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Solid polymer electrolytes from a fluorinated copolymer bearing cyclic carbonate pendant groups

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A poly(vinylidene fluoride-*co*-(2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoromethyl)acrylate) random copolymer, poly(VDF-*co*-MAF-cyCB), with a MAF-cyCB weight fraction of 59%, was synthesized by free radical copolymerization of VDF and MAF-cyCB, a methacrylate bearing cyclocarbonate side-chains. This copolymer showed a nano-structured morphology where crystalline PVDF-rich domains coexisted with amorphous poly(VDF-*co*-MAF-CyCB) segments. Solid polymer electrolytes were further obtained by loading the poly(VDF-*co*-MAF-cyCB) copolymer with various LiClO₄ amounts. The added lithium salt was dissolved in the poly(VDF-*co*-MAF-CyCB) amorphous phase and allowed the formation of an ionic conducting phase exhibiting ionic conductivity values as high as $2x10^{-4}$ S/cm at room temperature for an optimum cyCB/Li⁺ molar ratio of 5. The addition of LiClO₄ up to the optimum cyCB/Li⁺ molar ratio of 5 also increased the phase separation between the crystalline and amorphous phases, the mechanical properties of the material (up to 10^{-7} at 10^{2} rad/s) and the ionic conductivity (> 10^{-3} S/cm at 80 °C). Furthermore, an electrochemical stability window from 1.4 to 4.9 V vs Li/Li⁺ and relative high values for the measured lithium ions transference numbers (0.68 at 40 °C) were observed, making the investigated system a promising candidate for the next generation of solid polymer electrolytes.

Introduction

The development of safe, cheap and efficient batteries has become a necessity in our modern society. This implies an increase in energy density for batteries and the related development of new chemistries for both the active electrode materials and the electrolyte.¹⁻³ As far as the electrolyte is concerned, there is a need for replacing the current technologies based on liquid or gel electrolytes due to safety issues. Indeed, the formation of irregular metallic lithium electrodeposits during the recharge, which results in dendrites and explosion hazards, cannot be avoided whenever organic solvents are used.⁴⁻⁶

Nowadays, solid-state electrolytes are considered as an appropriate alternative to mitigate safety issues. The advantages of solid-state electrolytes compared to organic liquid-based electrolytes are (i) safety, (ii) the possibility of increasing energy density (if the used solid electrolyte can enable the use of a lithium metal anode), and (iii) potentially improving cycling, lifetime or rate performance. However, the problems faced by all-solid-state cells are considerable as detailed in recent reviews.⁷⁻⁹ One of the greatest challenges is the development of a solid-state electrolyte combining high ionic conductivity and suitable mechanical properties.

Two major classes of solid-state electrolytes are the focus of research, namely ceramic and solid polymer electrolytes (SPEs).¹⁰⁻¹¹ On the one hand, ceramic electrolytes, and more particularly sulfide-based electrolytes, have the advantages to exhibit ionic conductivities at room temperature in the range (and sometimes higher) of liquid electrolytes, but are characterized by typical mechanical properties which prevent them from keeping good contact with the electrodes during cycling. On the other hand, SPEs display the typical mechanical properties of polymers that allow good contacts with the electrodes but are still characterized by low ionic conductivities at room temperature (ca. 10⁻⁴ S/cm for the best systems). Moreover, SPEs are generally based on poly(ethylene oxide) (PEO) mixed with a lithium salt. The use of those systems is hampered by three issues: (i) the partial crystallization of PEO leading to slow diffusion of lithium ions in the crystalline areas, (ii) the unsatisfactory mechanical properties of PEO/Li⁺ SPEs require the addition of fillers or other polymer blocks as reinforcing agents,¹² and (iii) the motion of lithium ions carries only a fraction of the overall ionic current (low transference number).13 Finally, recent studies have reported a combination of both types of solid electrolytes and have designed hybrid solid electrolytes in which ceramic electrolytes are embedded in SPEs.¹⁴ Those efforts rely on the formation of a continuous network of

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ceramic (nano)particles in the SPE matrix. Although this last approach seems to be promising, a critical issue arises from the control of the SPE/(nano)particles interface in those hybrid systems, stemming for the development of novel types of SPEs.

The present work focusses on a new class of SPE based on poly(vinylidene fluoride-co-(2-oxo-1,3-dioxolan-4-yl)methyl а 2-(trifluoromethyl)acrylate) copolymer, abbreviated as poly(VDF-co-MAF-cyCB) (see chemical structure in Fig. 1). PVDF is a polymer widely used in Li-battery as binder or as separator due to its chemical inertness and its good mechanical properties. It has been often copolymerized with hexafluoropropylene (HFP) in order to control its crystallinity¹⁵ and to be used in gel polymer electrolytes.¹⁶ Moreover, fluorinated polymers are particularly interesting because of their good dielectric constant promoting ion-dissociation, as demonstrated by studies on SPEs prepared from poly(VDF-co-HFP) LiCF₃SO₃¹⁷ or Li *bis*(trifluoromethanesulfonyl)imide.¹⁸ Nevertheless, due to the lack of coordinating atoms for Li ions, Li salts crystallization is often observed in those SPEs, that can be suppressed by using a fluorophilic anion in the used Li salt.¹⁹ As far as MAF-cyCB units are concerned, those are analogues of the very well-known cyclic carbonates-based liquid electrolytes. The incorporation of cyclic carbonates into polymer architecture seems to be a promising approach towards high performance SPEs, as recently reviewed by Brandell and co-authors.²⁰ Here, we investigate the mechanical and electrochemical properties of poly(VDF-co-MAF-cyCB) copolymer.

Experimental

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Synthetic procedures

Materials. All reagents were used as received unless stated otherwise. 2-Trifluoromethyl acrylic acid (MAF) and vinylidene fluoride (VDF) were kindly offered by Tosoh F-Tech Company and Arkema, respectively. *Tert*-amyl peroxy-2-ethylhexanoate (TAPE, purity 95%) was supplied from AkzoNobel. Glycerol 1,2carbonate (purity > 90%) was acquired from TCI Europe N.V. ReagentPlus grade dimethyl carbonate (DMC, purity > 99%), dichloromethane (DCM), pyridine, thionyl chloride, laboratory reagent grade methanol and lithium perchlorate (LiClO₄, battery grade, 99.99%) were purchased from Sigma-Aldrich. Deuterated chloroform (CDCl₃) and dimethyl sulfoxide (DMSOd₆), used for NMR spectroscopy, were purchased from Eurisotop (purity > 99.8%).

(2-oxo-1,3-dioxolan-4-yl)methyl Synthesis of 2-(trifluoromethyl)acrylate (MAF-cyCB). 2-Trifluoromethyl converted acrvlic acid (MAF) was into 2-(trifluoromethyl)acryloyl chloride (MAF-COCl) using thionyl chloride following a procedure reported elsewhere.²¹ Glycerol 1,2-carbonate (25.27 g, 214 mmol) and pyridine (19.0 mL, 235 mmol) were added to dichloromethane (40.0 mL) in a twonecked round bottomed flask equipped with a dropping funnel. The mixture was then cooled to -10 °C in an ice-salt bath while being purged under nitrogen atmosphere for at least 20 min. MAF-COCI (33.96 g, 214 mmol) was transferred to the dropping funnel under N₂ atmosphere and added slowly into the reaction mixture (over the course of 30 min) while maintaining the flask temperature at -10 °C for another 2 h and finally at room temperature for additional 16 h. After that, the reaction was quenched by adding 8 mL of methanol. The reaction mixture was then washed three times with 40 mL of diluted HCl, once with saturated NaHCO₃ solution (until neutral pH) and finally with water. The organic layers were collected and dried over MgSO₄, filtered and the solvent was removed under vacuum. MAF-cyCB, obtained in 55% overall yield from MAF as a brownish viscous liquid, was characterized by ¹H and ¹⁹F NMR spectroscopy.

¹H NMR (400 MHz, CDCl₃, δ ppm, Fig. S1): 3.74 and 4.54 (2m, -O-CH₂-CH(O)-CH₂-O-); 4.29 (m, 2H, 2H. -O-C<u>H</u>2-CH(O)-CH2-O-); 4.96 (m, 1H. -O-CH₂-C<u>H(O)</u>-CH₂-O-); 6.47 and 6.72 (2 s, 2H, $H_2C=C(CF_3)(CO_2CH_2-).$

 ^{19}F NMR (376 MHz, CDCl₃, δ ppm): peak centred at -65.82 (- CF₃). $^{22-23}$

Radical copolymerization of VDF with MAF-cyCB.²¹The copolymerization of VDF with MAF-cyCB was performed in a 100 mL Hastelloy autoclave Parr system (HC 276) equipped with a Bourdon pressure gauge, a mechanical Hastelloy anchor, a rupture disk (3000 PSI), inlet and outlet valves and a Parr electronic controller (for stirring speed and heating control). A solution of TAPE (0.72 g, 3.12 mmol) and MAF-cyCB (5.00 g, 20.83 mmol) prepared in DMC (70 mL) was degassed by N₂ bubbling for 30 min. Before starting the reaction, the autoclave was pressurized with 30 bars of nitrogen to check for any leaks. It was then put under vacuum $(40 \times 10^{-3} \text{ bar})$ for 30 min to remove any residual traces of oxygen. The solution was transferred into the autoclave under vacuum through a funnel tightly connected to the introduction valve of the autoclave. The reactor was then cooled in a liquid nitrogen bath, and VDF gas (12 g, 187.5 mmol) was transferred into it under weight control. After this, the vessel was stirred mechanically and gradually heated up to 74 °C, the evolutions of pressure (P_{max} = 37 bar) and temperature being recorded. The reaction was stopped after 16 h (the pressure dropped to 22 bar) by placing the autoclave in an ice bath. The unreacted gaseous monomer was purged off. Then, the autoclave was opened, the solvent and unreacted liquid monomer (if there was any) were completely removed under vacuum. The crude product was then dissolved in acetone and precipitated from cold pentane, centrifuged, and then dried under vacuum (20 × 10^{-3} bar, 50 °C) for 16 h. The yield of the polymerization was determined by gravimetry (mass of the copolymer obtained/mass of monomers introduced in the reactor) (yield = 60%). The poly(VDF-co-MAF-cyCB) copolymer, as a brownish soft material, was characterized by ¹H and ¹⁹F NMR spectroscopy.

¹H NMR (400 MHz, DMSO-*d*₆, δ ppm, Fig. 2): 2.15 to 2.40 (m, $-CF_2CH_2-CH_2CF_2-$ reverse VDF-VDF tail-to-tail (T-T) dyad addition); 2.70 to 3.20 (m, $-CH_2CF_2-CH_2CF_2-$, normal VDF-VDF head-to-tail (H-T) dyad addition), 2.80 (- $CH_2C(CF_3)(CO_2CH_2)$ of

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MAF-cyCB); 3.73 and 4.60 (2m, 2H, $-O-CH_2-CH(O)-C\underline{H}_2-O-$); 4.30 (m, 2H, $-O-O-C\underline{H}_2-CH(O)-CH_2-O-$); 5.07 (m, 1H, $-O-CH_2-C\underline{H}(O)-CH_2-O-$); 6.05 to 6.45 (small tt, ²J_{HF} = 55 Hz , ³J_{HH} = 4.6 Hz), $-CH_2CF_2-\underline{H}$ end-group originated from the transfer (to solvent or polymer) or from backbiting reaction.^{24,25}

¹⁹F NMR (376 MHz, DMSO- d_6 , δ ppm, Fig. 3): -66 (-C<u>F</u>₃ of MAF-cyCB in the copolymer), -91.5 to -93 (-CH₂CF₂-CH₂CF₂-normal VDF-VDF H-T dyad addition); -93.5 to -95.5 (-CF₂ of VDF in the alternating VDF-MAF-cyCB dyad); -113.2 (-CH₂CF₂-CF₂CH₂-CH₂, reverse VDF-VDF H-H dyad addition); -114.8 (dtt, ${}^{2}J_{HF}$ = 55 Hz, ${}^{3}J_{HF}$ = 16 Hz and ${}^{4}J_{FF}$ = 6 Hz, chain-end transfer); CF_2 - CH_2CF_2 -H, from -116.5(-CH₂CF₂-CF₂CH₂-CH₂, reverse VDF-VDF H-H dyad addition).

Characterization methods

Nuclear magnetic resonance (NMR). The compositions and microstructures of the copolymer were determined by ¹H and ¹⁹F NMR spectroscopy, recorded on a Bruker AC 400 Spectrometer (400 MHz for ¹H and 376 MHz for ¹⁹F) using DMSO-d₆ or CDCl₃ as solvents. Coupling constants and chemical shifts are given in Hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording ¹H [or ¹⁹F] NMR spectra were as follows: flip angle 90 ° [or 30 °], acquisition time 4.5 s [or 0.7 s], pulse delay 2 s [or 5 s], number of scans 32 [or 64], and a pulse width of 5 µs for ¹⁹F NMR.

Size exclusion chromatography (SEC). Molecular weight (M_n) and dispersity (Đ) were assessed from size exclusion chromatography (SEC) with triple-detection GPC from Agilent Technologies using a PL0390-0605390 LC light scattering detector with two diffusion angles (15° and 90°), a PL0390-06034 capillary viscometer, and a 390-LC PL0390-0601 refractive index detector and two PL1113-6300 ResiPore 300 × 7.5 mm columns. DMF (containing 0.1 wt % of LiCl) was used as the eluent at a flow rate of 0.8 mL/min and toluene as the flow-marker. The entire SEC-HPLC system was thermostated at 35 °C. Poly(methyl methacrylate) standards were used for calibrating the SEC instrument and the results were processed using the corresponding Agilent software.

Electrolyte film preparation. The thick electrolyte films were prepared as follows: The poly(VDF-co-MAF-cyCB) was dissolved in acetone (30 wt%) with different molar ratios of LiClO₄. Acetone was slowly evaporated at 40 °C. The samples were casted on stainless steel electrodes and dried again overnight in vacuo at 40 °C. The thickness was kept constant with a 270 μ m thick PTFE spacer between two stainless steel electrodes into the Swagelok cell.

Differential scanning calorimetry (DSC). DSC measurements were carried out using a Mettler Toledo 822e calorimeter. The samples were analyzed under nitrogen atmosphere in a 40 μ L Al pan with an empty Al pan as reference cell. In order to erase their thermal history, the samples were initially heated from 25 °C to 200 °C and cooled down from 200 °C to -120 °C at a

heating rate of 10 °C/min. The temperature was maintained for 2 min before changing cycle. The samples were then heated from -120 °C to 200 °C at the same heating rate to determine the glass transition temperature (T_g), the melting temperature (T_m) and the melting enthalpy (ΔH_m) using the Stare software.

Atomic force microscopy (AFM). AFM was performed on a multimode scanning probe microscope (Bruker Multimode Nanoscope VIII). AFM imaging was operated in tapping mode using NCL cantilevers (Si, 48 N/m, 276 kHz, Nanosensors) at a scan rate of 1 Hz. The images were processed by Bruker Nanoscope Analysis software. Silicon wafers were washed with acetone and milli-Q water before treated with piranha solution, rinsed in milli-Q water and dried by spin-coating at 2000 rpm. A copolymer solution at 1 wt % in NMP was spin-coated onto silicon substrates of 1 cm² at rotation rates of 500 rpm, 1000 rpm then 2000 rpm, respectively.

Rheology. Rheological experiments were performed on a MCR 301 (Anton Paar, Germany) rheometer equipped with a convection oven operating under air. Measurements were conducted using 4 mm stainless steel parallel plate geometry. Oscillatory shear measurements were carried out in linear regime with a strain amplitude γ of 0.03 %. The gap was adjusted between 400 and 550 μ m and the temperature was fixed at 25 °C.

Electrochemical impedance spectroscopy (EIS). EIS measurements were performed using a Parstat 4000 apparatus over a frequency range of 1 MHz to 10 mHz and with an amplitude a.c. excitation voltage of 5 mV. The temperature dependence measurements were carried out from 25 °C to 80 °C by gradually increasing the temperature by steps of 10 °C with an equilibration time of 1 h between each step.

Electrochemical stability. The electrochemical stability window was determined on an Arbin Instrument battery tester BT-2043 by the method of the linear voltammetry. The polymer electrolyte ($\approx 270 \ \mu$ m) was sandwiched between a stainless steel working electrode and a lithium foil as counter and reference electrode. The Swagelok cell was assembled in an argon glove box and cycled from 0.5 V to 6 V vs. Li/Li⁺ at scan rate of 0.5 mV/s.

Transference number. Those measurements were carried out using Li|solid-polymer-electrolyte|Li symmetric cells, thermally equilibrated in oven at the desired temperature for 24h before measurement. The d.c. polarization measurements were performed on an Arbin Instrument battery tester BT-2043 with a d.c. bias of 10 mV. The EIS measurements were performed on Parstat 4000 with an a.c. bias of 10 mV.

Results and discussion

Synthesis of the solid polymer electrolytes

Recently, we have reported the synthesis of poly(vinylidene fluoride-co-trioxa-3,6,9-decyl-2-

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trifluoromethacrylate) copolymers, poly(VDF-co-MAFTEG),²³ with the aim to functionalize PVDF membranes with polar TEG units to be used as gel polymer electrolytes with an ionic liquid electrolyte. The obtained results demonstrated the success of this approach with the formation of gel electrolytes exhibiting ionic conductivities above 0.2 mS/cm at room temperature and close to the values of the pure ionic liquid (1-2 mS/cm). Nevertheless, silica nanoparticles were added to the gel electrolyte in order to guarantee good mechanical properties to the accordingly obtained gels. Moreover, the poly(VDF-co-MAFTEG) copolymer could not be used as SPE due to the low amount of MAFTEG units in the copolymer and the associated low content of coordinating oxygens for lithium ions (only 3 ethylene oxide units in each MAFTEG). The present research aims at replacing the MAFTEG units by MAF-cyCB ones that could also result in a better mobility for lithium ions and accordingly in enhanced ionic conductivity. Indeed, carbonate functional groups present high dipolar moment and dielectric constant enabling them to dissociate many types of salts.²⁶ They are found especially in five-membered cyclic form into commercial liquid electrolytes composition as ethylene carbonate and propylene carbonate. Carbonates were thus introduced into polymeric architectures in order to provide SPEs as demonstrated by the early work of Tarascon and coauthors.²⁷ A non-cyclic poly(propylene carbonate) providing an ionic conductivity of 10⁻⁴ S/cm at ambient temperature was described by Zhang et al.²⁸ Tominaga's team reported²⁹⁻³¹ a non-cyclic poly(ethylene carbonate) and further developed a hybrid membrane based on porous polyimide matrix supporting poly(ethylene carbonate)-based SPE able to reach an ionic conductivity of 10^{-5} S/cm at 30 °C. Recently, Chai et al.³² polymerized vinylene carbonate and obtained a polymer incorporating the cyclic carbonate function in the polymer backbone reaching an ionic conductivity of 5×10^{-4} S/cm at ambient temperature, good mechanical properties and an electrochemical stability window up to 4.8 V vs Li⁺/Li. Cyclic carbonates were also introduced as side-chains in polymer architectures as demonstrated by Lex-Balducci and coworkers^{33,34} who copolymerized a methacrylate bearing cyclic carbonate with oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and further studied gel polymer electrolyte obtained by swelling the copolymer in a carbonatebased electrolyte.

Here, we report on a poly(VDF-*co*-MAF-cyCB) copolymer synthesized via a conventional radical copolymerization of VDF with MAF-cyCB, a fluorinated methacrylate bearing a cyclic carbonate group as side-chain. The synthesis of the MAF-cyCB monomer was achieved by the esterification reaction of 2trifluoromethyl acrylic acid (MAF) with glycerol carbonate (Fig. 1). First, MAF was modified into 2-(trifluoromethyl)acryloyl chloride (MAF-COCI) using thionyl chloride (step A).³⁵ Then, the esterification reaction of MAF-COCI with glycerol carbonate led to MAF-cyCB, in 85% yield (step B, see NMR spectrum in Fig. S1 in ESI‡.). Similar to MAF and other MAF-esters,³⁵⁻³⁷ the homopolymerization MAF-cyCB failed under radical initiation. Page 4 of 10



Fig. 1. (Top) Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoromethyl)acrylate (MAF-cyCB). (Bottom) Radical copolymerization of VDF with MAF-cyCB initiated by *tert*amyl peroxy-2-ethylhexanoate (TAPE).

The copolymerization of VDF with MAF-cyCB was initiated radically by tert-amyl peroxy-2-ethylhexanoate (TAPE) at 74 °C in dimethyl carbonate (DMC) in a high pressure autoclave since VDF is a gas. In the course of the polymerization, an initial increase in pressure up to 37 bars along the increase in temperature was noted, followed by a decrease in pressure when the temperature reached 70 °C. This is explained by the dissociation of the initiator at this temperature that released radicals enabling the copolymerization to start. Then, the consumption of the monomers led to the decrease of the pressure down to 24 bars. After 16 hours, the pressure was 10 bars justifying the reactivity of VDF and, after opening the autoclave and purification, the copolymerization reached 60% obtained poly(VDF-co-MAF-cyCB) vield. The random copolymer presents an average content of 28 mol% (corresponding to 59 wt%) of MAF-cyCB units as determined by NMR (¹H NMR spectrum in Fig. S2 and ¹⁹F NMR in Fig. S3 in ESI[‡]), a molar mass (M_n) of 6,500 g/mol and a dispersity (D) of 1.67 as determined by SEC. SPEs were finally prepared by mixing the poly(VDF-co-MAF-cyCB) copolymer with various amounts of LiClO₄.

The distribution of comonomers was recently studied in similar terpolymers containing VDF, trifluoroethylene (TrFE) and MAF monomers.³⁸ Those previous results showed that VDF copolymerizes very quickly with MAF until its complete conversion, followed by the copolymerization of unreacted VDF with TrFE. Poly(VDF-*co*-MAF) segments are thus first obtained during the polymerization. The remaining VDF units are then polymerized leading to a (quasi) pure poly(VDF) segment at the end of the polymer chain. One can assume that the same situation prevails for the copolymer investigated here. The actual microstructure of the copolymer could be thus described as a poly(VDF-*co*-MAF-cyCB) block linked to a poly(VDF) block, although this copolymer will be named poly(VDF-*co*-MAF-cyCB) in the following.

Morphology of the solid polymer electrolytes

Before measuring the electrochemical characteristics of the studied SPEs, it is worth determining their morphology. The results obtained in this section could help to understand the ionic conductivities results studied below.

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First, structural information about the investigated SPEs can be obtained by differential scanning calorimetry (DSC) experiments. The DSC thermograms of the SPEs (Fig. S4 in ESI[‡]) reveal two typical transitions, i.e. a glass transition (T_g) and a melting peak (T_m) . The melting transition has been attributed to PVDF segments since the corresponding PVDF polymer is semi-crystalline. For the pure poly(VDF-co-MAFcyCB) copolymer without added salt, a T_m of 147 °C has been noted and a degree of crystallinity of 9% has been calculated (see ESI[‡]). These values have to be compared to pure PVDF for which a $T_{\rm m}$ of 177 °C and a degree of crystallinity of 50% are commonly observed.³⁹ The T_g of pure PVDF is reported³⁹ to be around -40 °C while the T_{g} for the poly(MAF-cyCB) is not available since this homopolymer cannot be synthesized by radical polymerization. The T_{g} measured for the poly(VDF-co-MAF-cyCB) copolymer investigated here is 11 °C. This value is substantially higher than for pure PVDF.

These observations can be understood on the basis of the microstructure of the copolymer discussed in the section above. Indeed, the copolymer chains are consisting of a poly(VDF-co-MAF-cyCB) segment followed by a pure PVDF sequence. Actually, the presence of both the trifluoromethyl and cyclocarbonate side groups imparts some bulkiness of the MAF-cyCB units. Therefore, we believe that crystallization is hampered in the poly(VDF-co-MAF-cyCB) segment. Moreover, MAF-cyCB units are believed to increase substantially the value of the Tg. In contrast, crystallization can be observed in the pure PVDF segments. On the basis of these considerations, we propose a microphase separated morphology in which PVDF crystalline domains are embedded in an amorphous matrix of poly(VDF-co-MAF-cyCB) segments (see Fig. 2). This picture is confirmed whenever the effect of the addition of salt is investigated. Indeed, addition of $LiClO_4$ does not affect T_m nor the degree of crystallinity in the SPE while it substantially increases the T_g . As a typical example, the T_g rises up to 31 °C for copolymer electrolyte with $cyCB/Li^+ = 5$ (Fig. S4 in ESI[‡]). This result points out towards a morphology where the mechanical properties are controlled by crystalline PVDF nanodomains and where ionic conductivity would be ensured by the amorphous poly(VDF-co-MAF-cyCB) matrix with dissolved LiClO₄.



This picture is further confirmed by AFM measurements on the poly(VDF-*co*-MAF-cyCB) SPEs. Indeed, the AFM images (Fig. 3) reveal a nano-structured morphology for the SPEs. The nanosized features observed in Fig. 3 (left) for the pure poly(VDF-co-MAF-cyCB) copolymer are attributed to the PVDF crystalline-rich phase and to the amorphous poly(VDF-co-MAFcyCB) domains. Addition of salt tends to increase the size of the nano-structured features (Fig. 3 right). The added salt is indeed expected to be incorporated in the amorphous poly(VDF-co-MAF-cyCB) zones to form an ionically conducting phase. Indeed, the added lithium ions can act as transient cross-linkers between poly(VDF-co-MAF-cyCB) domains, reducing segmental motion of amorphous chains (as evidenced by an increase in T_{g}) and enhancing microphaseseparation. The SEM images (Fig. S5 in ESI‡) confirm that a network has been formed in adding the LiClO₄ salt. AFM phase contrast images (data not shown) were blurry and did not allow obtaining further identification of a hard crystalline phase and a soft amorphous phase. This is the reason why a detailed analysis of the mechanical properties of the SPEs is detailed in the next section.

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Fig. 3. AFM images (height contrast) of poly(VDF-co-MAF-cyCB) copolymer without $LiClO_4$ (left) and with added $LiClO_4$ with cyCB/Li^{*} = 5 (right).

Mechanical properties of the solid polymer electrolytes

The mechanical properties of the SPEs were studied by oscillatory shear rheology. Initially, frequency sweep measurements were performed at 25 °C. The materials act as elastic solids in which the storage modulus G' remains always higher than the loss modulus G" for all the SPEs with or without LiClO₄ as reported in Fig. S6 (in ESI[‡]). The terminal regime is absent within the measurement range meaning that the materials do not dynamically flow. This elastic solid behavior is attributed to the phase separation within the poly(VDF-co-MAF-cyCB) copolymer as discussed in the above section. Hence, the investigated SPEs are composed of a hard phase which is originating from the crystallization of PVDF and an amorphous one from poly(VDF-co-MAF-cyCB) segments. The PVDF hard phases act as physical cross-linkers surrounded by the amorphous phase and these cross-linkers allow the formation of a network that prevents the material from flowing.

The addition of salts within the polymeric matrix tends to increase this phase separation where the lithium salts are dissolved in the amorphous phase of the polymer to reduce at maximum the surface contact with the crystalline PVDF domains. This increase in phase separation is confirmed in oscillatory shear measurements for which the elasticity of the

SPEs raises when the salt concentration increases (except when the cyCB/Li⁺ ratio is equal to one which will be explained below). For instance, for a fixed angular frequency, e.g. $\omega = 1$ rad/s, the storage modulus G' values of the reference copolymer along with SPEs are reported and compared in Fig. 4.



Fig. 4. Storage modulus G' values at angular frequency ω = 1 rad/s for different poly(VDF-co-MAF-cyCB) copolymers with and without LiClO₄ obtained through frequency sweep measurements at T = 25 °C and γ = 0.03%.

The reference sample displays a G' of 3.86 x 10^{5} Pa that is increased by 62% up to one order of magnitude depending on the amount of added lithium ions. There is no significant difference in mechanical properties between the SPEs with $cyCB/Li^+$ = 10 and $cyCB/Li^+$ = 20 (Fig. 4). But, when the concentration of salt raises up to cyCB/Li⁺ = 5, a storage modulus G' as high as 1.67 x 10⁶ Pa is observed (Fig. 4). As mentioned above, the increase in moduli upon addition of lithium salt could be attributed to an enhanced phase separation between the hard crystalline PVDF and the soft poly(VDF-co-MAF-cyCB) phases and to a reduced segmental motion of amorphous poly(VDF-co-MAF-cyCB) segments since lithium ions are expected to behave as transient cross-linkers between MAF-cyCB units. When the cyCB/Li⁺ ratio reaches 1, G' decreases to a value slightly lower than the one at cyCB/Li[†] = 5 but significantly higher than that assessed for the reference copolymer without any added salt (Fig. 4). We hypothesize that the salt concentration has reached a saturation level at $cvCB/Li^{+} = 1$ and that the excess of salt is not dissolved in poly(VDF-co-MAF-cyCB) amorphous phase and forms salt clusters compromising mechanical properties. This result also indicates that it is useless to further investigate SPEs with $cyCB/Li^{\dagger}$ ratio as low as 1.

Furthermore, the evolution of complex viscosity is also an interesting mechanical feature to investigate as shown in Fig. S7 (in ESI[‡]). Typically, all the studied systems display a shear-thinning behavior as the complex viscosities of the materials with salt decrease by three orders of magnitude when the shear rate varies from 0.003 to 3 s⁻¹. The high viscosities of these systems, e.g. 14.6 MPa.s for the reference and 82.9 MPa.s for cyCB/Li⁺ = 5 at low shear rate, clearly indicate that the materials behave as a solid in which the elasticity and the

stiffness of the sample both increase upon addition of lithium salts.

Ionic conductivity measurements on the solid polymer electrolytes

The SPEs consisting of poly(VDF-co-MAF-cyCB) copolymer loaded with various LiClO₄ amounts were studied by electrochemical impedance spectroscopy (EIS). Fig. 5 plots the ionic conductivity (σ) of the SPEs versus their lithium salt (LiClO₄) loading, at ambient temperature. The ionic conductivity increases when the amount of lithium salt incorporated into the polymer increases up to cyCB/Li⁺ equals to 5. An ionic conductivity value in the range of 2×10^{-4} S/cm is noted at room temperature for the $cyCB/Li^{+} = 5$. This value is quite interesting and renders our materials promising for possible application as SPE for Li-ion batteries. This rate is much higher than those observed at room temperature for classical PEO-based SPEs.⁴⁰ However, a drop in conductivity is noted thereafter for the highest salt concentration (cyCB/Li⁺ equals to 1), meaning that the mobility of ions is reduced for high salt loading. This result could be easily understood while remembering that ionic conductivity measurements depend on the concentration and on the mobility of the charge carriers in the matrix. Indeed, at high salt concentrations, free ions could recombine into aggregates or ions pairs, which do not contribute to the conductivity anymore.⁴¹⁻⁴³ This observation is consistent with the rheological characterization performed in the above section where a decrease in G' has been noted for a cyCB/Li⁺ ratio of 1 due to the possible formation of ionic clusters at high salt loading.



Fig. 5. Ionic conductivity vs. Lithium salt concentration (expressed as the CyCB/Li * ratio) at ambient temperature.

The ionic conductivities for the SPEs with different cyCB/Li⁺ molar ratios increase with temperature, as shown in Fig. 6. This increase in ionic conductivity with temperature is attributed to an enhanced mobility of the polymers segments and charge carriers. Competing values above 10^{-3} S/cm are reached at 80 °C for the sample with a cyCB/Li⁺ ratio of 5. According to the Volgel-Tamman-Fulcher (VTF) model, the activation energy (Ea) decreases when the salt concentration

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increases. The dispersion of a high amount of a salt with a low lattice energy in a polymer matrix containing high dielectric constant cyCB units leads to excellent ionic conductivity values.⁴⁴ Because of its interesting values, the SPE obtained from a cyCB/Li⁺ ratio of 5 was selected for further electrochemical characterizations.



Fig. 6. Temperature dependence of the ionic conductivity for the investigated SPEs using VTF model.

Electrochemical stability

The electrochemical stability window of the SPE with $cyCB/Li^{+} = 5$ was investigated by linear sweep voltammetry between 0.5 V and 6 V vs Li/Li⁺ at a scan rate of 0.5 mV/s (Fig. 7). The studied cell consisted in a sandwiched SPE film between a stainless steel working electrode and a Li-metal anode playing the role of reference electrode. The polymer appears to be electrochemically stable from 1.4 V to 4.9 V vs Li/Li⁺. This electrochemical window allows the poly(VDF-co-MAF-cyCB)/LiClO₄ SPEs to be compatible with e.g. Li-ion batteries based on lithium titanate anodes. Below 1.4 V and above 4.9 V, reactions of degradation occur. The cathodic peaks at potentials above 5 V are mainly attributed to the decomposition of the LiClO₄ and oxidative corrosion of stainless steel working electrode. For potentials below 1.4 V vs. Li/Li⁺, considerable SPE decomposition can be observed which is associated to complex surface reactions between the electrolyte components and the electrode materials (Li-metal in this case). In contact with the Li-metal electrode, the poly(VDF-co-MAF-cyCB) segments of the SPE decompose and form a solid-electrolyte interface (SEI).⁴⁵ The stability of this SEI was analyzed by galvanostatic cycling measurement on a Li/polymer-electrolyte/Li symmetrical cell at 40°C. Fig.S8 (in ESI[‡]) shows a stable voltage over a period of 107 hours, indicating an acceptable compatibility between the poly(VDFco-MAF-cyCB)/LiClO₄ SPE and the Li-metal electrode.



Fig. 7. Linear sweep voltammetry curves of polymer electrolyte with cyCB/Li * = 5. The scan rate is 0.5 mV/s.

Lithium transference number

The lithium ion transference number (t_{li}⁺) is another very important parameter for the characterization of lithium ion battery electrolytes. It represents the fraction of current carried by lithium ions and it should be close to 1. Fig. 8 shows the time-dependence of current flowing through the copolymer electrolyte with cyCB/Li $^{\!\!+}$ ratio of 5 at 40 °C. The inset in Fig. 8 shows the impedance measurements performed at the initial and steady states. The lithium ion transference number of the SPE was estimated by using Evans et al.'s equation⁴⁶ that combines the d.c. polarization and a.c. impedance techniques. The poly(VDF-co-MAF-cyCB) electrolyte displays a high t_{1i}^+ of 0.68 at 40 °C compared to the $t_{\text{Li}}^{\phantom{\text{t}}}$ values reported for PEO-based SPEs. 40,42,43 This can be explained by a weaker interaction of lithium ions with cyCB units compared to the PEO matrix which displays coordinating feature. Moreover, the high dielectric constant anticipated for the MAF-cyCB matrix allows efficient dissociation and solubilisation of the ions, further enhancing the transport of lithium ions. Finally, the nano-structured morphology of the investigated poly(VDF-co-MAF-cyCB)/LiClO₄ SPE could also promote ion diffusion in the amorphous phase, as discussed above.

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Fig. 8. Time-dependence response of dc polarization for a Li|poly(VDF-co-MAF-cyCB)/LiClO₄|Li symmetric cell configuration at an applied d.c. bias of 10 mV and at 40 °C. The inset shows the impedance spectra of the initial and steady states of the cell with a.c. bias of 10 mV (cyCB/Li⁺ = 5).

Conclusions

In this contribution, we have disclosed a novel fluorinated copolymer bearing cyclic carbonate pendant groups that fulfils the criteria to be used as solid polymer electrolyte after loading with a lithium salt. The interesting features of this system are triggered by the microphase separation between crystalline PVDF and amorphous poly(VDF-*co*-MAF-cyCB) nano-domains. Indeed, the presence of reinforcing crystalline PVDF nano-domains brings decent thermal and mechanical properties with moduli values ranging between 10^5 and 10^6 Pa. The addition of LiClO₄ further enhances the mechanical properties up 10^7 Pa at 10^2 rad/s for a poly(VDF-*co*-MAF-cyCB) copolymer with a cyCB/Li⁺ ratio of 5. These high shear rates moduli, which are typically observed for elastic solid materials, could mitigate or even prevent the formation of lithium dendrites into batteries.

The added LiClO₄ dissolved in the amorphous poly(VDF-*co*-MAF-cyCB) phase leads to excellent ionic conductivity values. Indeed, amorphous PVDF is known for its ability to dissolve lithium salts. Similarly, the MAF-cyCB counterpart is also capable to dissociate large amounts of lithium salt because of the high dielectric constant of cyclocarbonate unit. Moreover, the localization of this moiety as a pendant group to the polymer backbone imparts a good mobility to the system. These positive features are also reflected in the rather high lithium ion transference numbers (0.68 obtained at 40 °C). Finally, the studied SPE displays an electrochemical stability window ranging from 1.4 V to 4.9 V vs Li/Li⁺.

It should be however noted that the addition of LiCIO_4 above a critical threshold leads to the probable formation of ionic clusters inducing a detrimental effect on the mechanical properties as well as on the ionic conductivity features.

On the basis of these observations, we believe that $poly(VDF-co-MAF-cyCB)/LiClO_4$ SPEs are valuable and promising candidates for further use in all-solid-state batteries.

Conflicts of interest

There are no conflicts to declare.

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