



Research Papers

Unconventional PEO-PPC quasi-solid state blend polymer electrolyte for high efficiency solid-state Li-metal batteries

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ARTICLE INFO

Keywords:

Quasi-solid polymer electrolytes
Solid state batteries
Lithium
Polyethylene oxide
Polypropylene carbonate

ABSTRACT

Polymer electrolytes represent a safer alternative over traditional liquid electrolytes, enabling the use of higher energy density active materials as electrodes for batteries. Among the wide variety of different polymeric matrix that are currently been proposed, polyethylene oxide (PEO) is considered one of the most promising. In this work, a PEO-based quasi-solid polymer electrolyte (QSPE) was produced by easily scalable solution casting technique, optimized with addition of plasticizers and blended with polypropylene carbonate (PPC). The resulting polymer electrolyte was ultimately supported to glass fiber separator. Improvement of ionic conductivity, transfer number and electrochemical stability window of the different formulations was confirmed through electrochemical impedance spectroscopy and linear sweep voltammetry. Plating and stripping tests in symmetric Li–Li cells and charge–discharge tests in half-cell configuration (Li vs LFP) were performed to evaluate the cyclability and stability of the QSPEs. The PEO-PPC polymer electrolyte showed improved efficiency and stability during charge–discharge cycles, at room temperature, suggesting the positive effect of the presence of carbonate groups in the polymer matrix. The promising results demonstrate that the as-prepared QSPE could represent a feasible and viable alternative to conventional liquid electrolytes and could accelerate the adoption of high energy density storage systems, like Li-metal batteries.

1. Introduction

The effects of climate change are everyday more evident, and the rate of extreme events seems to be increasing faster than expected. Moreover, the rapidly evolving society and technology demand huge amount of power and it becomes therefore necessary to have reliable and sustainable way of generating and storing energy. Li-ion batteries are the most promising technology for storing energy efficiently and they are indeed essential components of portable devices, electric vehicles and basically any other smart device [1]. Despite the great commercialization, Li-ion batteries still face some challenges and risks to be addressed to fully reach the goals of sustainability, safety and performance.

In this regard, Li-metal batteries (LMBs) are considered promising candidates due to the high energy density of the Li metal anode, offering a theoretical specific capacity of 3862 mAh g^{-1} , which is almost ten times higher than graphite (372 mAh g^{-1}). Li-metal also shows the lowest negative electrode potential of all elements (-3.04 V vs SHE), thus guaranteeing high voltage systems [2,3]. Although Li-metal anodes have been studied extensively, commercialization has been limited to

primary batteries with only a few exceptions. This is primarily because the presence of liquid organic electrolytes which involve critical risks and safety hazards [4–6] and affect the Li-metal plating reaction during the charging phase, resulting in uneven deposition. This ultimately leads to dendrite formation, short-circuits, and device failure [7]. Therefore, the use of liquid electrolytes is incompatible with high energy density systems that directly exploit lithium metal, like anode-free batteries, Li–S and Li-air batteries [8].

Solid-state electrolytes (SSEs), represent an optimal candidate to substitute liquid electrolytes, leading the way for the adoption of high energy density systems, like Li-metal batteries [9–12]. SSEs could address the main problems affecting liquid electrolytes, i.e. dendrites growth, leakage risks and thermal runaway. Among SSEs, inorganic (ISE) and polymer (SPE) solid-state electrolytes have been proposed, but at the current state none of them can be considered the ultimate solution due to their limitations. They both have their own advantages and disadvantages. ISEs show a high ionic conductivity but they are generally brittle, on the other hand SPEs show great flexibility and conformality with the electrodes interface but have intrinsic low ionic conductivity

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[13–19]. Despite many years of research, these issues are still hampering a definitive integration and commercialization of solid-state batteries. In this work, attention was given to polymeric electrolytes (PEs), in particular polyethylene oxide (PEO), with the main aim to improve the ionic conductivity and allow stable cyclability at room temperature, the main limitations of PEs [20,21].

PEO was the first reported polymer electrolyte enabling conduction of Li^+ ions at the solid-state and it is still the most studied polymer matrix due to its peculiar properties, like low T_g and high Li-salt dissociation [22,23]. Despite these peculiar properties, PEO suffers from low ionic conductivity due to a high degree of crystallinity [24]. As consequence, testing of PEO-based electrolytes is generally limited to high-temperatures ($T > 60^\circ\text{C}$), limiting its practical application [25–31]. The ionic conductivity of PEO can be enhanced by increasing the mobility and free volume of PEO chains: one method for decreasing crystallinity and increasing amorphous phase is plasticization. Introducing a plasticizer in the formulation helps to separate the polymer chains improving their mobility and allowing a reorganization of the polymeric chains [32]. Adding liquid plasticizers to the polymer matrix, such as aprotic organic solvents and low molecular weight glycols, is considered a promising method for increasing the ionic conductivity. This type of polymer system is considered a quasi-solid polymer electrolyte (QSPE). One of the most used approaches is to add low molecular weight PEG molecules [33], but $-\text{OH}$ groups of PEG tend to react with the Li-metal anode, leading to possible incompatibilities and rapid capacity fading [34]. Therefore, $-\text{OH}$ end groups were herein substituted by methyl ethers, selecting triethylene glycol dimethyl ether (TEGDME) as plasticizer for the PEO-system, due to the optimal combination of short chains and its compatibility with both the polymer matrix and Li-metal.

Moreover, polypropylene carbonate (PPC) was blended with the PEO-QSPE. PPC is an amorphous low-cost and biodegradable polymer, containing carbonate groups in the main chain [35]. Carbonate groups possess a lower donor number than ether groups of PEO, showing a weaker coordination with Li^+ ions. Therefore, polymers containing carbonate groups in the main chain (like PPC) show an improved transference number of Li^+ ion, as shown in previous works [36–38]. Solution casting method is selected to produce the polymeric membranes through an easily scalable process, that can be integrated in the already available Li-ion battery production line at industrial level. In-depth electrochemical characterization is performed to verify the effect of PPC on the ionic conductivity and the transference number. The as-developed QSPE is further improved by the integration of glass fiber (GF) separators as scaffold for the SPEs. The addition of a scaffold aims at enhancing the mechanical properties of the system, which are not sufficient to allow stable cycling experiments, especially for the PEO-PPC system. With respect to previously available literature [39], this QSPE contains a much lower amount of PPC and a plasticizer (TEGDME) which guarantees higher ionic conductivities, transference number and a stable cyclability at room temperature.

2. Materials and methods

2.1. Quasi-solid polymer electrolyte preparation

Acetonitrile (ACN, anhydrous 99.8 % Sigma Aldrich) has been selected as solvent to easily dissolve the PEO polymer. Polyethylene oxide (PEO $M_v \approx 600,000$, Sigma-Aldrich), LiTFSI (Sigma Aldrich) and additives were dissolved in anhydrous acetonitrile and stirred overnight before being cast in PTFE molds and dried in controlled atmosphere. ACN boiling point ($T_m = 82^\circ\text{C}$) also guarantees easy removal at room temperature, evaporation was completed by vacuum drying at 50°C for 12 h in Buchi oven (BÜCHI B-525) (Fig. S1). PEO and LiTFSI were carefully dried overnight at 80°C in vacuum oven before use. Triethylene glycol dimethyl ether (TEGDME, Sigma Aldrich) and polypropylene carbonate (PPC, Sigma Aldrich) were used as received and

stored in controlled environment. All the steps of preparation of the quasi-solid polymer electrolyte (QSPE) were carried out in Ar atmosphere inside the glovebox (O_2 and $\text{H}_2\text{O} < 0.5$ ppm, MBraun). The thickness of the polymer electrolytes had an average value of $50\ \mu\text{m}$, measured with micrometer and SEM. In order to obtain a constant thickness value, the quantity of poured solution into the molds was kept constant. Glass microfiber (Whatman GF/C) was also used as support for the QSPE. In case of supported polymer, the solution was poured onto the membrane and the same drying procedure was later followed. Each sample was labeled depending on its most relevant component, M being TEGDME and C being PPC. The concentration was also indicated, and the number was referred to wt% with respect to PEO mass. GF-supported samples were highlighted by the letter G.

2.2. Characterization methods

Accurate electrochemical characterization was performed in coin cell configuration (CR2032, Tob New Energy), assembled using a hydraulic press (TOB-YP180) at 1000 psi pressure. The QSPEs were punched with diameter $\phi 15$ mm. The ionic conductivity of the quasi-solid polymer electrolytes was evaluated through electrochemical impedance spectroscopy (EIS). EIS was performed using a Biologic VSP300 potentiostat, applying a single-wave potential perturbation with an amplitude of 10 mV around the OCV, between 10 MHz and 1 Hz, in the temperature range $22\text{--}50^\circ\text{C}$. The ionic conductivity can be calculated with $\sigma = d/(R_b S)$, where d is the thickness of the QSPE, S is the electrode/electrolyte contact area and R_b is the bulk resistance. The bulk resistance (R_b) of the QSPE was determined by fitting a Debye circuit using EC-Lab software. The activation energy (E_a) was evaluated through the Arrhenius equation, for the ionic transport. Electrochemical stability window (ESW) of the polymer electrolytes was determined through linear sweep voltammetry (LSV) using a Li/QSPE/SS coin cell configuration, with a sweep rate of $1\ \text{mV s}^{-1}$. Lithium transference number (t_+) was calculated through Bruce-Vincent potentiostatic polarization method, assuming perfectly dissociated ions [40]. The value of t_+ was therefore computed using equation:

$$t_+ = \frac{I_{SS}(V - I_0 R_0)}{I_0(V - I_{SS} R_{SS})}$$

where I_{SS} is the current registered in steady state and I_0 is the initial current detected. R_0 is the interfacial resistance at initial time while R_{SS} is the final resistance, V is the applied potential difference (10 mV). Galvanostatic plating–stripping tests were performed to assess stability of the QSPE towards Li-metal deposition at $0.25\ \text{mA cm}^{-2}$ and room T. To define the critical current density (CCD), a sequence of plating/stripping cycles at increasing current densities were performed, with steps of $0.1\ \text{mA cm}^{-2}$ and fixed time. Galvanostatic charge–discharge (GCPL) tests were performed to investigate the cyclic behaviour of QSPEs, employing $\phi 10$ mm commercial LFP electrodes (NEI Corp., active loading: $8.34\ \text{mg cm}^{-2}$) as cathode and $\phi 12$ mm Li foil ($100\ \mu\text{m}$ thick, Gelon LIB), with the QSPEs in between. Coin cells were cycled at 0.1 C ($0.14\ \text{mA cm}^{-2}$) in a voltage range of 2.6–4.0 V. Galvanostatic tests were performed using a Neware BTS4000 battery tester. Charge–discharge tests were performed at room temperature, which is a challenging condition for polymer electrolytes which are generally tested at higher temperatures.

X-ray Diffraction (XRD) (Philips model PW1830. $K\alpha_{\text{Cu}} = 1.54058\ \text{\AA}$) was used to analyse the degree of crystallinity of the QSPEs, while scanning electron microscopy (SEM) (Zeiss EVO 50 EP) was used to analyse the morphology of the films. Chemical characterization of the PEO-PPC blend was performed through Fourier transform infrared spectroscopy (FTIR), using a Nicolet 380 spectrometer (Nicolet Instrument Corp., Madison, WI, USA) in the $2100\text{--}1500\ \text{cm}^{-1}$ range.

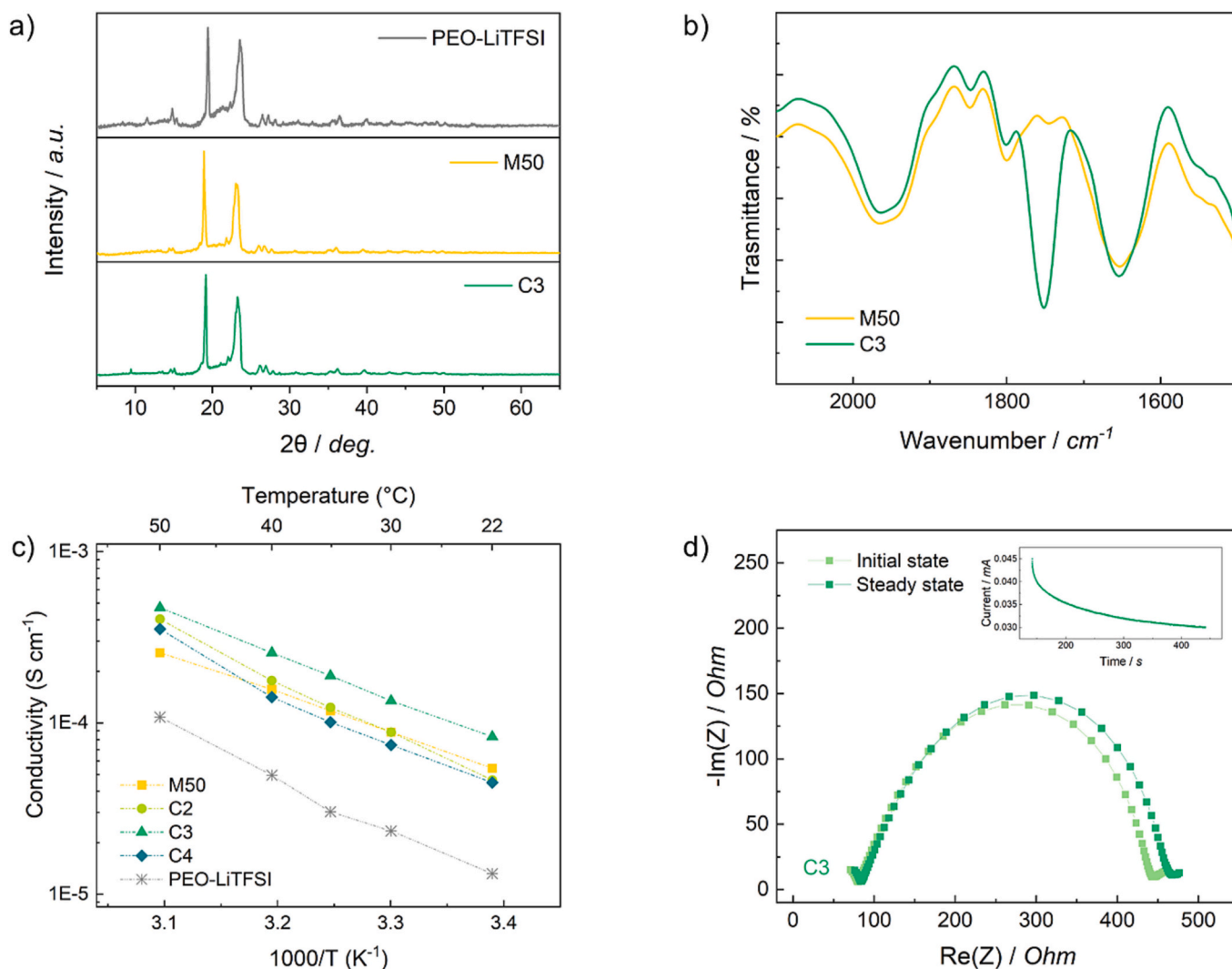


Fig. 1. (a) XRD patterns of QSPes, PEO-LiTFSI, M50, C3. (b) FTIR spectra of quasi-solid polymer electrolytes M50, C3. (c) Ionic conductivity of QSPes comparing different amount of PPC (2, 3, 4 wt%) with PEO-LiTFSI and M50. (d) Transference number test of C3. [PEO-LiTFSI (EO/Li = 10), M50 (TEGDME 50 wt%), C3 (TEGDME 50 wt%, PPC 3 wt%)].

3. Results and discussion

PEO was employed as main polymer matrix, showing peculiar properties in terms of ion solvating ability, but still suffering from low conductivity at room temperature and low transference number [41]. Moreover, PEO was selected for its solubility in lower boiling point solvent, viz. acetonitrile (ACN), for easier removal through a mild drying procedure. PEO concentration was kept constant at 3 wt%, for optimal viscosity and casting. Concentration of LiTFSI was optimized to an EO/Li = 10 for the best combination of high conductivity and mechanical properties. A TEGDME amount of 50 wt% was selected since too low amount was not able to improve effectively the ionic conductivity and too high amount would lead to unmanageable and porous membranes (Fig. S2). Different amounts of PPC were studied to further improve ionic conductivity and transference number, by modifying Li^+ ion movement through physical and chemical interactions. The use of PPC to create a blend with PEO has been therefore investigated. Pure PPC, like most polycarbonates, it's completely amorphous thus a small amount was dissolved along with PEO in acetonitrile aimed at compensating the high degree of crystallinity of PEO, the optimal PPC amount was found from ionic conductivity results (Fig. 1c). Impedance analysis was performed by varying the temperature from room temperature to 50 °C, below the melting temperature of PEO ($T_m \approx 60$ °C)

Table 1

Comparison of ionic conductivity and activation energy for QSPes.

	Ionic conductivity ($S\ cm^{-1}$, RT)	Activation energy (eV)
PEO-LiTFSI	1.32×10^{-5}	0.59
M50	5.44×10^{-5}	0.44
C2	4.64×10^{-5}	0.58
C3	8.32×10^{-5}	0.49
C4	4.49×10^{-5}	0.60
GM50	1.70×10^{-4}	0.45
GC3	2.46×10^{-4}	0.60

and comparing the PPC-containing samples with the bare PEO-LiTFSI and the PEO-TEGDME (M50) QSPE. From conductivity results reported in Fig. 1c, 3 wt% was found to be the optimal concentration of PPC, which was used for further characterization. Room temperature conductivity and activation energy are summarized in Table 1: sample containing PPC 3 wt% (C3) showed highest value of room temperature conductivity $8.32 \times 10^{-5}\ S\ cm^{-1}$, and activation energy of 0.49 eV, highlighting good transport of ions in the PPC-containing QSPE. It was found that over the 3 wt% threshold, PPC reduces the conductivity of the system. Moreover, the crystallinity of the different QSPes was compared through XRD analysis (Fig. 1a). By addition of TEGDME and PPC the

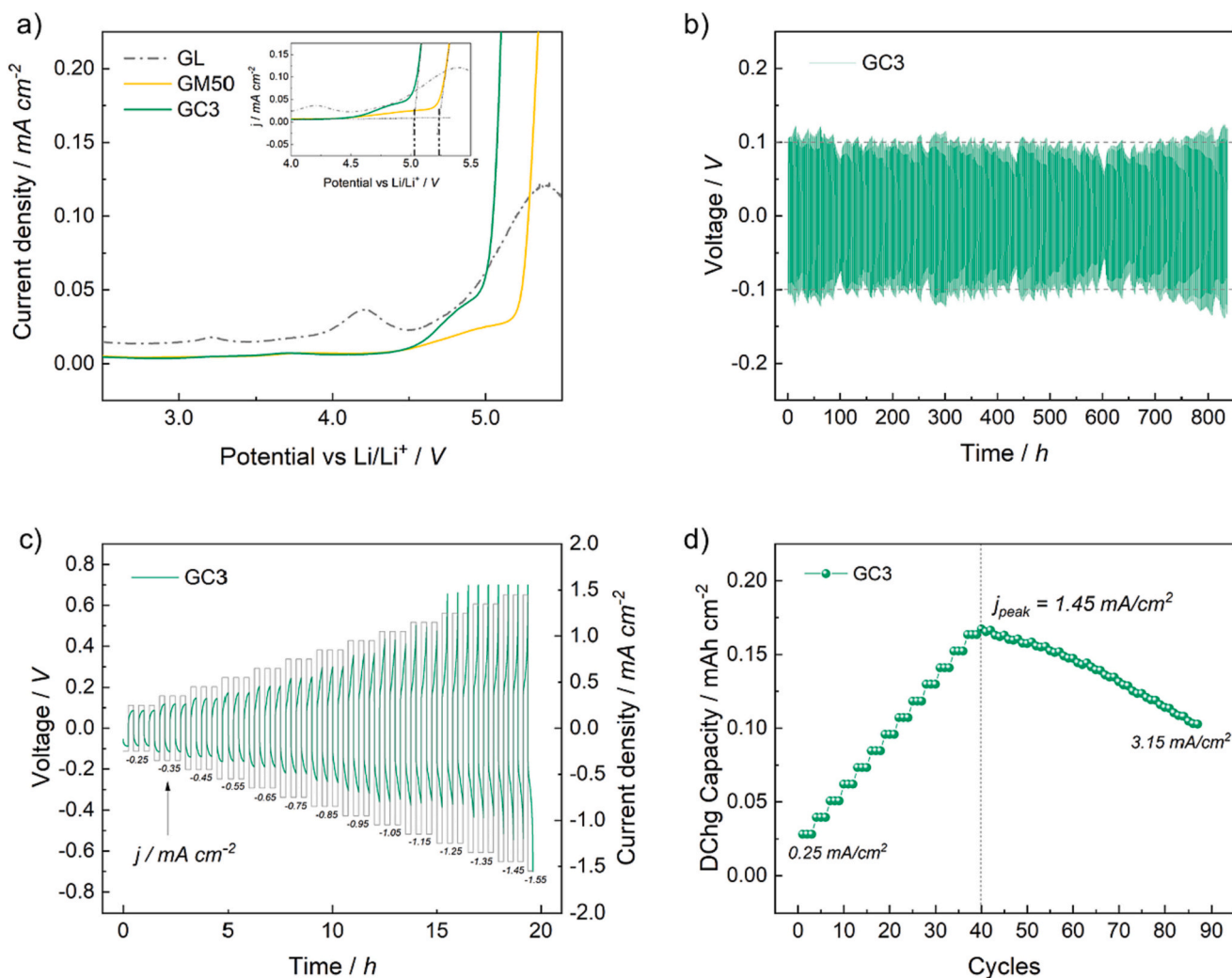


Fig. 2. (a) Cathodic LSV scan for the GF-supported QSPEs: GL, GM50, GC3. Scan rate: 1 mV s⁻¹. (b) Plating/stripping test of GC3, 0.25 mA cm⁻² (0.1 C), 0.125 mA cm⁻². (c) Critical current density protocol of GC3. 0.25–1.55 mA cm⁻², $t_{\text{cycle}} = 30$ min. (d) Discharge specific capacity of GC3, for each cycle of the critical current density test. [GL (DEC-EC 1:1, 1 M LiPF₆), GM50 (TEGDME 50 wt%), GC3 (TEGDME 50 wt%, PPC 3 wt%)].

peak at 23.72°, associated to the (112) crystalline plane, was reduced compared to the PEO-LiTFSI case. This suggests a reduction of the crystalline planes with (112) orientation, this is in accordance with the increase of the ionic conductivity previously analysed. Between the samples with and without PPC no clear change in the (112) orientation is found, this is also consistent with the ionic conductivity which showed comparable results, confirming a connection between the two properties. FTIR was performed to visualize the effective integration of PPC into the QSPE (Fig. 1b): the characteristic peak of the C=O stretching of the carbonyl group was found in the 1730–1750 cm⁻¹ region of the spectrum for the PEO-PPC sample C3. Indeed, the addition of a polycarbonate polymer, like PPC, was aimed at exploiting the presence of carbonate groups C(=O)(O—)₂ able to solvate lithium ions keeping a good transfer number. Compared to traditional PEO-based systems, the transference number for sample C3 was indeed found to be greatly improved (0.59), confirming the good influence of the carbonyl group of PPC (Fig. 1d). The transference number assumed the same value for all the three PEO-PPC compositions, suggesting that small amount of carbonate groups is needed to improve the Li⁺ movement.

The membranes with the best performing compositions were prepared to complete the electrochemical characterization through charge-discharge cycles. However, none of the self-standing membranes tested was able to show a good cycling behaviour; this was expected since the addition of TEGDME and PPC both have a negative effect in

terms of mechanical properties of the QSPE. To increase the cyclic performances of the membranes, glass fiber (GF) commercial separators were introduced as support to the polymeric membranes. GFs were therefore integrated into QSPE formulations previously selected and the morphology was analysed through SEM analyses (Fig. S3), showing good homogeneity and wettability of the glass fibers. The ionic conductivity was again assessed as previously described (Table 1), showing higher values with the addition of the GF. This behaviour can be justified by the better homogeneity of the GF-samples, which guarantees better interfacial contact and electrochemical properties. LSV was performed to evaluate the ESW of the GF-supported QSPEs (Fig. 2a). Stability window was found to be higher than 5 V for both TEGDME and PPC-containing samples, generally comparable with the stability window of liquid electrolytes. The plating-stripping test in symmetric Li—Li coin cells ($j = 0.25$ mA cm⁻², room T) of PEO-PCC QSPE revealed its outstanding stability against Li electrodes for over 800 h, with a stable overpotential of 0.1 V, demonstrating effective behaviour against dendrites (Fig. 2b). A critical current density (CCD) protocol was designed to evaluate the ultimate current density at which the membrane could exchange lithium ions without dendrites and irreversible damage to its structure. As reported in Fig. 2c–d the PEO-PPC blend could withstand a peak current density (j_{peak}) up to 1.45 mA cm⁻². No short circuit was found up to 3.15 mA cm⁻² but capacity decay was evident after j_{peak} . The critical current density has been evaluated also for the QSPE

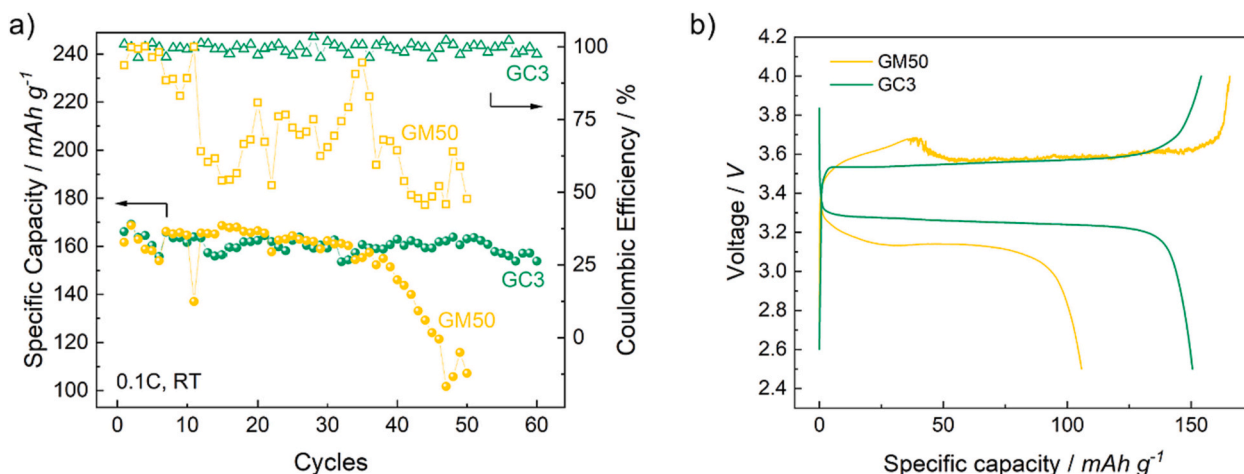


Fig. 3. (a) Charge–discharge cycles for GF-supported QSPEs: GM50 and GC3. 0.1 C, room T. (b) Last charge–discharge cycle for GF-supported QSPEs: GM50 and GC3. 0.1 C, room T. [GM50 (TEGDME 50 wt%), GC3 (TEGDME 50 wt%, PPC 3 wt%)].

without PPC (Fig. S5), showing a j_{peak} of 0.95 mA cm^{-2} . This result confirms the improved behaviour at high current rates for the sample containing PPC with respect to the sample without PPC and the better ability to withstand Li-metal growth.

Finally, cycling behaviour of the GF-supported QSPEs was evaluated through charge–discharge tests at 0.1 C and room temperature in Li-LFP configuration. The specific capacity upon discharge and coulombic efficiencies are reported in Fig. 3a. Both GM50 and GC3 samples showed high specific capacities in the first cycles, reaching values very close to the theoretical one (170 mAh g^{-1}). But only GC3 was able to stably cycle for >50 cycles with an average discharge specific capacity of 160 mAh g^{-1} and stable coulombic efficiency. Fig. 3b compares the last recorded cycle for the two QSPEs, and by the irregular charging phase it is clearly showed how dendritic growth is affecting sample GM50 much more than GC3, containing PPC. The instability and dendrites formation in GM50 was evident from the irregular behaviour upon charge, leading to local puncturing of the polymer electrolyte, loss of electrical connections and consequent instability of the charging phase at high capacity. The morphology of the GC3 QSPE after cycling test has been reported in Fig. S4, showing a change in the surface appearance with respect to the fresh one, but overall homogeneity over large areas. Moreover, the thickness was also slightly reduced probably due to the effect of the coin cell pressure.

4. Conclusions

In this study, a polymer electrolyte based on polyethylene oxide (PEO) was optimized by incorporating triglyme (TEGDME) as a plasticizer and poly(propylene carbonate) (PPC) as an additional polymer matrix. A highly scalable process was developed using solvent casting. In the final configuration an efficient and long-lasting quasi-solid polymer electrolyte (QSPE) was obtained with an optimized PEO-PPC composition. Overall, the blend exhibited improved ionic conductivity of the order of $10^{-4} \text{ S cm}^{-1}$ at room T and good transference number (0.59) which clearly demonstrated the positive influence of the carbonate group to the behaviour of Li^+ ions in polymer electrolytes. By supporting the PEO-PPC blend to a glass fiber separator, it was possible to obtain outstanding stability against Li-metal electrodes in plating-stripping test for $>800 \text{ h}$ and a high critical current density of 1.45 mA cm^{-2} was demonstrated. Additionally, stable discharge specific capacity and coulombic efficiency was verified for the PEO-PPC blend at 0.1C and room temperature. An average discharge capacity of 160 mAh g^{-1} was indeed maintained almost constant for >50 cycles, while keeping a stable CE around 100 %. The possibility to efficiently work at room temperature and to easily scale-up the production process and the

compatibility with Li-metal electrodes make the QSPE based on the PEO-PPC blend a promising candidate for next-generation high energy density Li-metal systems, such as Li–S and anode-free batteries, and solid-state batteries in general.

Author statement

Due to the nature of the project, raw data would remain confidential and would be shared upon request.

Data not available/The data that have been used are confidential.

CRediT authorship contribution statement

Luca Bertoli: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Giacomo Gabriele:** Investigation. **Eugenio Gibertini:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Luca Magagnin:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Methodology, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors would like to thank Piergiorgio Marziani for the help with FTIR measurements.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.est.2024.110456>.

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