



A concentrated poly(ethylene carbonate)/poly(trimethylene carbonate) blend electrolyte for all-solid-state Li battery

Zhenguang Li¹ · Jonas Mindemark² · Daniel Brandell² · Yoichi Tominaga¹

Received: 11 January 2019 / Revised: 11 February 2019 / Accepted: 17 February 2019 / Published online: 12 March 2019
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Abstract

Electrochemical and ion-transport properties of polymer blend electrolytes comprising poly(ethylene carbonate) (PEC), poly(trimethylene carbonate) (PTMC) and lithium bis(fluorosulfonyl) imide (LiFSI) were studied in this work, and the electrolyte with the best blend composition was applied in all-solid-state Li batteries. The ionic conductivity of both PEC and PTMC single-polymer electrolytes increased with increasing Li salt concentration. All PEC and PTMC blend electrolytes show ionic conductivities on the order of 10^{-5} S cm⁻¹ at 50 °C, and the ionic conductivities increase slightly with increasing PEC contents. The PEC₆PTMC₄-LiFSI 150 mol% electrolyte demonstrated better Li/electrolyte electrochemical and interfacial stability than that of PEC and PTMC single-polymer electrolytes and maintained a polarization as low as 5 mV for up to 200 h during Li metal plating and stripping. A Li|SPE|LFP cell with the PEC₆PTMC₄-LiFSI 150 mol% electrolyte exhibited reversible charge/discharge capacities close to 150 mAh g⁻¹ at 50 °C and a C/10 rate, which is 88% of the theoretical value (170 mAh g⁻¹).

Introduction

Solid-state lithium batteries (SSLBs) have attracted a great deal of attention because they are safer and more thermally and electrochemically stable than typical Li batteries with liquid electrolytes [1–5]. The solid electrolyte is one of the most important components in SSLBs. Previously developed solid electrolytes can be classified into two main types: inorganic ceramic and organic polymer electrolytes. Inorganic electrolytes are basically Li-ion conductors; their ionic conductivity can exceed 10^{-2} S cm⁻¹ at ambient temperature [3]. However, problems at the interface between the electrolyte and the electrode and a complex manufacturing process are formidable issues facing their application in batteries [6–8]. By contrast, organic-based solid polymer electrolytes (SPEs) solve those problems associated with solid electrolytes because of their flexibility [9]. Moreover, SPEs have been

praised as safe electrolytes for application in SSLBs because of their advantages of nonvolatility, no leakage of liquids, and suppression of Li dendrites [10–12]. Over the past few decades, SPEs have mainly been studied for poly(ethylene oxide) (PEO)-based systems due to the good ion-conductive behavior and high solubility of numerous metal salts in this host material [13–16]. However, the ionic conductivity at room temperature and poor cation transference number of PEO-based electrolytes are still considered unsolved problems [14, 17, 18].

Recently, polycarbonates such as poly(ethylene carbonate) and poly(trimethylene carbonate) (PTMC) have been attracting much attention as new hosts for SPEs because their electrolytes' exhibit completely different ion-conductive behavior and better cation-conductive properties compared with those of typical polyether-based electrolytes [19–21]. Furthermore, polycarbonate-based electrolytes show good electrochemical stabilities, such as anodic oxidation stability at voltages as high as 5 V and the ability to protect the cathode current collector [22, 23]. However, further improvements in the conductivity, thermal stability and mechanical properties are still needed for the

Supplementary information The online version of this article (<https://doi.org/10.1038/s41428-019-0184-5>) contains supplementary material, which is available to authorized users.

✉ Yoichi Tominaga
ytominag@cc.tuat.ac.jp

¹ Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Tokyo

184-8588, Japan

² Department of Chemistry - Ångström Laboratory, Uppsala University, SE-75121 Uppsala, Sweden

development of polymer batteries with good long-term stability.

Over the years, polymer blending has shown to be a promising process for improving polymer performances. In previous studies, PEO/PEC and PEO/PTMC blend electrolytes have been reported [24, 25], and we have also very recently reported fundamental properties of a miscible blend electrolyte composed of two polycarbonates, PEC and PTMC, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) [26]. Electrochemical properties such as the battery performance and cation transference characteristics are still unknown for the blend electrolytes, and detailed electrochemical investigations are therefore needed.

In the present study, several blend electrolytes of PEC and PTMC were prepared, and the battery performance of a Li half-cell with a LiFePO₄ cathode was investigated for the first time. Lithium bis(fluorosulfonyl)imide (LiFSI) has been used as an appropriate salt due to its high ionic conductivity and ability to form a stable solid-electrolyte interphase (SEI) layer on various electrodes, resulting in good electrochemical properties for the corresponding SPEs [20, 27, 28].

Experimental

Materials and sample preparation

Poly(ethylene carbonate) (PEC; $M_w = 2.4 \times 10^5$, QPAC[®]25) and lithium bis(fluorosulfonyl)imide (LiFSI, battery grade) were purchased from Empower Materials, USA, and Kishida Chemical Co., Japan, respectively. Poly(trimethylene carbonate) (PTMC) was synthesized via ring-opening polymerization. Trimethylene carbonate (TMC) and Sn(Oct)₂ solution were used as a monomer and a polymerization catalyst, respectively. The synthesis was performed in a stainless steel reactor at 130 °C for 3 days. The detailed polymerization processes have been described in a previous paper [22]. The structures of PEC and PTMC are shown in the inset of Fig. 1. Self-standing electrolytes were prepared by a simple casting method, and acetonitrile (electrochemical grade) was used as the solvent. The LiFSI concentrations of the electrolytes were set by the ratio of LiFSI and carbonyl groups (C=O) in the polymers ($([Li^+]/[C=O]) \times 100 = a \text{ mol}\%$). Furthermore, the ratio of the PEC and PTMC blend was determined by the molar ratio of C=O units and distinguished as PEC_{*x*}PTMC_{*y*} ($9 \geq x \geq 1$ and $1 \leq y \leq 9$, such that $x + y = 10$). To prepare the electrolyte samples, PEC and PTMC were dissolved in acetonitrile at room temperature for 8 h. All electrolyte solutions were dried in a vacuum oven at 60 °C for 72 h to eliminate all residual solvent.

Cathodes were prepared by blending LiFePO₄ (LFP, Tating Fine Chemicals Co., Taiwan) as active material with poly(vinylidene fluoride) (PVdF, KYNAR 741, ARKEMA Co., France) as binder and acetylene black (Denka Black[®], Denka Co., Japan) as conductive additive in the weight ratio 90:6:4 in *N*-methyl-2-pyrrolidinone (NMP, >99.5%, Kanto Chemical Co., Japan). The obtained slurry was cast onto an Al current collector using a doctor blade, and the cast electrode sheet was then dried under vacuum at 85 °C for 12 h.

Characterization

The thermal properties of the original polymers, electrolytes and the blend electrolytes were characterized by differential scanning calorimetry (DSC) using a DSC7020 (Hitachi High-Tech Co., Japan). All samples for measurement were loaded into Al pans and sealed under dry Ar. The DSC measurements were performed using the following procedure: The sample was rapidly heated from room temperature to 80 °C to make it uniform in the pan and then cooled to -60 °C. The sample was then heated at 10 °C min⁻¹ to 80 °C under dry flowing N₂.

Ionic conductivities were measured by electrochemical impedance spectroscopy (EIS) using a SP-150 potentiostat/galvanostat (Bio-Logic Instrument Co., France). The conductivity cell consisted of two stainless steel (SS) blocking electrodes sandwiching the electrolyte. The EIS measurements were performed every 10 °C from 100 to 25 °C with a signal amplitude of 10 mV in the frequency range from 100 mHz to 1 MHz. DC polarization and AC impedance measurements were carried out using an 1280 C impedance analyzer (Solartron) for symmetric Li|SPE|Li cells at 50 °C to estimate the Li⁺ transference number (t_+) under potentiostatic polarization [29]. The symmetric cells were assembled and thermally equilibrated at 50 °C for 12 h to improve contact between SPE and Li before the measurement.

Lithium stripping/deposition tests were carried out on Li|SPE|Li cells using coin-type cells (CR2032) without a separator by applying a constant current density of 0.1 mA cm⁻² with a step duration of 1 h using a HJ1001SM8A battery test system (Hokuto Denko Co., Japan). The Li/electrolyte interfacial stability of the original polymers and blend electrolytes was evaluated by performing EIS tests on symmetrical Li|SPE|Li coin-type cells. The EIS measurements were performed at 50 °C with a signal amplitude of 30 mV in the frequency range 100 mHz to 7 MHz using a SP-200 potentiostat/galvanostat (Bio-Logic Instrument, France). For comparison, SS|SPE|SS coin cells were also prepared and their EIS measurements were performed under the same conditions. All electrochemical processes were carried out in a strictly controlled Ar-gas-filled glove box.

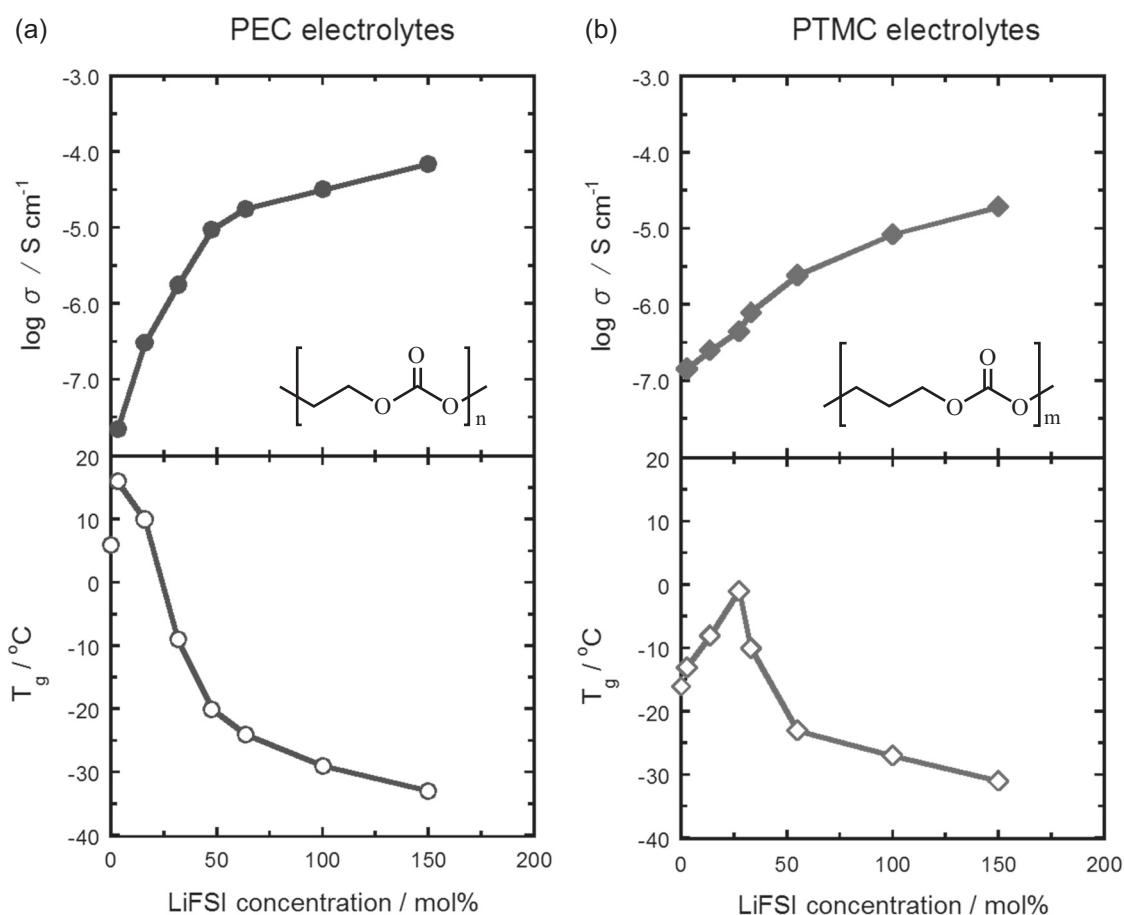


Fig. 1 Dependence of the ionic conductivity at 50 °C and the glass-transition temperature (T_g) on the salt concentration for (a) PEC-LiFSI and (b) PTMC-LiFSI electrolytes

CR2032 coin-type LiSPE|LFP half-cells were assembled for the battery tests. An acetonitrile solution of the electrolyte was cast onto the cathode, and the solvent was removed via the same drying procedure used in the electrolyte preparation process. The galvanostatic cycling tests were performed using a HJ1001SM8A battery test system at 50 °C. The cells were electrochemically activated by a galvanostatic cycle at $C/10$ rate ($1 C = 170 \text{ mA g}^{-1}$) within a voltage range from 2.5 to 4.0 V. The cells were kept at 50 °C for 12 h before the cycling.

Results and Discussion

Polymer electrolytes with a low glass-transition temperature (T_g) generally exhibit high ionic conductivity because the low T_g reflects a more active segmental motion of the polymer chains in the SPE, which is correlated with fast ionic transport [30]. The dependence of ionic conductivity and T_g on the salt concentration in PEC- and PTMC-based electrolytes is shown in Fig. 1. The ionic conduction and

glass-transition behavior of the PEC-LiFSI electrolytes were confirmed in our previous research [20]. The same results were also obtained in the present study, and the highest conductivity was achieved at a salt loading of 150 mol% (Fig. 1a). Higher salt loadings, however, generated electrolytes with poor mechanical properties. Similarly, the conductivity of the PTMC-LiFSI electrolytes increases with increasing salt concentration (Fig. 1b); however, the change is smoother than for the PEC system. Neat PEC and PTMC show completely different values of T_g at 6 °C for PEC and -16 °C for PTMC, whereas their chemical structures are very similar. Moreover, the changes in the T_g values for the PTMC electrolytes differ from those observed for the PEC system in the low salt concentration range. The values of T_g for PEC electrolytes basically continues to decrease with increasing salt concentration after the addition of LiFSI (Fig. 1a); however, the PTMC system increases T_g with increasing concentration at lower salt concentrations below 30 mol% (Fig. 1b). Similar behavior of the PTMC system has been reported previously; [22] this behavior likely directly influences the conductivity change observed in

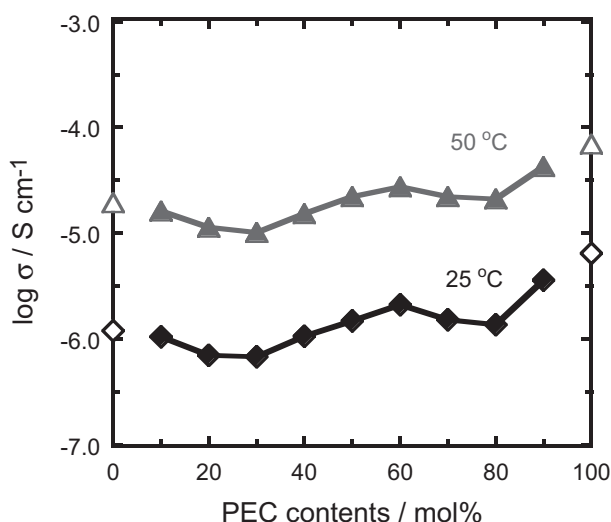


Fig. 2 Dependence of the ionic conductivity of $\text{PEC}_x\text{PTMC}_y\text{-LiFSI}$ 150 mol% electrolytes on their PEC content

Fig. 1b. Furthermore, the T_g of the PTMC system decreased with a further increase of the salt concentration, which is behavior similar to that observed in the concentrated PEC system (Fig. 1a) in that the T_g decreases as a result of the aggregation of numerous ions without stable solvation between the polymer chains and Li ions, which increases the conductivity [31].

Figure 2 shows dependence of the conductivity on the PEC content for $\text{PEC}_x\text{PTMC}_y\text{-LiFSI}$ 150 mol% blend electrolytes at 50 °C and 25 °C. All of the polymer electrolytes show acceptable conductivities on the order of $10^{-5} \text{ S cm}^{-1}$ at 50 °C and $10^{-6} \text{ S cm}^{-1}$ at 25 °C. The conductivity of the blend electrolytes slightly increases with increasing PEC content, and the $\text{PEC}_6\text{PTMC}_1$ electrolyte exhibits the highest conductivity among all of the investigated blend electrolytes. This behavior is similar to that of the PEC/PEO blend electrolyte system reported previously [24]. Moreover, the local maximum in conductivity displayed for $\text{PEC}_6\text{PTMC}_4$ is the same as that observed for the LiTFSI-based system [26]. The PEC may function as a better ion-conductive phase in the blend electrolyte. However, the PEC-rich electrolytes, such as pure PEC and the $\text{PEC}_9\text{PTMC}_1$ blend electrolytes, appear to be unsuitable for battery applications because of their lower decomposition temperature [26, 32]. Therefore, a $\text{PEC}_6\text{PTMC}_4$ blend electrolyte was chosen for further measurements.

Polycarbonate-based electrolytes can exhibit excellent Li-ion transport properties, such as a high Li-ion transference number (t_+) [20, 21, 32]. In the present study, the values of t_+ for PEC, PTMC, and their blend electrolytes were measured, where the t_+ value is given by the following

equation [29]

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

where ΔV is the DC voltage applied to the cell, I_0 and I_{SS} are the initial current and steady-state current, respectively, and R_0 and R_{SS} are the Li/electrolyte interphase resistances before and after the polarization, respectively. The results of t_+ measurements are arranged in Table 1, and chronoamperometry profiles and the Nyquist plots of the impedance spectra for all samples are shown in Figure S2 in the Supplementary Materials. All electrolytes exhibited a very high t_+ greater than 0.6; the values were determined as 0.63 for PEC-LiFSI 150 mol%, 0.61 for PTMC-LiFSI 150 mol%, and 0.73 for $\text{PEC}_6\text{PTMC}_4\text{-LiFSI}$ 150 mol%. These values are substantially higher than those of typical PEO-based electrolytes [20]. Excellent t_+ values for the concentrated PEC-based electrolytes were reported in our previous papers; [20, 32–34] and the PTMC system also exhibits good Li-ion transport properties [21]. Moreover, the blend electrolyte displayed slightly higher and stable values of current with the smallest impedance response (Figure S2 in the Supplementary Materials). This result implies that there are many mobile Li-ions and that they can move faster and easier in the blend electrolyte than in the original polymer electrolytes. These observations suggest that the combination of carbonyl-group-containing polymers that separately have good t_+ can result in electrolytes with improved Li-ion transport properties.

In Li metal batteries, electrolytes, solvents and salts react with exposed Li during battery cycling, resulting in consumption of the electrolyte and the formation of detrimental degradation layers and Li dendrites on the surface of the anode, which degrade the batteries [35–37]. The battery performance is therefore influenced directly by the interfacial stability between the Li-metal anode and the electrolyte. A comparison of the electrochemical features for PEC, PTMC, and $\text{PEC}_6\text{PTMC}_4\text{-LiFSI}$ 150 mol% in terms of the Li/electrolyte interface stability is shown in Fig. 3. At the early stages of cycling for cells with both PEC and PTMC electrolytes, very unstable voltage profiles appear with high overpotentials, which means poor interfacial stability between the Li-metal anode and the electrolyte (Fig. 3a, b). However, these voltage profiles became stable after cycling for more than 10 h. The polymer in the concentrated electrolytes may decompose to a cyclic carbonate and various other degradation products through the reaction with Li metal under continuously applied current during electrochemical cycling [36, 38]. The concentrated polycarbonate-based electrolytes have many benefits, including excellent Li-ion transport, a wide electrochemical window and good inhibition of corrosion of the Al current

Table 1 Current (I_0 , I_{ss}), charge transfer resistance (R_0 , R_{ss}) and lithium transference numbers (t_+) data, as determined electrochemically [29] for (a) PEC-LiFSI 150 mol%, (b) PTMC-LiFSI 150 mol%, and (c) PEC₆PTMC₄-LiFSI 150 mol% electrolytes at 50 °C (the related chronoamperometry profiles and Nyquist plots are reported in Figure S2 in the Supplementary Materials)

Sample	I_0 (μ A)	I_{ss} (μ A)	R_0 (Ω)	R_{ss} (Ω)	t_+
(a) PEC-LiFSI 150 mol%	0.45	0.32	11254	13542	0.63
(b) PTMC-LiFSI 150 mol%	0.35	0.24	8546	8784	0.61
(c) PEC ₆ PTMC ₄ -LiFSI 150 mol%	0.50	0.38	8177	9881	0.73

collector; [20, 32, 39] however, polymer decomposition is one of the issues that needs to be resolved. In contrast to both original polymer electrolytes, the blend electrolyte shown in Fig. 3c displays a stable voltage profile; the PEC₆PTMC₄-LiFSI 150 mol% cell maintains a polarization as low as 5 mV. This result clearly demonstrates that the PEC₆PTMC₄ electrolyte has better interfacial stability against the Li anode and a more stable SEI than that of the original electrolyte system, which can mitigate degradation upon cycling.

To investigate the stability of the Li anode in contact with three kinds of electrolytes, EIS analysis was further carried out. Figure 4 shows Nyquist plots related to EIS measurements performed during storage of SSISPEISS coin cells for PEC, PTMC, and PEC₆PTMC₄-LiFSI 150 mol% electrolytes at 50 °C. For the fresh cells at 0 h only a single semicircle due to the bulk resistance was observed for all of the electrolytes. However, another semicircle at lower frequencies due to the interfacial resistance between the SS electrode and the electrolyte clearly appeared after more than 17 h for the PTMC (Fig. 4b) and PEC₆PTMC₄ blend electrolytes (Fig. 4c). In contrast, the interfacial semicircle for the PEC electrolyte is difficult to observe (Fig. 4a), which means that the behavior of the PEC₆PTMC₄ blend electrolyte was derived from that of the PTMC system. In addition, no changes in the bulk resistance for any of the electrolytes are observed with increasing time, which indicates that no bulk degradation or reaction occurs during the measurement.

In case of the Li|SPE|Li cell, the bulk and interfacial resistances during storage of the PEC, PTMC, and the PEC₆PTMC₄-LiFSI 150 mol% electrolytes were also investigated; the results are summarized in Fig. 5 (all corresponding Nyquist plots are shown in Figure S3 in the Supplementary Materials). Certain increases in both the bulk and interfacial resistances were observed for all of the electrolytes during the first 17 h. These results may indicate decomposition of the electrolyte and an increase in the bulk resistance of the electrolyte through contact between the Li electrode to the concentrated electrolytes [40, 41], thus

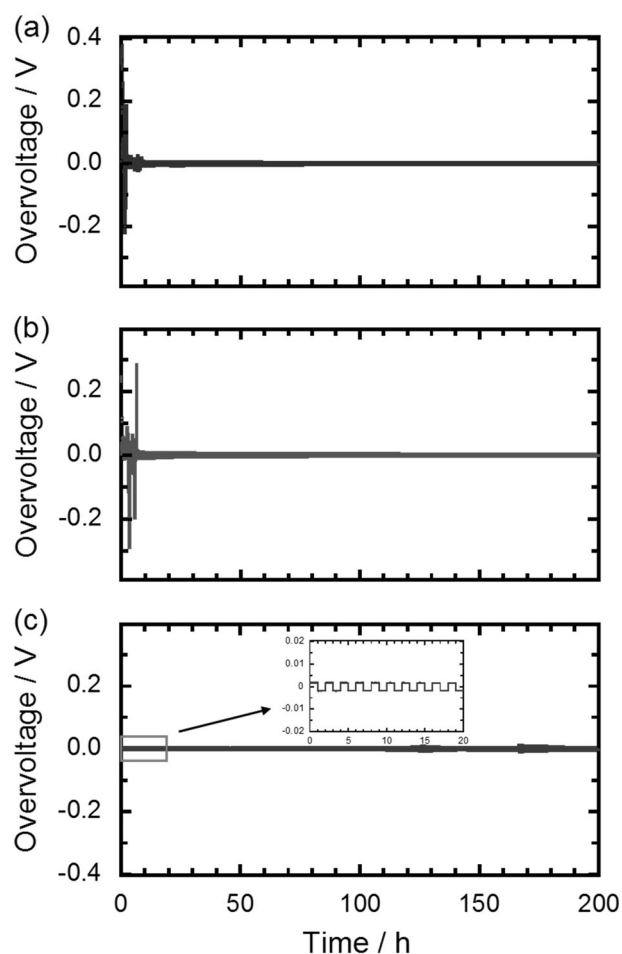


Fig. 3 Lithium stripping/deposition tests for (a) PEC-LiFSI 150 mol%, (b) PTMC-LiFSI 150 mol%, and (c) PEC₆PTMC₄-LiFSI 150 mol% electrolytes in symmetrical Li/Li cells at a constant current density of 0.1 mA cm⁻² (voltage limit: +1 V and -1 V; step time 1 h each)

causing an instability between the Li electrode and the concentrated electrolytes. As seen in Fig. 5a, both original electrolytes exhibit a continuous increase in bulk resistance; however, the bulk resistance of the PEC₆PTMC₄ blend electrolyte is almost constant after 17 h. The change in the interfacial resistance for all of the electrolytes is similar to that of the bulk, and the PEC-based electrolyte exhibits a significant increase in both resistances compared with the other systems. This increased resistance may be due to the poor chemical stability of the PEC-based concentrated electrolyte in contact with the Li electrode. However, the blend electrolyte has a relatively stable resistance, exhibiting the lowest values. The combination of PEC and PTMC could therefore improve the stability of the electrolyte in contact with the Li electrode.

Figure 6 shows galvanostatic charge-discharge properties of Li/LFP cells based on PEC, PTMC, and PEC₆PTMC₄-LiFSI 150 mol% electrolytes at 50 °C. The cell with the PEC-based electrolyte delivers a discharge capacity of

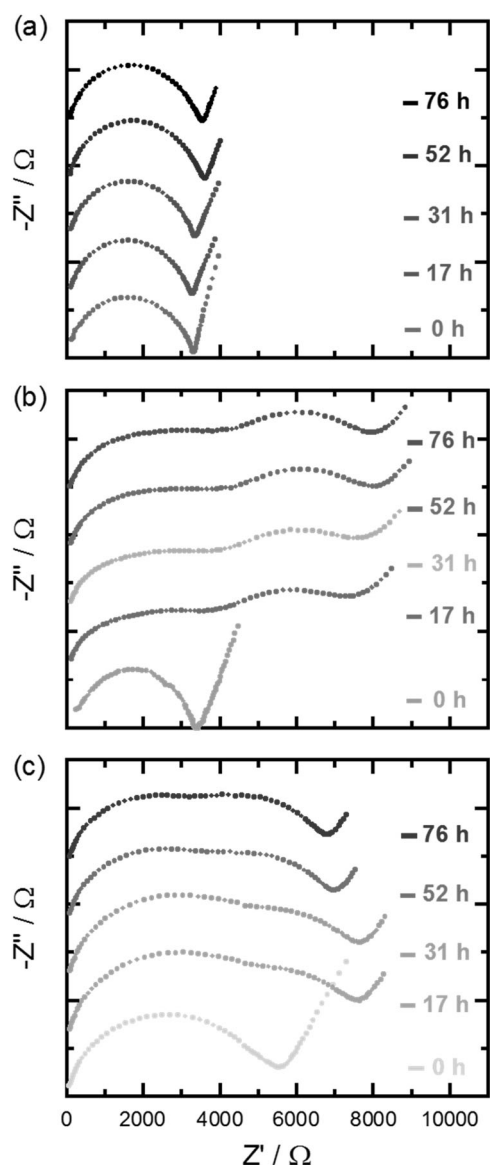


Fig. 4 Nyquist plots related to EIS measurements performed during storage of SSISPE|SS symmetrical cells using (a) PEC-LiFSI 150 mol%, (b) PTMC-LiFSI 150 mol%, and (c) PEC₆PTMC₄-LiFSI 150 mol% electrolytes at 50 °C

approximately 160 mAh g⁻¹ in the first cycle (Fig. 6a). However, a decrease in the capacity was observed, which is mainly due to the degradation in the concentrated electrolyte. A similar behavior was also confirmed via the Li/electrolyte impedance analysis, as shown in Fig. 5a. The cell with the PTMC-based electrolyte also exhibited a reversible capacity approaching 140 mAh g⁻¹ in the first cycle, and its capacity increased with continued cycling (Fig. 6b); the same tendency has been observed in previous work [42]. These data are comparable to those of PEC- and PTMC-based electrolytes reported previously [39, 42]. In contrast, the cell with the blend electrolyte exhibited the most stable charge/discharge performance and its initial

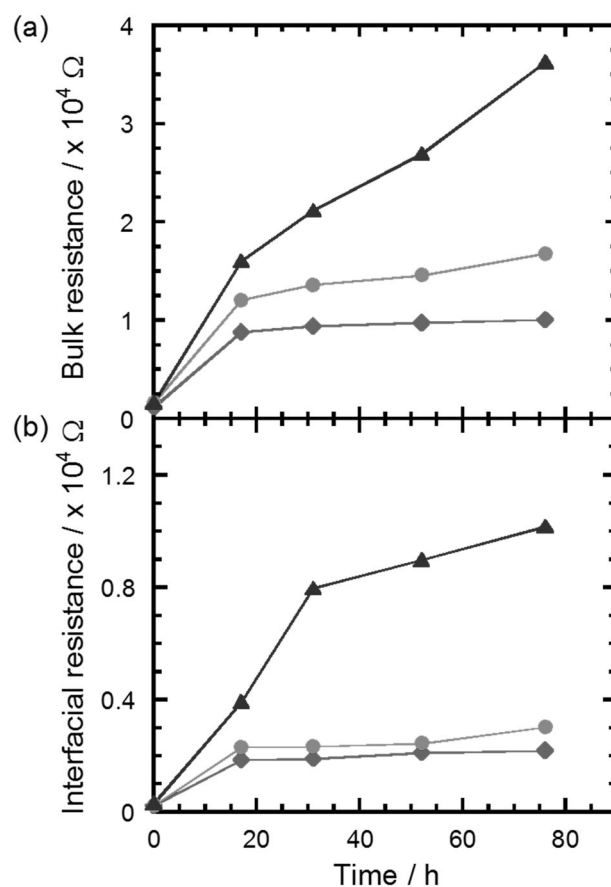


Fig. 5 Changes in the (a) bulk resistance and (b) interfacial resistance of Li|SPE|Li cells for PEC-LiFSI 150 mol% (▲), PTMC-LiFSI 150 mol% (●), and PEC₆PTMC₄-LiFSI 150 mol% (◆) electrolytes at 50 °C (see also Figure S3 in the Supplementary Materials for the corresponding Nyquist plots)

capacity approached 150 mAh g⁻¹, which is 88% of the theoretical value. Indeed, these results are likely due to a combination of the formation of a stable Li/electrolyte interface and a good interface with the LFP cathode induced by the blend of PEC and PTMC, as confirmed by the galvanostatic tests in Fig. 3 as well as by the EIS in Fig. 5. Moreover, the extended cycling performance of the blend electrolyte cell is shown in Fig. 6d, and further cycling results for PEC- and PTMC-based electrolytes are shown in Figure S4 in the Supplementary Materials. Both original electrolytes exhibit large decreases in the capacity at approximately 10 cycles, and the cells exhibit poor cycling stability. However, the cell with the blend electrolyte exhibits better and stable cycling performance compared with the original electrolytes. The combination of PEC and PTMC may improve the interface between Li and the electrolyte, as well as the stripping/deposition process of the original electrolytes. The effects of the blend electrolyte have thus been demonstrated also for battery performance.

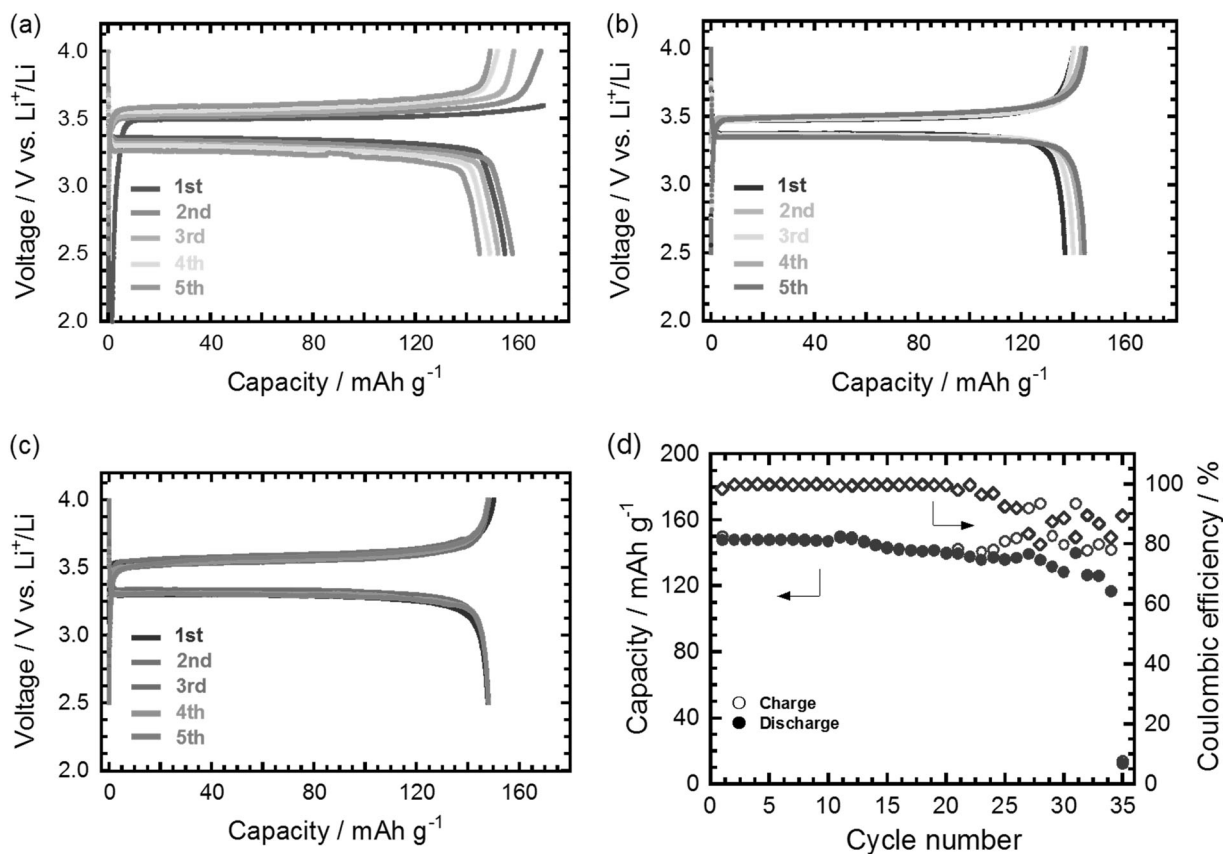


Fig. 6 Galvanostatic charge/discharge curves of Li|SPE|LFP cells: (a) PEC-LiFSI 150 mol%, (b) PTMC-LiFSI 150 mol%, and (c) PEC₆PTMC₄-LiFSI 150 mol%, and (d) cycle performance of Li|PEC₆PTMC₄-LiFSI 150 mol%|LFP cells at a C/10 rate (1 C = 170 mA g⁻¹) and 50 °C

Conclusions

Solid polymer electrolytes of PEC, PTMC, and their mixture with LiFSI were prepared, and high-concentration polymer electrolytes were investigated in all-solid-state Li|SPE|LFP cells. Both PEC and PTMC single-polymer electrolytes reveal increasing ionic conductivity with increasing LiFSI salt concentration. Meanwhile, the glass-transition temperature of the PTMC-based electrolytes showed an increase with increasing salt concentration in the low-concentration regime but a decrease in the concentrated regime. All of the PEC and PTMC blend electrolytes with LiFSI 150 mol% showed ionic conductivities on the order of 10⁻⁵ S cm⁻¹, and their ionic conductivities increased slightly with increasing PEC content. The electrochemical investigation revealed t_+ values greater than 0.6 for both PEC and PTMC single-polymer electrolytes, whereas the PEC₆PTMC₄-LiFSI 150 mol% electrolyte had a t_+ value as high as 0.73 at 50 °C. Furthermore, the PEC₆PTMC₄-LiFSI 150 mol% electrolyte demonstrated better Li/electrolyte electrochemical and interfacial stability than the PEC and PTMC single-polymer electrolytes. The Li|SPE|LFP cells with PEC and PTMC single-polymer electrolytes showed poor cycling performances,

whereas the battery cell with PEC₆PTMC₄-LiFSI 150 mol% electrolyte exhibited better cycle stability than the others and delivered a reversible charge-discharge capacity of approximately 150 mAh g⁻¹ at 50 °C and a C/10 rate, which is 88% of the theoretical value (170 mA h g⁻¹). Therefore, the PEC and PTMC blend electrolyte is more suitable for batteries than either of the original electrolytes.

Acknowledgements This work was supported financially by a Grant-in-Aid for Scientific Research (B) from JSPS KAKENHI (No. 16H04199), Japan, and STandUP for Energy, Sweden.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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