

Designing boron-based single-ion gel polymer electrolytes for lithium batteries by photopolymerization

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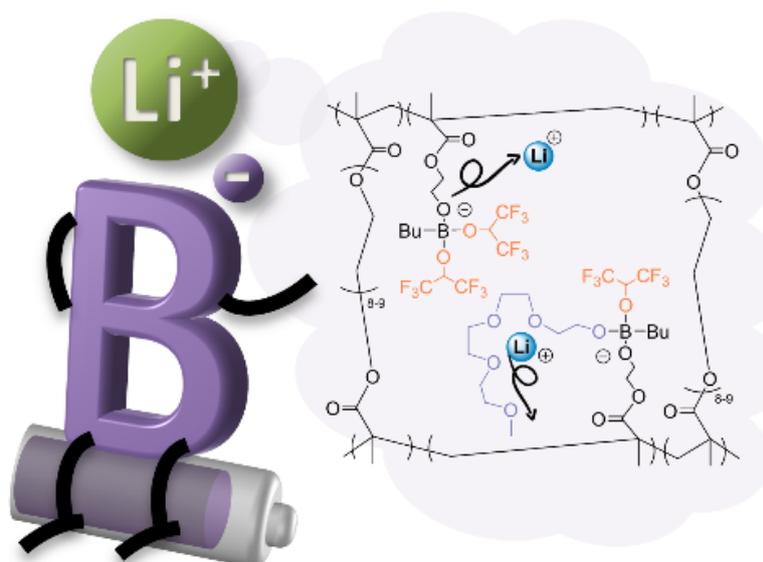
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ABSTRACT

Single-ion lithium conducting polymer electrolytes based on delocalized borate groups have been designed and synthesized by rapid UV-photopolymerisation. For this purpose, three different functional lithium boron sp^3 anionic monomers, containing fluorinated, ethoxy, or a blend of both functionalities have been synthesized. These monomers were photopolymerized in the presence of a PEG-di-acrylate crosslinker and tetraglyme as plasticizer. By this method, gel polymer electrolytes (SIPes) endowed with lithium single-ion conduction were prepared. The impact generated by the different functionalities of the borate groups and the addition of plasticizer on the electrochemical and ion conducting properties of the synthesized polymer electrolytes are analyzed in detail. These polymer electrolytes showed high ionic conductivity ($1.71 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at $25 \text{ }^\circ\text{C}$) and high lithium transference number values (up to 0.85). Finally, they were investigated as solid electrolytes in lithium metal symmetrical cells showing good performance ($<0.85 \text{ V}$ at $\pm 0.2 \text{ mA} \cdot \text{cm}^{-2}$ for 175 h).



1. Introduction

In recent decades, the demand for lithium-ion batteries (LIBs) has experienced a rapid increase, mainly due to their lightweight, high energy density, and versatility for use in portable electronic devices and battery electric vehicles (BEVs)[1]. The efficiency of electrolytes for LIBs is crucial for their electrochemical performance and safety during the charging and discharging processes. Currently, liquid electrolytes based on lithium salts dissolved in organic carbonates are the most widely used in LIBs[2], however, they may present severe safety issues such as flammability, volatility, leakage or toxicity. Solid polymer electrolytes (SPE) have been proposed as one of the most feasible solutions to mitigate these safety issues although their ionic conductivity is still far from current liquid electrolyte cells. One compromising solution could be the use of gel polymer electrolytes (GPEs). In general, GPEs can be obtained by plasticizing SPE with an organic solvent, forming polymeric structures interconnected by liquid electrolyte-filled pores that serve as conduction pathways for ionic transport[1]. In this way, GPEs can synergize the properties of high ionic conductivity (fast cation diffusion) and electrode/electrolyte interfacial properties of liquid electrolytes[3], with the beneficial mechanical properties (strength, flexibility, etc.) of solid polymer electrolytes[4]. Nevertheless, one of the main limitations of conventional GPEs is associated with their low lithium transference number (t_{Li^+}) values, as a consequence of the dual-ion motion of lithium salts used in the network-entrapped liquid electrolytes[5]. Recently, lithium single-ion conducting polymer electrolytes (SIGPE) prepared from polymerizable lithium salts such as lithium 1-[3-(methacryloyloxy)-propylsulfonyl]-1-(trifluoromethylsulfonyl)imide (LiMTFSI)[6], have been reported with high lithium transference number (close to 1) and excellent performance in lithium metal batteries. Researches also proved that the anionic immobility decreases the

overpotential generated by anionic concentration gradients and slows down the dendritic growth rate on the negative electrode during the charge-discharge cycles of lithium metal batteries[7–9].

On the other hand, the use of boron-based molecules, either as additives or primary salts, has become popular in electrolyte development[10], as these have shown a positive effect on the formation of more stable solid electrolyte interphase (SEI) layers on the negative electrode surface and improved electrochemical performance in LIBs cyclability tests[11]. For example, Jimin Shim et al.[12], developed a series of semi-interpenetrated polymeric networks (IPNs) containing PVDF and boron-based trimethacrylate cross-linkers with different lengths of their ethylene oxide (EO) chains, which exhibited excellent ability as anion-trapping groups when combined with liquid electrolytes based on LiTFSI salt and organic carbonates, obtaining t_{Li^+} values ranging from 0.4 to 0.8. These values were associated to the length of the EO chains[13], which determined the amount of adsorbed liquid electrolyte[14]. Other boron-based GPEs that exhibited single lithium-ion conduction properties (t_{Li^+} close to 0.85) were obtained by preparing IPNs through the condensation reaction of lithium tetramethoxy borate and dicarboxylic acids[9] (that facilitate the dissociation between lithium-ion and borate group) or 1,2,3,4-Butanetetracarboxylic acid[15] and tartaric acid[16], both in PVdF-HFP. In other strategies, such as the one developed by Y. Meng et al.[17], a single-ion conducting electrolyte was prepared by coupling lithium bis(allylmalonate) borate (LiBAMB) and pentaerythritol tetrakis (2-mercapto acetate) via an *in situ* UV-photoinitiated click-reaction, achieving the incorporation of up to 85 %wt. of gamma-butyrolactone (GBL) as a plasticizer and obtaining t_{Li^+} values of 0.85 and an ionic conductivity of $1.47 \cdot 10^{-3} \text{ S cm}^{-1}$ at 25°C. In general, it is well-known that anionic centers based on sp^3 -coordinated boron atoms reside tetra-coordinated

with oxygen atoms forming rigid polymeric frameworks, which lowers ionic conductivity[1,17,18]. To improve it, I. Gonzalez et al.[19] employed both partial crosslinking and tuning of electron-withdrawing substituent groups attached to the BO_4 groups. Electrochemical impedance spectroscopy (EIS) results and theoretical calculations revealed that the electron-withdrawing substituents are insufficient to significantly improve the ionic conductivity, due to the limited mobility of the polymer chains at room temperature[20–22]. Hence, substituents that improve this chain mobility are desirable for achieving higher conductivities in polymers containing this type of borate group[23].

In this work, single-ion gel polymer electrolytes (SIGPEs) were prepared by UV-photopolymerization based on three borate lithium methacrylate monomers[24] and poly(ethylene glycol) dimethacrylate (PEGDM) and tetraethylene glycol dimethyl ether (tetraglyme, G4) as a plasticizer. The effect of the substituents in the boron atom of the different monomers and the impact of G4 glyme plasticizer on the thermal, mechanical and electrochemical properties of the developed SIGPEs are deeply analyzed. The optimization of the ionic conductivity and lithium transference number of the SIGPEs was pursued. Finally, their performance in lithium symmetrical cells was investigated.

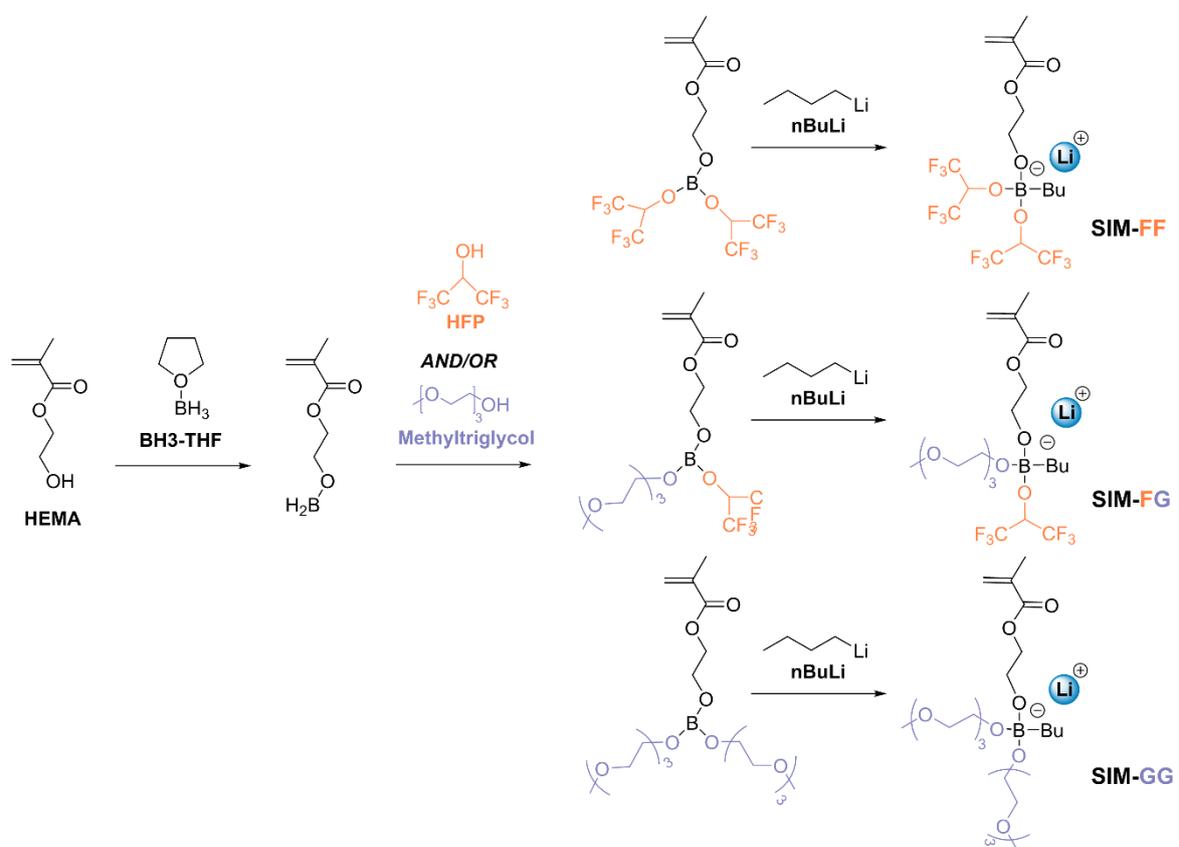
2. Results and Discussion

2.1. Single-ion Gel Polymer Electrolytes (SIGPEs)

2.1.1. Synthesis of lithium borate methacrylic monomers SIM-FF, SIM-FG, and SIM-GG

In this work, three anionic methacrylic monomers based on highly delocalized asymmetric borate groups were synthesized according to **Scheme 1** as recently

reported[24]. In the first one, 2-hydroxyethyl methacrylate (HEMA) was covalently bonded to a boron atom (-C-O-B- bond) via the dropwise addition of BH₃-THF complex. In the second step, the desired functionality was added to the methacrylic-molecule via the addition of triethylene glycol monomethyl ether (methyltriglycol) and/or hexafluoroisopropanol (HFP). Finally, n-butyllithium (n-BuLi) was added to generate the formation of the boron-lithium anionic group, this experimental procedure is described in detail in the **SI**.



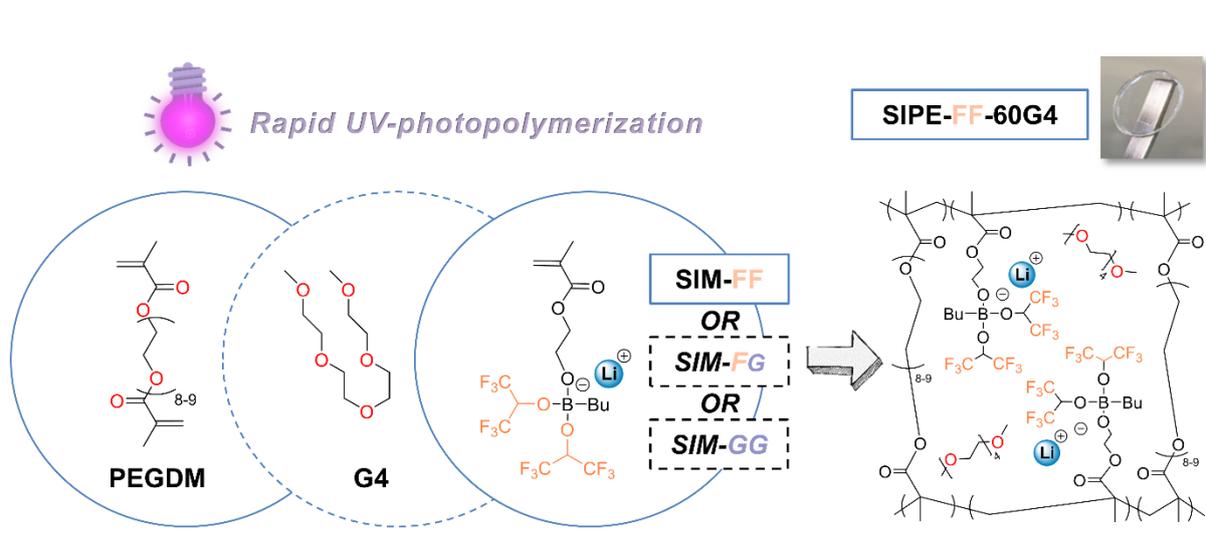
Scheme 1. Synthetic route for the preparation of borate-based single-ion monomers SIM-FF, SIM-FG, and SIM-GG[24].

Thus, the chemical structures of these SIM-xx are composed of an ethoxy-methacrylate group (polymerizable group), a butyl group through a (B-C-) bond (stabilizing agent-decreasing hygroscopicity), and two oxy- (B-OR) substituents, which aimed to modulate the electron-withdrawing ability of borate groups and/or create

lithium-ion mobility pathways. Thus, three custom-made sp^3 boron-based single-ion monomers (SIMs) named as SIM-FF, SIM-FG, and SIM-GG; where F or G represent the functional substituent groups ($F = 1,1,1,1,3,3, 3\text{-hexafluoropropan-2-yl}oxy$ and/or $G = bis((2-(2-(2-(2\text{-methoxy ethoxy})ethoxy) ethyl) boryl)oxy))$) were synthesized. The arrangement of these substituents within the polymer network may the modulation of the electron density of the borate groups (given by the fluorinated functionality, F) and/or the promotion of dissociation and solvation of the lithium ions (given by the presence of ethoxy groups in G).

2.1.2. Synthesis of single-ion gel polymer electrolytes by UV photopolymerization

Single-ion Gel Polymer Electrolytes (SIGPEs) were prepared by rapid UV-photopolymerisation process following the success of previous works[6,25] (**Scheme 2**). SIM-FF, SIM-FG, and SIM-GG methacrylic monomers were co-polymerized (independently) with the crosslinker poly(ethylene glycol) dimethacrylate (PEGDM) in the presence of 2-Hydroxy-2-methylpropiophene (DAROCUR) as the radical photoinitiator. In some cases, tetraethylene glycol dimethyl ether (tetraglyme, G4) was added as a plasticizer at different ratios.



Scheme 2. Lithium single-ion polymer electrolyte (SIGPE) synthesis process by UV-photopolymerization. SIPE-FF-60G4 chemical structure is illustrated as an example.

Table S1 shows the different formulations of the nine SIGPE electrolytes synthesized in this work. For each of the three monomers, three SIGPE formulations containing increasing amounts of G4 plasticizer were designed: SIPE-xx-60G4 (60 %wt. of G4), SIPE-xx-30G4 (30 %wt. of G4), and SIPE-xx (solvent-free solid polymer electrolyte). In all cases, the obtained SIGPEs were self-standing and visually transparent, and monomer conversions were monitored before and after UV-irradiation by Fourier Transform Infrared Spectroscopy (FT-IR) (**Figure 1**). After photopolymerization, the UV-cured gel polymer electrolytes showed high monomer conversions $\geq 95\%$ conversions as seen by the disappearance of the 1635 cm^{-1} band, associated with the stretching of the carbon double bonds of acrylic functionalities[26]. This confirms the photopolymerization process and the viability of the proposed synthetic method.

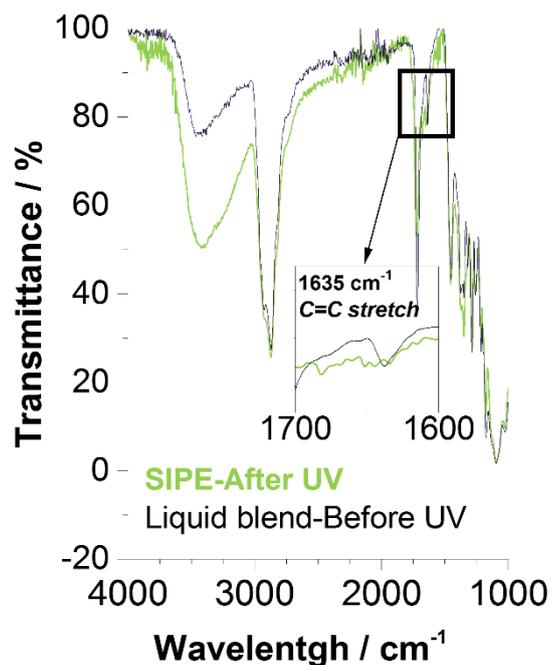


Figure 1. FT-IR spectra of a SIGPE membrane before (black line) and after (green line) UV-photopolymerization. *Inlet:* disappearance of the band associated with the carbon double bond of acrylic functionalities (1635 cm^{-1} band)[26] after UV irradiation.

2.2. Characterization of lithium borate single-ion gel polymer electrolyte

Firstly, thermal and mechanical testing was undertaken to evaluate the potential use of these membranes as electrolytes in operating battery cells. Similarly to previous works using cross-linked and plasticized membranes[6], two consecutive degradation areas were observed in SIPE-FF-60G4 and SIPE-FF-30G4 samples on the thermal gravimetric analysis (TGA) curves (**Figure 2a**): one between 100 and $280\text{ }^{\circ}\text{C}$ (associated with the evaporation of the plasticizer and initial decomposition of the weaker bonds of the polymeric network), and the second one at around $280\text{ }^{\circ}\text{C}$ (associated with the degradation of the polymeric network with stronger bonds). TGA profiles of the other families of solvent-free solid polymer electrolytes were also completed (**Figure S1**). SIPE-FG and SIPE-GG also exhibited two polymeric thermal

decomposition areas, but with a less pronounced decomposition than the plasticized membranes. Overall, membranes were thermally stable until ~ 110 °C, well above LIBs operating temperature (e.g. -20 to 60 °C)[27,28].

Mechanical stability through dynamic mechanical thermal analysis (DMTA) was also investigated (**Figure 2b**) on membranes of the same family containing different amounts of plasticizer (SIPE-GG-xx). All electrolyte membranes presented a stable storage modulus from 0 to 100 °C (in between $10^5 - 10^7$ Pa), which increased with lower plasticizer content, having its maximum with the SIPE-GG solvent-free membrane ($\sim 5 \cdot 10^6$ Pa). Additionally, DMTA measurements at lower temperature range revealed that all membranes were amorphous at RT, having their glass transition temperature, T_g , at -21.0, -37.0, and -33.71 °C for the SIPE-GG, SIPE-GG-30G4, and SIPE-GG-60G4, respectively. This amorphous condition allowed small polymeric segment motions, improving lithium-ion mobility. Hence, these results make these membranes suitable materials as electrolytes for battery cells from a mechanical perspective, sufficiently strong and flexible to withstand the stresses caused during cells assembly and thickness cells variation during use, without affecting ion transport properties[9].

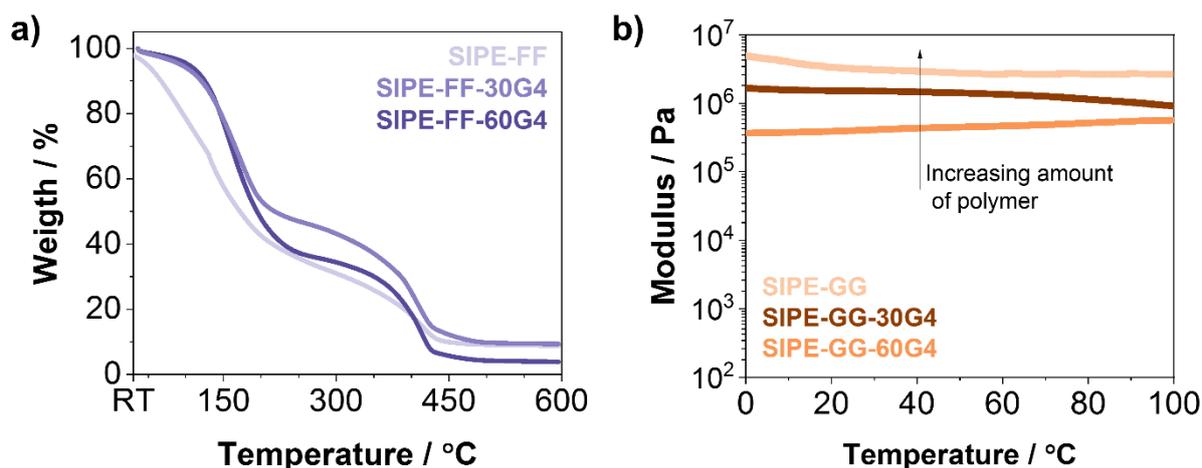


Figure 2. a) Thermal gravimetical analysis (TGA) curve of SIPE-FF-x family of electrolytes undertaken under nitrogen atmosphere and 10 °C·min⁻¹; and b) Dynamic mechanical thermal analysis (DMTA) of SIPE-GG-x family membranes at compression from 0 to 100 °C.

Ionic conductivities (σ) of the developed SIGPEs were deeply analyzed as a function of the plasticizer content, as well as the impact of the Li⁺ interaction with the functional moieties of the selected membrane (FF, FG, or GG). Regarding the plasticizer content, it was common to all membranes that the presence of the plasticizer leads to higher ionic conductivity values (**Figure 3a-c**) compared to solvent-free ones. More particularly, membranes containing 30 %wt. of G4 (SIPE-xx-30G4) had the highest σ values also due to the higher Li⁺ ratio in the gel polymer electrolyte formulation.

The impact of the plasticizer was especially noticeable in the SIPE-FF-xx family (**Figure 3a**), in which there was a difference of 2 orders of magnitude between the ionic conductivity (σ) value at 25 °C of the solvent-free SIPE-FF ($3.92 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$) and the SIPE-FF-30G4 ($1.71 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$). This difference was partly due to the presence of G4 and partly due to the type of functional group present in the polymeric network. SIPEs containing borate-fluorinated groups (SIPE-FF-xx), due to their high electron-withdrawing capability, were expected to weaken the association between the lithium

ions and the anionic pendant group, and therefore, ease Li⁺ mobility from the charged group. In opposition to solvent-free SIPE-FF membranes, the ethoxy groups of the G4 plasticizer present in SIPE-FF-30G4 and SIPE-FF-60G4 provided additional pathways for ion conduction across the electrolyte, hence, enhancing σ and probably explaining the big gap observed between the solvent-free and plasticized membranes.

On the other hand, SIPEs with borate-ethoxy pendant groups (SIPE-GG-xx), in which the moieties had similar chemical structure to glymes (i.e. G4) were designed to enhance ion mobility through the self-solvating capability of its –C–O– moieties. For this reason, the addition of G4 did not improve significantly the σ of the SIPE-GG-xx family of electrolytes (**Figure 3c**).

Lastly, SIPE with asymmetric borate-fluorinated-ethoxy groups (SIPE-FG-xx) were designed to combine both ion delocalization (fluorinated moiety) and ion mobility-pathways capabilities (ethoxy moiety). This effect is observed in the σ of the solvent-free membranes, where SIPE-FG showed the highest value (e.g. $6.47 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ at 25 °C) (**Figure 3b**); but it was less significant with the addition of G4 plasticizer.

Furthermore, ionic conductivities increased linearly with temperature and followed Arrhenius-type thermally activated behavior (**Equation 1** and **Figure S2**)[29,30]:

$$\sigma = \sigma_o \cdot \exp\left(\frac{-E_a}{kT}\right) \quad (1)$$

, where σ_o is the pre-exponential factor (ionic conductivity at $x = 0$ (T_o)), E_a is the activation energy, and k is the Boltzmann constant. The effect of the borate-pendant group in the ion transport mechanism was also detected in the SIPEs activation energies (**Figure 3d**). Within the solvent-free membranes, SIPE-FF presented a much

higher activation energy than SIPE-FG and SIPE-GG due to the lack of ion mobility-pathways provided by the borate-ethoxy pendant groups. As expected, this energy was significantly reduced by the addition of G4.

Overall, the achieved ionic conductivity values in this work are in line with the ones reported in literature[9] for solvent-free single-ion electrolytes ($<10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at $25 \text{ }^\circ\text{C}$) and plasticized SIPEs ($< 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at $25 \text{ }^\circ\text{C}$). The SIPE-FF-xx family had the highest ionic conductivity values, but needed the presence of a plasticizer, i.e. G4, to optimize performance. SIPE-FF-30G4, SIPE-FF-60G4, and SIPE-FG-60G4 showed the highest σ values ($1.71\cdot 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, $9.95\cdot 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ and $5.4\cdot 10^{-5} \text{ S}\cdot\text{cm}^{-1}$, respectively), making them suitable candidates as solid electrolytes in battery cells from an ion conductive perspective.

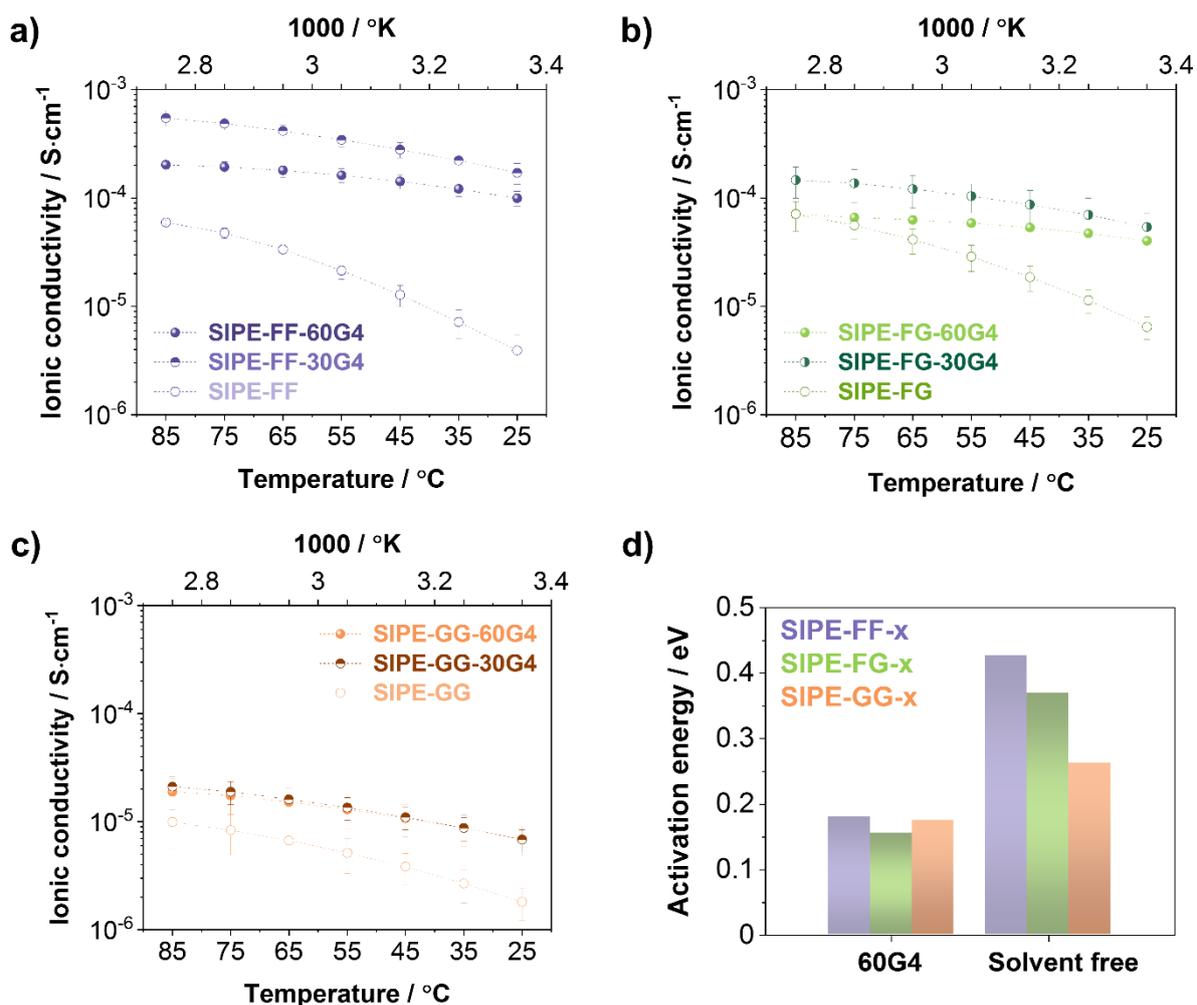


Figure 3. Ionic conductivity values at different temperatures of a) SIPE-FF-x electrolytes containing increasing amounts of tetraglyme (G4) plasticizer, b) SIPE-FG-x electrolytes family and c) SIPE-GG electrolytes family; d) Activation energies (eV) calculated following Arrhenius fittings of thermally-activated processes[30].

Then, lithium transference number (t_{Li^+}) of relevant SIPEs were calculated following **Equation 2**, proposed by Evans-Vincent-Bruce[31]:

$$t_{Li^+} = \frac{I_s(\Delta V - I_0 \cdot R_0)}{I_0(\Delta V - I_s \cdot R_s)} \quad (2)$$

A DC bias (ΔV , 10 mV) is applied to polarize the SIPEs during a chronoamperometry, I_0 is the initial value of the current upon polarization, I_s is the current reached in the steady-state for the sample polarized, and R_0 and R_s are the resistances of the SEI

before and after the polarization, respectively, obtained by electrochemical impedance spectroscopy (EIS). As an example, **Figure 4a** shows both the response of the current overtime during the ΔV polarization and the correspondent Nyquist plots for the SIPE-FF-60G4 cell at 60 °C. The t_{Li^+} of the solvent-free SIPE-FG electrolyte was found to be 0.85.

Solvent-free single-ion conducting polymer electrolytes are close to unity due to the anchoring of the anion group to the polymeric network, thus lowering the accumulation of anions at the electrolyte/negative electrode interface and depressing polarization and resistances due to ion concentration gradients[9,32]. However, these unique transport properties can be slightly affected in plasticized SIPEs, in which there is a partial movement of the anionic groups and polar groups of the polymeric matrix contributing to the solvation of lithium complexes. These partial movements are more significant with increasing lengths of the linking chains between the anionic groups[17,18] and/or the amount/type of solvent incorporated in the polymeric matrices[13]. This behavior was observed in **Figure 4b**, in which t_{Li^+} decreased with higher plasticizer content (0.65 and 0.80 for SIPE-FG-60G4 and SIPE-FF-60G4, respectively). This might be explained by the formation of lithium-ion solvation complexes by the long G4 glyme plasticizer and the mobile cations. In SIPE-FF-60G4 cell, due to the presence of the borate-fluorinated groups, the negative charge is more delocalized and the Li^+ cations disassociate easier.

In accordance, the SIPE-FG-30G4 cell, with intermediate-plasticizer containing electrolyte, had a midway result (0.79) between the solvent-free cell (SIPE-FG) and the high-plasticizer content cell (SIPE-FG-60G4).

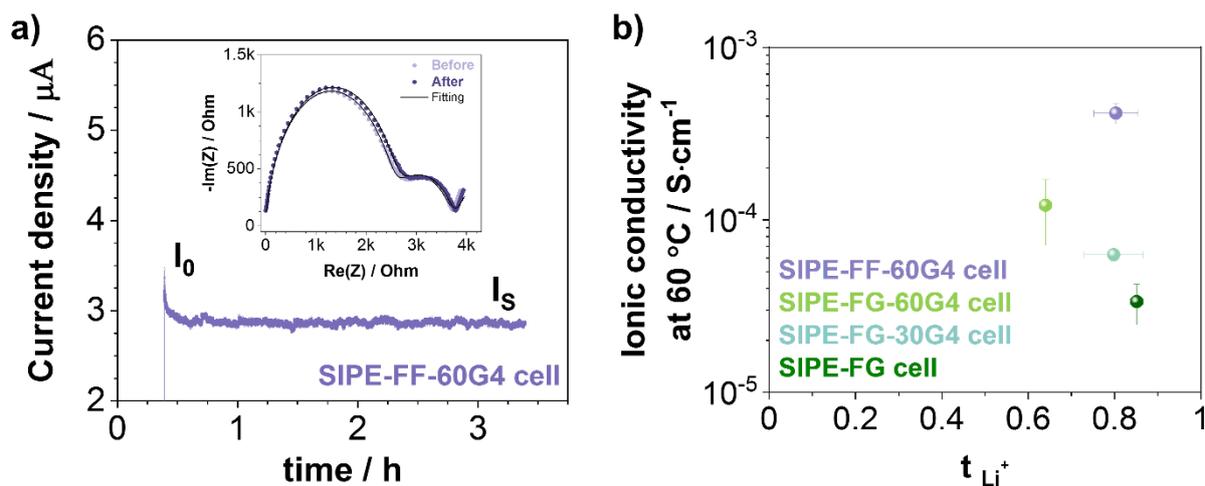


Figure 4. a) Chronoamperometry plot for the lithium transference number calculation following the Evans-Vincent-Bruce method[31] of SIPE-FF-60G4 electrolyte. *Inlet:* Nyquist impedance plots before and after polarization, including fitting curves by equivalent circuits; and b) Ionic conductivities against lithium transference number of SIPE-FF-60G4 electrolyte and SIPE-FG-x family of electrolytes containing different amounts of G4 plasticizer.

The reversible lithium plating and stripping on/from copper electrodes of $\text{Li}^0/\text{SIPE-FG-xx family}/\text{Cu}$ cells (**Figure S3c**) were investigated by cyclic voltammetry (CV) at $60\text{ }^\circ\text{C}$. As observed, the improvement of the wettability of the electrode surface, generated by increasing amounts of plasticizer, resulted in better interfacial transport during the plating-stripping tests. To evaluate this further, the chemical stability window of SIPE-FF-60G4 and SIPE-FG-60G4 (**Figure 5**) were also investigated.

The cathodic scans on $\text{Li}/\text{Electrolyte}/\text{Cu}$ cells, showed a couple of reversible redox peaks, stronger on the SIPE-FF-60G4 cells (-0.5 V and 0.17 V vs Li^0/Li^+). **Figure S3a** shows the first 5 cycles of this cell (SIPE-FF-60G4) during the cathodic scan. There was a very clear irreversible peak at 0.79 V vs Li^0/Li^+ during the first cycle and 1.42 V vs Li^0/Li^+ on the second one. These peaks disappeared in the following cycles. We believe this might be a contribution to the formation of the solid electrolyte interphase (SEI) although a deeper analysis (e.g. such as *in situ* micro-FTIR spectroscopy[33] or X-ray photoelectron spectroscopy (XPS)[34]), which is outside the

scope of this work, would be needed to study this phenomenon further. During the anodic scans ($\text{Li}^0/\text{Electrolyte/Stainless-steel}$ cells), no oxidation currents were observed up to 2.49 V vs Li^0/Li^+ for the SIPE-FG-60G4 cell and 3.91 V vs Li^0/Li^+ for the SIPE-FF-60G4 cell (**Figure 5**). Although these stability windows for upper potentials were not as high as expected, the stability over cycling was promising for the SIPE-FF-60G4 cell (**Figure S3b**) as the oxidation current occurred at the same potential during the first four cycles analyzed.

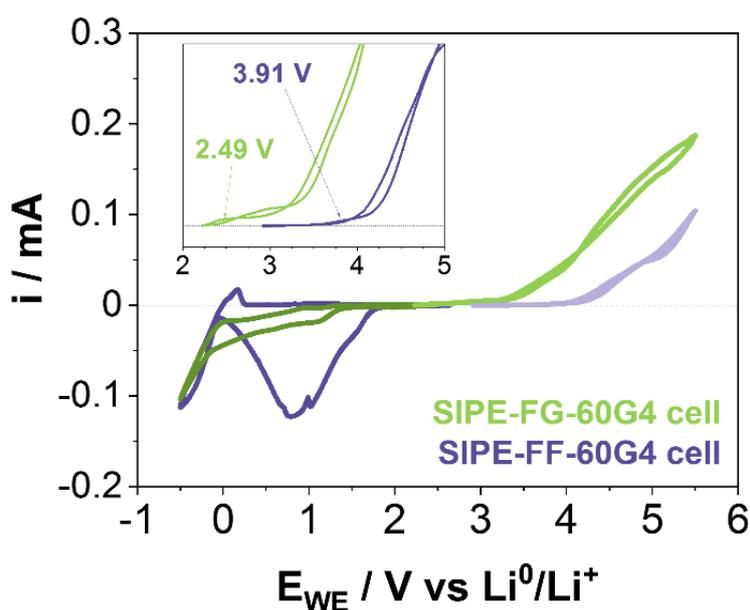


Figure 5. Voltammograms of SIPE-FG-60G4 and SIPE-FF-60G4 electrolytes at 60 °C and a scan rate of $0.2 \text{ mV}\cdot\text{s}^{-1}$. Scans were undertaken in Li^0/Cu^0 (from OCV to -0.5 V) and $\text{Li}^0/\text{Stainless steel}$ (from OCV to 5.5 V) cells.

Lastly, lithium symmetrical cells were assembled to evaluate the polarization potentials at consecutive current rates of ± 0.01 , ± 0.1 , ± 0.2 , ± 0.5 and $\pm 0.8 \text{ mA}\cdot\text{cm}^{-2}$ at 60 °C of the most promising SIGPE membranes: SIPE-FF-60G4 and SIPE-FG-60G4, as well as SIPE-GG-60G4 for comparison (**Figure 6a**). For each current density, the cells were cycled three times (2 hours/cycle). According to previous results in this work, SIPE-FF-60G4 and SIPE-FG-60G4 presented better performance. The critical current

density (CCD) was $\pm 0.2 \text{ mA}\cdot\text{cm}^{-2}$ for both cells, achieving overpotentials of $<0.34 \text{ V}$ and $<1.23 \text{ V}$ for SIPE-FF-60G4 and SIPE-FG-60G4, respectively. The same test was undertaken for the rest of the SIPE-FG-xx family of electrolytes. As shown in **Figure S4**, CCD was quickly achieved for the solvent-free SIPE-FG cell ($\pm 0.01 \text{ mA}\cdot\text{cm}^{-2}$, 2.36 V). SIPE-FG-30G4 CCD was $\pm 0.2 \text{ mA}\cdot\text{cm}^{-2}$ (1.87 V), concluding that the presence of G4 plasticizer helped to lower the overpotentials when samples are polarized, as seen in literature[35,36].

Furthermore, long-term cycling stability of the most promising lithium symmetrical cells (SIPE-FF-60G4 and SIPE-FG-60G4) were investigated at their CCD ($\pm 0.2 \text{ mA}\cdot\text{cm}^{-2}$) during 175 hours after a 3 h conditioning at OCV. **Figure 6b** shows that SIPE-FF-60G4 was able to retain overpotentials $<1.20 \text{ V}$ for around 50 h, following a slow and continued overpotential increase until cell death after 135 hours. On the other hand, the SIPE-FG-60G4 cell kept the polarization potentials $<0.85 \text{ V}$ during the whole testing.

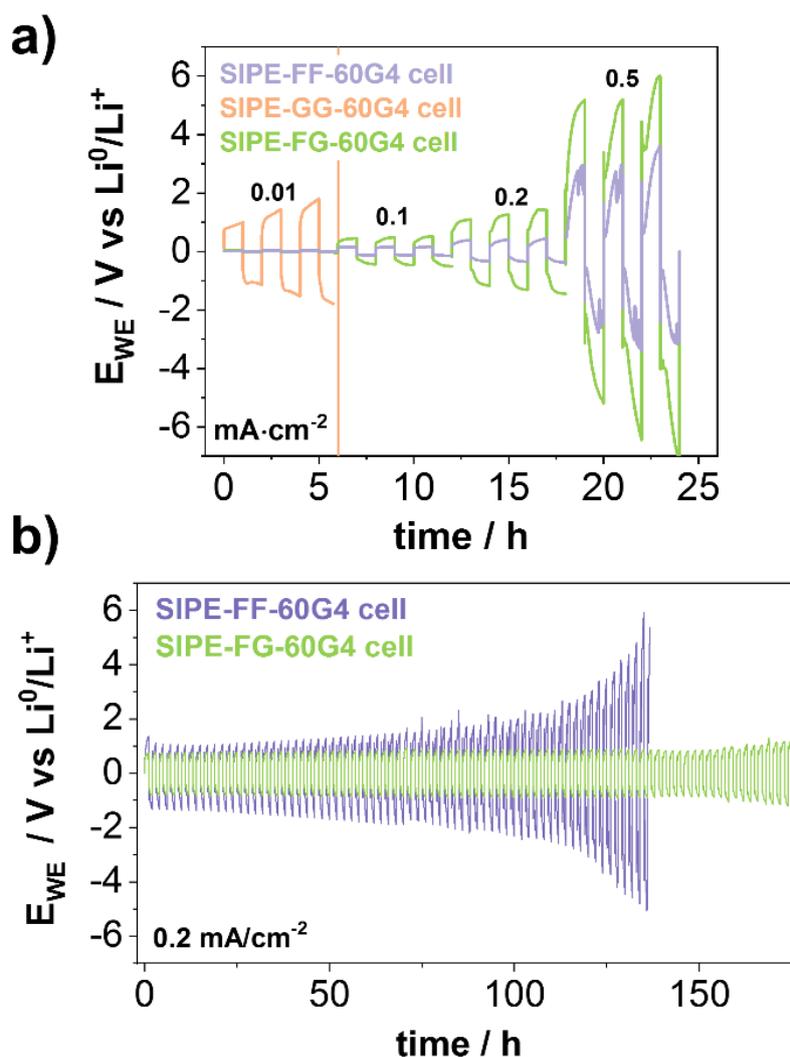


Figure 6. a) Lithium stripping/plating curves at increasing current densities from 0.01 to 0.5 $\text{mA}\cdot\text{cm}^{-2}$ in symmetrical lithium cells of SIPE-FF-60G4 cell, SIPE-FG-60G4 cell and SIPE-GG-60G4 cell; and b) Long cycling of Li/Li cells at 0.2 $\text{mA}\cdot\text{cm}^{-2}$.

3. Conclusion

A new family of lithium single-ion polymer electrolytes (SIGPEs) based on tailored designed borate-based lithium conducting monomers were designed by UV-photopolymerization. Three functional lithium borate monomers, based on fluorinated (SIM-FF), ethoxy (SIM-GG), or a combination of both functionalities (SIM-FG), have been photopolymerized in the presence of G4 plasticizer. As a result, self-standing and visually transparent gel polymer electrolytes were obtained in a clean and fast way. All

membranes presented good thermal and mechanical stability up to 100 °C and then the evaporation of the G4 glyme was observed. The role of the different substituents in the boron atom on electrochemical properties was analyzed based on Li^+ transport characteristics in solvent-free electrolytes. SIPEs with asymmetric borate-fluorinated-ethoxy groups (SIPE-FG-xx) combined both Li^+ ion delocalization (fluorinated moiety) and ion mobility-pathways capabilities (ethoxy moiety), which translated on the highest conductivity value of the solvent-free SIPE electrolytes ($6.47 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ at 25 °C for SIPE-FG) and t_{Li^+} (0.85). The addition of plasticizer into the membranes created new pathways for the Li^+ transport, which turned into a significant decrease of the activation energy of the ionic conduction process and a massive improvement of the SIPE-FF-30G4 and SIPE-FF-60G4 ionic conductivities at RT ($1.71 \cdot 10^{-4}$ and $9.95 \cdot 10^{-5} \text{ S} \cdot \text{cm}^{-1}$, respectively), the highest values achieved in this work. Furthermore, the optimized single-ion gel polymer electrolytes presented a reversible plating/stripping of lithium and the lowest overpotentials on lithium symmetrical cells with a critical current density of $\pm 0.2 \text{ mA} \cdot \text{cm}^{-2}$. Overall, the boron-based SIGPEs synthesized in this work show mechanical and electrochemical characteristics suitable for use in lithium metal batteries.

4. Experimental Section/Methods

SIGPE electrolytes: SIGPE liquid blend mixtures were prepared by mixing the selected SIM-xx monomer with PEGDM and G4 at the ratios described in **Table S1**. The mixture was stirred for at least 2 hours at RT. DAROCUR photoinitiator was then added at 3% w/w of the monomers and mixtures were drop-casted on a silicon mold (Φ 11.28 mm) and irradiated with a UV-LED lamp for 5 minutes (300 – 400 nm, 385 nm peak).

Lightningcure® V3, Hamamatsu). All materials were dried before use by 4Å molecular sieves (Aldrich) and cell assemblies were carried out inside an argon-filled glovebox ($H_2O < 0.01$ ppm, $O_2 < 0.01$ ppm).

Polymeric characterization: Chemical characterization via Fourier transform infrared spectroscopy (FTIR ATR, Bruker Alpha I Spectrometer) at RT and air atmosphere. Thermal degradation via TGA Q 500 (TA instruments). Samples were heated from RT to 600 °C at 10 °C/min under N_2 . Mechanical properties via Dynamic Mechanical Analyzer, Triton 2000 DMA (Triton Technology) at compression from -100 to 0 °C at 4 °C/min and 1.0 Hz.

Impedance spectroscopy: Ionic conductivities were measured by electrochemical impedance spectroscopy (EIS) using an Autolab 302N Potentiostat Galvanostat coupled to a Microcell HC temperature controller. SIPE membranes (Φ 11 mm) were sandwiched between two stainless steel electrodes and sealed under argon atmosphere. Temperature screening from 85 °C to 25 °C (30 minutes dwell), frequency range from 1 MHz to 0.1 Hz, and 10 mV amplitude. Ionic conductivities can be calculated following **Equation 3**[37]:

$$\sigma = \frac{1}{R_b} \cdot \frac{d}{S} \quad (3)$$

where σ is the ionic conductivity ($S \cdot cm^{-1}$), d is the thickness (cm) of the SIPE, S is the area of the stainless-steel electrodes (cm^2), and R_b (\square) is the bulk resistance of the SIPE.

Lithium symmetrical cells: SIGPE electrolytes (Φ 11.28 mm) were sandwiched between two circular lithium metal circular thin sheets (Φ 8 mm, Rockwood Lithium

(USA)), and placed between two stainless steel electrodes hold together by a PEEK Swagelok cell.

SUPPORTING INFORMATION

Supporting Information is available.

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