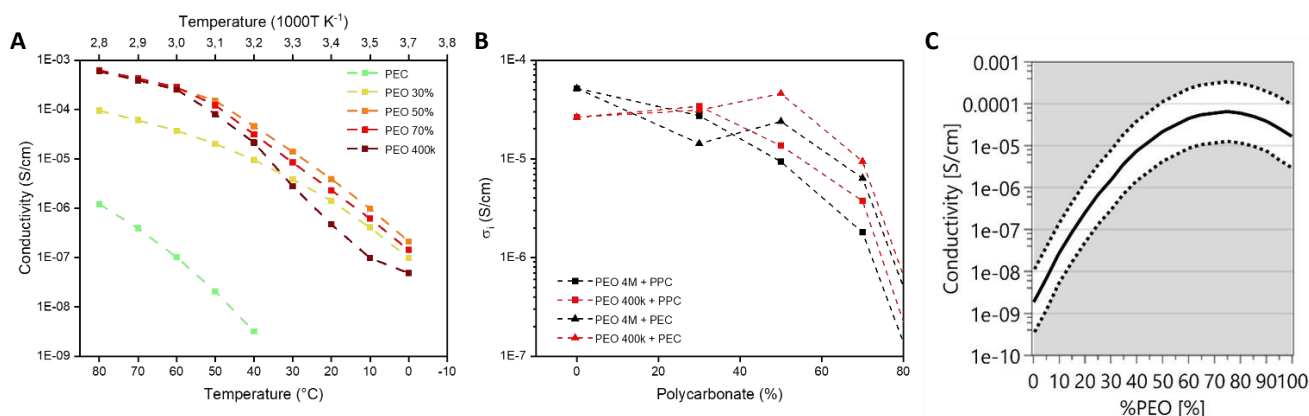


Figure 3. Arrhenius plot of ionic conductivity versus inverse temperature determined by EIS in the range of 0–80 °C for PEO 400k/PEC formulations (A). Comparison of the conductivity values at 40 °C varying the percentage of polycarbonate in the blend (B). Effect of the % PEO on the conductivity calculated from DoE analysis (C).

PEO at temperatures above 50 °C displayed similar conductivity to the blends due to the melting of PEO crystalline domains that occurs at around 50 °C. Above this temperature, the material is completely amorphous with improved ion transport. However, at lower temperatures, the electrolytes made of PEO/PC show better ionic conductivity compared to the pure PEO. This is related to the reduction in crystallinity of PEO in the system, as demonstrated by the DSC thermograms. Thus, at lower temperatures, the blend of PEO with amorphous PCs possesses higher ion conduction properties. Moreover, the curve slope in the high-temperature region (80 – 50 °C) is different from the slope in the low-temperature region (50 – 0 °C). The reason behind this effect is the recrystallisation of PEO that occurs at temperatures lower than 50 °C. This effect is less pronounced in the curves of the PEO/PC blends due to the lower crystallinity of these systems. The σ_i values at 40 °C are reported in Figure 3B.

The effects of PC and PEO types, as well as the % PEO, on the conductivity have been evaluated at 40 °C through DoE analysis. Among them, the main influential variable is the percentage of PEO in the blend (Figure S4). Generally, conductivity at values 40 °C improved from 10^{-9} to 10^{-5} S cm⁻¹ with increasing the quantity of PEO from 0 % to 50 %, respectively. Above such percentage, the values remained quite stable, and only a slight decrease is observed with pure PEO (Figure 3C). In addition to % PEO, the type of PC shows a minor effect on the conductivity, where the use of PEC, instead of PPC, leads to slightly higher values. On the contrary, the molecular weight of PEO does not show a relevant effect on the conductivity. Among all the polyelectrolytes tested, PEO 400k:PEC 1:1 exhibited the highest ionic conductivity ($4.584 \cdot 10^{-5}$ S cm⁻¹).

When comparing membranes with the same PC content, it is evident that the type of PC plays a role in determining ionic conductivity. PEC-based membranes generally exhibited higher conductivity compared to PPC-based membranes and the reason can be attributed to the intrinsic higher conductivity of the pure PEC, which is higher than PPC (Figure S5). Moreover, the molecular weight of PEO influenced the conductivity of the electrolyte when considering samples with only PEO. Despite a high conductivity of PEO 4M, the membranes with PEO 400k showed close conductivity compared to the same blends made with PEO 4M. The electrochemical stability window of PEO/PC blends was evaluated using LSV at 40 °C. Initially, the anodic stability of the pure compound (Figure 4A) was measured. The stability of the two PEOs was quite similar and superior compared to the stability of the two PCs. A slight difference in the stability is also noticed between the two PCs, with PPC resulting in more stability than PEC. Notably, the oxidation peak of water is not observable in all cases, meaning that the drying process is efficient enough to remove all traces of water that can eventually be contained in both PEO and LiTFSI components.

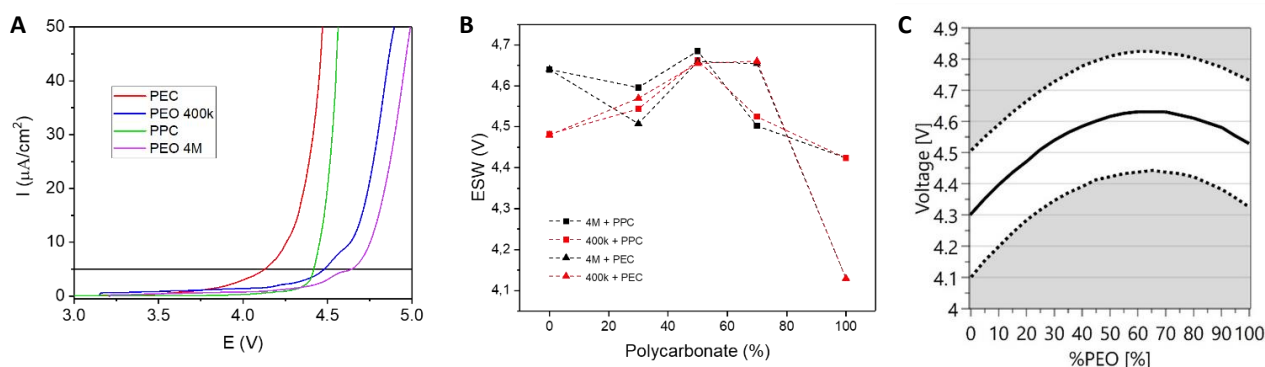


Figure 4. The measured electrochemical stability window (ESW) for pure compound (A) and for all the samples (B). Effect of the % PEO on the voltage calculated from DoE analysis (C).

This result, along with no substantial weight loss at around 100 °C in the TGA, suggests that the extrusion process allowed the production of polymeric blends without water contamination or degradation of the polymers.

Then, the oxidation stability was evaluated for all the blends (Figure 4B) through the multivariate analysis. The analysis shows that the % PEO is the sole influential variable with a quadratic effect on the electrolyte stability of the blend (Figure S4). In particular, the predicted voltages increase with the addition of PEO up to a maximum of 60 % (Figure 4C). Among the experimental trials, PEO 4M:PPC 1:1 exhibited the highest electrochemical stability (4.68 V). Above this percentage, the electrolyte stability tends to decrease to lower voltages. On the contrary, the PC type and molecular weight of PEO do not directly affect the voltage stability. Varying the weight ratio of PEO and PC within the polymeric blend, leads to a variation in the electrochemical stability with a general improvement, reaching a maximum around the ratio 1:1 of PEO/PC. Further increases in the quantity of PCs is detrimental to the stability of all PPC blends, while PEO/PEC blends witnessed an improvement in the anodic stability of up to 70% of PEC. Within each PC type, the electrochemical stability did not change significantly, varying the molecular weight of PEO. Differently, the type of PC has a relevant influence on the oxidation potential, and the membranes containing PPC have been proved to have slightly better electrochemical stability.

4. Conclusions

In this work, a polymeric electrolyte was realised by incorporating two types of polycarbonates, polyethylene carbonate (PEC) and polypropylene carbonate (PPC), in a PEO-based matrix. Different PEO molecular weights (400 000 g/mol and 4 000 000 g/mol) and compositions (0%, 30%, 50%, 70%, and 100% of PEO) were investigated to optimise the final polyelectrolyte's properties, such as crystallinity, electrochemical stability window, and conductivity. The blend polymer was successfully produced by employing a mini-compounder that was able to mix the starting materials all together. The process developed can be easily scaled up, finding industrial applications and avoiding the use of organic solvents. A homogeneous and interpenetrated mixing was confirmed by SEM, which did not reveal any distinct domain. We observed that the addition of amorphous PCs led to a substantial decrease in crystallinity, which is attested to around 10 % when 50 % of PEO is used. No relevant effect was induced by the type of PC used. Also, all blends exhibited improved ionic conductivity until a threshold of 50 % of PEO, while further decreases in the PEO percentage were detrimental to conductivity. The sample PEO400k, with 50% of PEC, displayed the best ionic conductivity among the series with $4.6 \cdot 10^{-5} \text{ S cm}^{-1}$ at 40 °C, showing an increase of 57 % with respect to the membrane with only PEO 400k. The ESW also took advantage of the addition of PCs, reaching a maximum in the anodic stability for the formulation with 50% of PEO. Improved values of 4.68 V were reached for PEO4M with 50% of PPC, indicating a beneficial role of PCs. The statistical analyses of the experimental results within a DoE approach confirmed that the most important parameter that should be taken into account is the quantity of PEO, showing an excellent trade-off among all properties for a ratio of PEO 400k:PEC 1:1. The possibility of readily scale up the solvent-free production process and the improved mechanical and electrochemical performances make the PEO/PC blended polymer a good candidate for lithium solid-state batteries, offering promising prospects for next-generation energy storage technologies.

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