

# Electrochemical properties of a poly(ethylene carbonate)-LiTFSI electrolyte containing a pyrrolidinium-based ionic liquid

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**Abstract** A novel polymer electrolyte membrane comprising poly(ethylene carbonate) (PEC), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt, and *N-n-butyl-N-methylpyrrolidinium* bis(trifluoromethanesulfonyl)imide (Pyr<sub>14</sub>TFSI) ionic liquid is prepared by a solvent-free procedure, combining annealing and hot-pressing. The electrochemical properties of the electrolyte are investigated in terms of ionic conductivity, Li transference number ( $t_{Li^+}$ ), and electrochemical stability by a combined study involving electrochemical impedance spectroscopy (EIS), chronoamperometry, and voltammetry. The thermal characteristics are assessed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results reveal an ionic conductivity of a PEC-Pyr<sub>14</sub>TFSI-LiTFSI electrolyte of the order of  $10^{-5}$  S cm<sup>-1</sup> at 80 °C and  $t_{Li^+}$  as high as 0.66 with the intrinsic amorphous nature of the PEC matrix. Furthermore, a Li polymer cell coupling LiFePO<sub>4</sub> cathode and the electrolyte is assembled and galvanostatically cycled. The result of this charge-discharge test demonstrates a 3.5-V battery which can be used at 80 °C and a current rate of C/20, delivering a reversible capacity of the order of 150 mAh g<sup>-1</sup>.

**Keywords** Solid polymer electrolyte · Poly(ethylene carbonate) · Ionic liquid · Lithium battery

## Introduction

Li rechargeable batteries are presently the power sources of choice for common consumer electronics. However, safety hazards associated with the use of flammable organic solutions as electrolytes so far have hampered their integration in emerging fields, such as electric vehicles (EVs) or renewable energy plants (REPs) [1]. Therefore, solid polymer electrolytes (SPEs) which are principally based on mixtures of flexible polymer matrices, such as poly(ethylene oxide) (PEO) and metal salts, are very promising candidates as safe alternatives because they are nonvolatile and leakage free [2]. Since the initial discovery in the 1970s [3], many attempts have been made to improve properties of the polyether-based electrolytes, especially in terms of ionic conductivity and Li transference number ( $t_{Li^+}$ ) [4–6]. Nevertheless, excessive crystallinities of the polymer matrices and strong ion-dipole interaction between the cation (Li ion) and the polar ether oxygen atom have caused relatively scarce success so far obtained.

In this work, we report a ternary solid polymer electrolyte formed by renewing its composition, i.e., passing from PEO to poly(ethylene carbonate) (PEC) in a mixture with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as a salt and *N-n-butyl-N-methylpyrrolidinium* bis(trifluoromethanesulfonyl)imide (Pyr<sub>14</sub>TFSI) ionic liquid as a plasticizer. Several polycarbonate-based electrolytes have so far been investigated [7, 8], which confirmed the amorphous natures of the polycarbonate matrices and high dissolution powers for various metal salts. Additionally, poly(alkylene carbonate)s, such as PEC, are synthesized by

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the alternating copolymerization of carbon dioxide (CO<sub>2</sub>) with epoxides [9–11], which is a quite promising way for fixations of the undesired greenhouse gas into functional plastic materials. This technique, first reported by Inoue and coworkers in the 1960s [9], is still under vigorous study to develop novel active catalysts aimed at precisely controlling configurations of the resulting copolymers, as well as at improving yields [10, 11]. Following these trends, we have first proposed to utilize the CO<sub>2</sub>/epoxide copolymers for polymer hosts of the SPEs [12, 13]. Notably, as in fact demonstrated in our previous works [14, 15], quite a large amount of Li salts can be dissolved without aggregation in the PEC matrix, resulting in highly concentrated PEC-based electrolytes with quite intriguing features, including relatively high ionic conductivity and extremely high Li transference number ( $t_{\text{Li}^+}$ ) which, in some cases, exceeds 0.7 [15].

To further improve the PEC-based electrolytes, a pyrrolidinium-based ionic liquid, i.e., Pyr<sub>14</sub>TFSI, was added as a plasticizing additive to enhance electrochemical characteristics, in particular ionic conductivity and electrode compatibility. As is well known, ionic liquids (ILs) [16] basically comprise bulky organic cations and weakly interacting anions, which assures numerous benefits regarding safety of the eventual devices, including, for instance, negligible vapor pressure and nonflammability. Incorporation of the ILs into polymer electrolytes has recently attracted much interest as one of the most promising approaches to make them feasible in view of the battery applications [17–20]. In this work, we selected Pyr<sub>14</sub>TFSI as an IL because pyrrolidinium-based ILs are expected to be quite suitable due to their reasonable ionic conductivities and extended electrochemical stability windows [21, 22].

In this short communication, we describe a solvent-free preparation of a PEC-Pyr<sub>14</sub>TFSI-LiTFSI ternary polymer electrolyte composite and evaluations of it in terms of physicochemical and electrochemical characteristics. Furthermore, we demonstrate that this electrolyte behaves as a promising material in a prototype Li/LiFePO<sub>4</sub> polymer battery, to the best of our knowledge for the first time, suggesting possibilities of the PEC-based electrolytes for the future applications in all solid-state Li polymer batteries.

## Experimental

### Electrolyte preparation

PEC (QPAC®25, Empower Materials, USA,  $M_w=238,000$ ) and LiTFSI (Solvionic, France) were dried under vacuum at 60 and 120 °C for 24 h before use, respectively. Pyr<sub>14</sub>TFSI (99.9 %, Solvionic, France) was stored as received in a dry argon-filled glove box with a moisture and oxygen level below 1 ppm and used. The P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI

electrolyte sample was prepared by setting up the molar ratio of the number of monomer unit in PEC to LiTFSI as 2:1 and Pyr<sub>14</sub>TFSI to P(EC)<sub>2</sub>LiTFSI as 1:0.2. The preparation involved first heating a LiTFSI-Pyr<sub>14</sub>TFSI mixture at 100 °C for 24 h. Next, PEC was added into the obtained dense mixture and heated at 80 °C for 24 h. Finally, the obtained gel-like mixture was sealed in a bag filled with dry argon and hot-pressed at 70 °C using 1 ton of force to promote the diffusion of the Li salt and the ionic liquid into the polymer, to form an electrolyte membrane with the thickness of 300 μm. The entire preparation procedure was performed in a dry argon-filled glove box.

### Electrochemical characterizations

Ionic conductivity of the electrolyte was determined by an electrochemical impedance spectroscopy (EIS) on a coin-type cell over a frequency range from 100 kHz to 5 Hz and by an applied voltage of 30 mV using a frequency analyzer VersaSTAT 3 F (Princeton Applied Research, USA). The cell was kept at each selected temperature value for at least 2 h to achieve thermal equilibria. Li transference number ( $t_{\text{Li}^+}$ ) was evaluated according to a Bruce-Vincent-Evans method combining EIS and chronoamperometry [23] by using a potentiostat/galvanostat VSP (Bio-Logic Instrument, France). A symmetric Li/Li cell was prepared and maintained at 80 °C for 3 days to achieve a stable electrolyte/electrode contact prior to the measurement. In the EIS measurement, the amplitude of the applied voltage and the frequency range were fixed at 30 mV and 300 kHz to 100 mHz, respectively. The  $t_{\text{Li}^+}$  of the electrolyte was calculated using the following equation:

$$t_{\text{Li}^+} = \frac{I_{\text{ss}}(\Delta V - R_0 I_0)}{I_0(\Delta V - R_{\text{ss}} I_{\text{ss}})} \quad (1)$$

where  $I_0$  is the initial current,  $I_{\text{ss}}$  is the steady-state current,  $\Delta V$  is the applied voltage (10 mV in this study), and  $R_0$  and  $R_{\text{ss}}$  are the resistances of the passivating film on the surface of the electrodes before and after DC polarization (determined by the EIS). The electrochemical stability window was investigated by cyclic voltammetry (CV) for a cathodic scan and linear sweep voltammetry (LSV) for an anodic scan by using the potentiostat/galvanostat VSP. A Li/Super-P carbon (Timcal, Switzerland) coated on Cu foil cell and a Li/Super-P carbon coated on Al foil cell were assembled for the CV and the LSV measurement, respectively. In these tests, the Super-P electrodes were used as working electrode, and the Li foils were used as both counter and reference electrodes. The measurements were performed at 80 °C with a scan rate of 0.2 mV s<sup>-1</sup>, and cycles of the CV were repeated in a voltage range of 0.01 to 2.0 V vs. Li/Li<sup>+</sup>.

## Thermal characterization

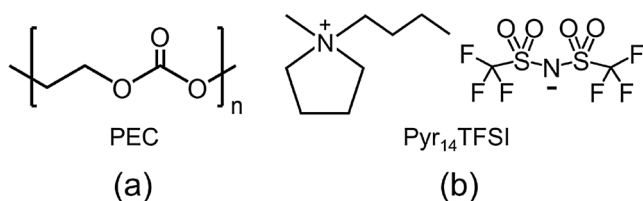
A differential scanning calorimetry (DSC) was performed on the P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI electrolyte by using a DSC/821 (Mettler Toledo, Switzerland). The sample was sealed in an aluminum pan in a dry argon-filled glove box, and a heating/cooling cycling was performed under N<sub>2</sub> gas flow over a temperature range of −120 to 130 °C at a scan rate of 5 °C min<sup>−1</sup>. A thermogravimetric analysis (TGA) was carried out on the P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI electrolyte by using a TGA/SDTA 851 (Mettler Toledo, Switzerland). The measurement was performed under N<sub>2</sub> gas flow over a temperature range of 25 to 500 °C at a scan rate of 10 °C min<sup>−1</sup>.

## Battery test

A Li/P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI/LiFePO<sub>4</sub> cell was assembled by using a cathode prepared by blending LiFePO<sub>4</sub> (Clariant, Switzerland) as active material (80 wt%) with the Super-P carbon as electron-conductive additive (10 wt%) and PVdF (Solvey, USA) as binder (10 wt%) in *N*-methyl-2-pyrrolidone (NMP) as solvent. The blended mixture was cast onto an aluminum current collector, dried in the air at 80 °C for 6 h, and finally dried under vacuum at 110 °C for 3 h. A galvanostatic charge-discharge cycling was carried out by using a series 4000 battery test system (Maccor, USA) over a voltage range of 2.8 to 4.1 V at a current rate of C/20 (1 C is 0.19 mA with respect to the theoretical specific capacity of LiFePO<sub>4</sub>, i.e., 170 mAh g<sup>−1</sup>) at 80 °C. The cell was maintained at 80 °C for 24 h for aging prior to the test.

## Results and discussion

Figure 1 shows the structure of PEC and Pyr<sub>14</sub>TFSI ionic liquid additive. The combination obtained by mixing these two compounds with the addition of LiTFSI as a Li salt yielded a freestanding and flexible electrolyte membrane. Notably, this mechanically strong membrane was obtained by an environmentally friendly procedure without using any organic solvent, but rather, the ionic liquid which served as a solvent for the electrolyte preparation was used. In addition,

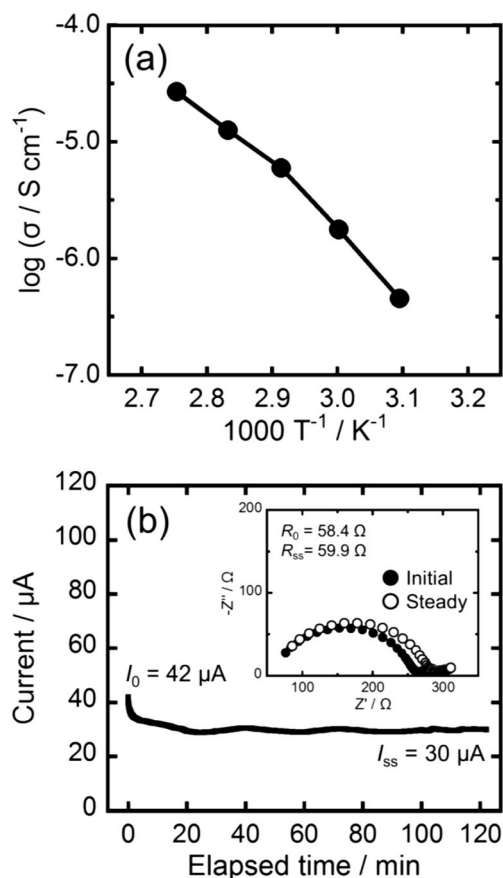


**Fig. 1** Chemical structure of **a** poly(ethylene carbonate) (PEC) and **b** Pyr<sub>14</sub>TFSI ionic liquid

we selected a Li salt concentration higher than those commonly employed in the PEO- or other polyether-based electrolytes with the aim of increasing the number of carrier ions. This strategy was based on the results of our previous studies which revealed that quite a large amount of Li salts can be in fact homogeneously dissolved in PEC with the resulting relatively fast Li-ion transport [14, 15].

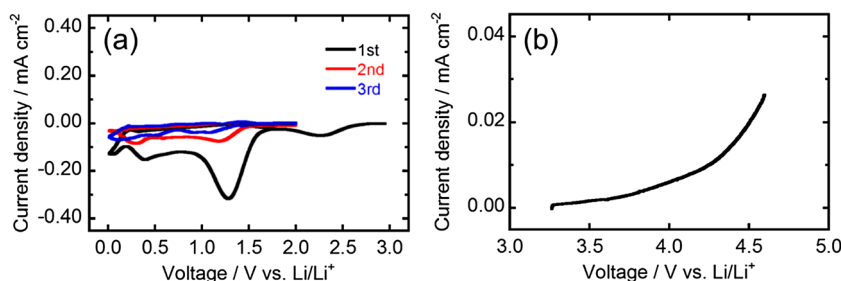
Figure 2a shows an Arrhenius plot of ionic conductivity of the P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI electrolyte. The conductivity values ranging from  $5 \times 10^{-7}$  S cm<sup>−1</sup> at 50 °C to  $2 \times 10^{-5}$  S cm<sup>−1</sup> at 90 °C are shown. These values are relatively low for the battery applications where the conductivity of the electrolyte is generally expected to be of the order of 10<sup>−3</sup> S cm<sup>−1</sup>. However, this apparent drawback is counterbalanced by the quite high value of the Li transference number ( $t_{Li^+}$ ) (see below).

Figure 2b shows a current-voltage curve obtained by the DC polarization of the symmetric Li/P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI/Li cell at 80 °C with an inset showing Nyquist impedance plots of the same cell which were measured before and after the polarization. The Li transference number ( $t_{Li^+}$ )



**Fig. 2** **a** Arrhenius plot of ionic conductivity of the P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI electrolyte. **b** Polarization curve of chronoamperometry and Nyquist impedance plots before and after polarization (*inset*) of the symmetric Li/P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI/Li cell at 80 °C

**Fig. 3** **a** Cyclic voltammogram of the Li/P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI/Super-P carbon coated on Cu foil cell at 80 °C. **b** Linear sweep voltammogram of the Li/P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI/Super-P carbon coated on Al foil cell at 80 °C



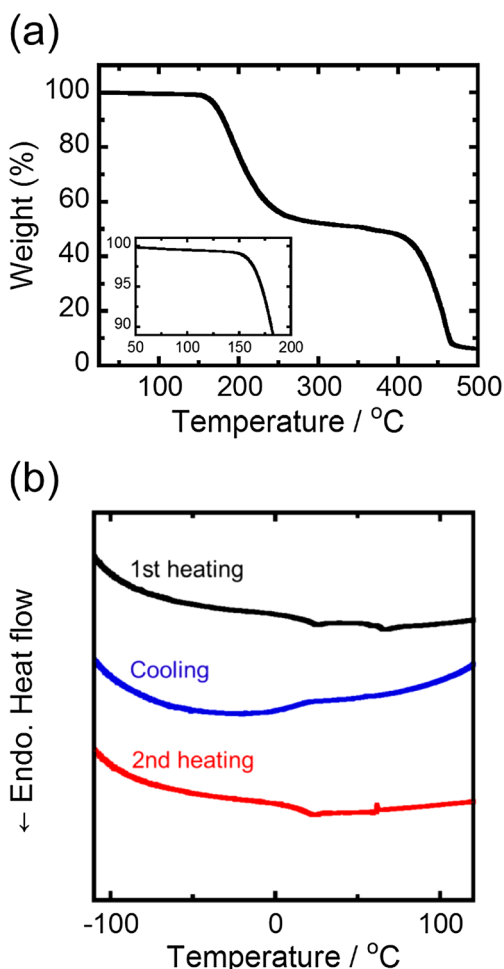
estimated from Eq. (1) (see the experimental part) was as high as 0.66, which is a value rarely obtained in common PEO-based electrolytes, where the  $t_{\text{Li}^+}$  values are typically of the order of 0.1–0.3. For instance, we have previously obtained a  $t_{\text{Li}^+}$  of the order of 0.2 for a PEO-LiCF<sub>3</sub>SO<sub>3</sub> mixture-based electrolyte containing Pyr<sub>14</sub>TFSI with a nearly identical experimental condition in our previous result [20]. Although the relatively high Li/electrolyte interfacial resistance value with respect to the electrolyte resistance (Fig. 2b) may have an effect on the precision of the calculation to some extent, this outstanding  $t_{\text{Li}^+}$  is well accorded with our previous study which demonstrated extremely high  $t_{\text{Li}^+}$  of PEC-LiTFSI electrolytes by employing a solid-state pulse-field-gradient (pfg) NMR technique [15]. Such a very high value is basically seen in single-ion conductive polymers and can effectively increase the cycling ability of the Li cells as a consequence of the reduced polarization upon battery charge-discharge process [24]. This quite favorable  $t_{\text{Li}^+}$  value of our PEC-based electrolyte would be accounted for by considering the moderate ion-dipole interactions between Li ions and polar carbonate groups.

Figure 3 summarizes the electrochemical stability of the electrolyte investigated by voltammetry techniques for a Li/P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI/Super-P carbon cell. Cyclic voltammograms in Fig. 3a show several peaks in a voltage range of 0.1–2.2 V vs. Li/Li<sup>+</sup> during the first scan. These peaks are gradually diminishing during the following cycles, and this behavior may be attributed to a partial decomposition of the electrolyte components and impurities, leading to the formation of a stable passivating film on the surface of the Super-P carbon electrode. Figure 3b shows the linear sweep voltammogram of the anodic (oxidation) scan of the Super-P carbon electrode in a Li cell with the PEC-Pyr<sub>14</sub>TFSI-LiTFSI electrolyte. The trend reveals a stable behavior with very low current up to 4.3 V vs. Li/Li<sup>+</sup>. At higher potential values, an increase in current, which may be associated with a partial oxidative electrolyte decomposition, is observed. By setting the anodic limit as the voltage at which the current density value exceeds 0.01 mA cm<sup>-2</sup>, we may assume that the PEC-Pyr<sub>14</sub>TFSI-LiTFSI electrolyte has an anodic stability of

the order of 4.3 V vs. Li/Li<sup>+</sup>. On the basis of the trend of the anodic LSV and of the cathodic CV scans, we can finally conclude that the electrochemical stability window of the electrolyte ranges from 0 to 4.3 V vs. Li/Li<sup>+</sup>.

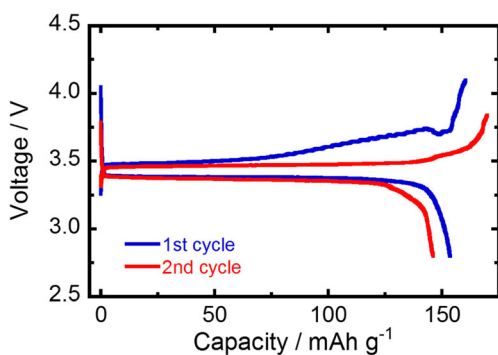
The thermal characteristics of the P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI electrolyte are shown in Fig. 4. The TGA response reveals almost no weight loss up to 150 °C and only a 5 % loss at 172 °C (see Fig. 4a). The significant loss at about 200 °C is most likely associated with the decomposition of PEC, while the following drastic loss at about 400 °C may be attributed to the decomposition of the LiTFSI-IL electrolyte component. This high thermal stability, extended up to 150 °C, suggests that the eventual Li batteries exploiting this electrolyte, when compared with those based on the conventional liquid solution electrolytes, are expected to assure higher safety levels in cases of unexpected thermal runaways as well as during normal operations. The DSC traces (Fig. 4b) indicate glass transitions at 10 °C in both the first and second heating scans and at 20 °C in the cooling scan. A small endothermic peak observed at 70 °C in the first heating scan may be associated with a melting of tiny crystalline phases induced by the interactions between the polymer chains and the ionic species, or small fraction of aggregated ions, exhibited as the effect of the high salt concentration employed in the present work. In contrast, there was no indication of crystallization during the cooling scan. This thermal behavior confirms that the PEC matrix is intrinsically able to dissolve a large amount of Li salts in a highly homogeneous manner while still keeping its amorphous nature.

The suitability of the P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI electrolyte for future applications in Li polymer batteries was assessed by testing the response of a Li cell using a LiFePO<sub>4</sub> cathode. The LiFePO<sub>4</sub> is an active material presently considered as one of the most promising materials for the development of Li rechargeable batteries to be applied for the EV applications because of its high specific capacity of 170 mAh g<sup>-1</sup>, high thermal and electrochemical stability, low cost, and environmental compatibility [25]. Figure 5 shows voltage profiles of the Li/P(EC)<sub>2</sub>LiTFSI+0.2Pyr<sub>14</sub>TFSI/LiFePO<sub>4</sub> battery



**Fig. 4** **a** TGA trace of the  $\text{P}(\text{EC})_2\text{LiTFSI}+0.2\text{Pyr}_{14}\text{TFSI}$  electrolyte under a heating scan rate of  $10\text{ }^\circ\text{C min}^{-1}$ . **b** DSC traces of the heating and cooling scans for the  $\text{P}(\text{EC})_2\text{LiTFSI}+0.2\text{Pyr}_{14}\text{TFSI}$  electrolyte under a scan rate of  $5\text{ }^\circ\text{C min}^{-1}$

cycled at  $80\text{ }^\circ\text{C}$  at a current rate of  $C/20$ . As expected, the battery operates on a plateau centered at about 3.4–3.5 V, reflecting the two-phase electrochemical process of  $\text{LiFePO}_4$ , delivering a specific capacity of  $150\text{ mAh g}^{-1}$ , i.e., a value corresponding to 90 % of the



**Fig. 5** Voltage profile of the galvanostatic charge-discharge cycling performed for the  $\text{Li}/\text{P}(\text{EC})_2\text{LiTFSI}+0.2\text{Pyr}_{14}\text{TFSI}/\text{LiFePO}_4$  cell at  $80\text{ }^\circ\text{C}$  and  $C/20$  rate

theoretical one although there were several indications of uncertain instabilities of the capacity and the cell voltage. We would assume the small initial irreversible capacity as a partial decomposition of the electrolyte with the formation of a passivating layer on the surface of the Li anode, as well as a structural reorganization of the active material which is generally seen in the  $\text{LiFePO}_4$  cathode. We are aware that the performance of our battery cannot directly compete with those of the current commercially available Li-ion batteries; they are not too far from those obtained with high temperature-operated, PEO-based Li polymer batteries. Further efforts aimed at improving the performance of our battery, in particular for operations at lower temperature and long-term cycling, are actively in progress. In addition, given the good anodic stability of our PEC-based electrolyte (extended up to 4.3 V vs.  $\text{Li}/\text{Li}^+$ ), we are motivated to assess the use of other cathode materials with higher operating voltages than that of  $\text{LiFePO}_4$ , e.g.,  $\text{LiCoO}_2$  or  $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$  in the next study, in the aim of achieving higher energy densities of the batteries.

## Conclusion

In this work, we have reported a “freestanding” polymer electrolyte membrane based on a combination of poly(ethylene carbonate) (PEC), LiTFSI salt, and  $\text{Pyr}_{14}\text{TFSI}$  ionic liquid. This electrolyte, denoted as  $\text{P}(\text{EC})_2\text{LiTFSI}+0.2\text{Pyr}_{14}\text{TFSI}$ , was used to assemble a prototype Li polymer battery with a  $\text{LiFePO}_4$  cathode. The resulting 3.5-V battery delivered a discharge capacity close to  $150\text{ mAh g}^{-1}$ , which is about 90 % of the theoretical value, at  $80\text{ }^\circ\text{C}$  under a galvanostatic cycling with a current rate of  $C/20$ . In summary, although the performance of this battery is far from being optimized at present, we demonstrated the unique properties of the electrolyte, including the extremely high Li transference number, i.e., 0.66, combined with the remarkable safety level assured by the absence of flammable organic liquids. We conclude that this work may eventually contribute to the progress of future Li polymer battery technologies and will open the door to utilize  $\text{CO}_2$  as a low carbon source for highly demanded functional polymer materials.

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