Boosting Lithium Ion Conduction of Carboxylate-Type Single-Ion Conducting Polymers through Complexation with Ionic Liquids for Lithium-Ion Batteries

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Single-ion conducting (SIC) polymers, wherein anions are covalently bonded to the polymer chain, selectively facilitate the movement of lithium ions, making them promising polymer electrolytes for lithium-ion batteries because only lithium ion acts as a charge carrier. Carboxylate-type SIC polymers offer cost advantages and are facilely prepared compared to conventional types like sulfonylamide-type SIC polymers. However, they are known to suffer from inefficient dissociation of lithium ions due to their high basicity. In this study, enhancement of lithium-ion dissociation in carboxylate-type SIC polymers is investigated by complexing them with ionic liquid (IL). Incorporation of IL with the SIC polymer significantly improves electrochemical properties, achieving a high ionic conductivity close to 2 mS cm^{-1} and a critical current density of 2.1 mA cm^{-2} in a Li symmetric cell at 25 °C. The interaction between the SIC polymer and IL is confirmed through infrared and Raman spectroscopy. Electrochemical tests of the Li/LiFePO$_4$ cell exhibit a high reversible capacity of 128.6 mAh g^{-1} with a cycle retention of 89.9% after 100 cycles at 1 C (1 C = 170 mA g^{-1}) and an excellent recuperation even after rate tests at 6 C.

Introduction

Lithium-ion batteries (LIBs) have been widely used for energy storage in portable electronic devices and hybrid/electric vehicles due to their high energy density and versatility.[1–5] The electrolyte in the LIB system plays a crucial role in battery performance.[6,7] Commercial LIBs commonly employ a solution of blended of cyclic or linear organic carbonates with lithium salt as the primary electrolytes (e.g., LiPF$_6$ in EC/DMC (ethylene carbonate/dimethyl carbonate).[8–10] While such electrolytes exhibit high ionic conductivities,[11,12] they have drawbacks in safety, arising from the high volatility of solvents.[13,14]

In addressing these shortcomings, solid-state batteries (SSBs) utilizing solid-state electrolytes (SSEs) have gained attention to ensure high thermal stability and high ionic conductivity ($\sigma \geq 1$ mS cm^{-1}).[15–18] Particularly, polymer-type SSEs are promising due to their lightweight, cost-effectiveness, and high interfacial compatibility to electrode materials.[17,19] However, practical implementation is hindered by their poor ionic conductivity, and large polarization caused by concentration gradients.[20,21]

A single-ion conducting (SIC) polymer has its anions covalently bonded to the polymer backbone, allowing only the countercations to move (Li$^+$ for LIBs).[22–24] Hence, it is highly desirable to overcome the drawbacks of conventional polymer electrolytes with dual-ion conducting mechanism.[22–24] Additionally, recent studies reported the ability of SIC polymers to suppress Li dendrites formation.[25,26] Various anions, such as sulfonylamide,[27,28] sulfonate,[29,30] and carboxylate,[31,32] etc.,[33,34] are utilized as the anionic part of the SIC polymers. Among them, carboxylate-type SIC polymers stand out due to their significant cost advantage in preparation, making them industrially favorable. However, their application is hindered by the higher basicity compared to sulfonylamide- and sulfonate-type SICs, which poses challenges for lithium-ion dissociation.[23,31,32] To address the poor ionic conductivity of SIC homopolymer, improvements were made through blending with other polymers and copolymerization with different monomers.[27,31,32,35] Additionally, ionic conductivity significantly varies, depending on the sequence control of the copolymer (alternating > block > random > homopolymer).[27,36]

In this study, sequence-controlled alternating copolymers were employed as the carboxylate-type SIC polymer and combined with different ionic liquids (ILs) to demonstrate the improvement in ionic conductivity, enhancing the dissociation of lithium ions. Here, ILs were added to weaken the interaction between lithium ions and SIC polymer, dissociating the lithium ion from the anionic part of the polymer chain. The physiochemical and electrochemical properties of the composite electrolytes were evaluated using diverse techniques such as electrochemical impedance spectroscopy (EIS), vibrational spectroscopy (infrared (IR) and Raman), Li plating/stripping tests,

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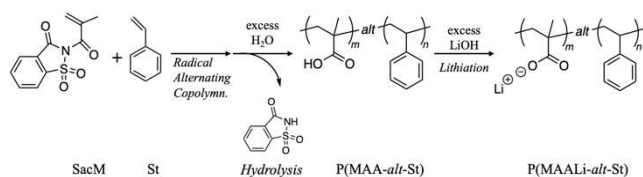   E-mail: matsumoto.kazuhiko.4c@kyoto-u.ac.jp

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and charge-discharge tests. The resulting composite polymer electrolyte demonstrates an outstanding ionic conductivity close to 2 mS cm^{-1} at room temperature and a critical current density (2.1 mA cm^{-2}) in a Li/Li symmetric cell. Furthermore, charge-discharge test of a Li/LiFePO$_4$ were carried out to verify the actual electrolyte chemical performance of the composite electrolytes. This research aims to explore the potential of carboxylate-type SIC polymers and its IL-complexed forms as high-performance electrolytes for LIBs, providing insights into the enhancement of lithium-ion dissociation.

Results and Discussion

Synthesis of the Alternating Sequence-Controlled Carboxylate-Type SIC Polymer

An alternating sequence-controlled carboxylate-type single-ion conducting (SIC) polymer was synthesized by radical copolymerization of saccharin methacrylamide (SacM), which is characterized by being bulky, highly conjugated, and electrodeficient, and styrene (St) with electro-abundant (Scheme 1).[37,38] The preparation of the polymer was carried out in three steps. Firstly, SacM and St monomers (1:1) and initiator (azobis(isobutyronitrile) (AIBN)) was added to 1,4-dioxane/acetonitrile=1:1 (v/v) and polymerized at 60°C for 24 hours. Excess water was directly added to the polymer solution at the end of the reaction and hydrolyzed by stirring at 60°C for 24 hours to give poly(methacrylic acid-*alt*-styrene) [P(MAA-*alt*-St)]. At this time, phenothiazine was added as an inhibitor to prevent further copolymerization of the remaining monomers.[39] The hydrolyzed polymer was lithiated by the treatment with excess LiOH at room temperature for 3 days to give poly(lithium methacrylate-*alt*-styrene) [hereafter, PMA-S]. The resulting polymer was dialyzed with methanol and vacuum-dried at room temperature for 1 day. The composition ratio (MAALi:St=1:1) of the obtained polymer was confirmed by ^{1}H NMR in DMSO-d_6.[37,38]

Scheme 1. Synthesis of the alternating sequence-controlled carboxylate-type SIC polymer.

Properties of PMA-S/P-H

The selected properties of PMA-S are presented in Table 1. The polymer electrolyte was prepared by mixing the PMA-S with the poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVdF-HFP) as the binder at a ratio of 2:1 [hereafter, PMA-S/P-H]. EC/PC (1/1 in volume) was added as a plasticizer (200 wt% based on the polymer membrane). PMA-S/P-H shows poor ionic conductivity ($\sigma = 7.13 \times 10^{-4}$ mS cm^{-1} at 25°C) with the activation energy of 24.0 kJ mol^{-1} according to the Arrhenius plot.[40] It was much larger compared to other SIC polymers (5~18 kJ mol^{-1}).[28,29] Li plating/stripping tests using a Li/Li symmetric cell revealed the direct current exceeded 2 V (so-called critical current density, CCD, based on cell failure) even at 0.1 mA cm^{-2} (Figure 1a), which indicates that the highly basic carboxylate group of the PMA-S/P-H hinders ion dissociation and impedes the flow of direct current.

Complexation of PMA-S/P-H and Ionic Liquids

To mitigate the interaction between the anionic part of the polymer chain and lithium ions in PMA-S/P-H and enhance lithium-ion dissociation, the PMA-S/P-H was complexed with two ILs (P$_{14}$FSA and P$_{14}$TFSA, where P$_{14}$: 1-butyl-1-methylpyrrolidinium, FSA$^-$: bis(fluorosulfonyl)amide, and TFSA$^-$: bis(trifluoromethanesulfobyl)amide). The ILs were added in 2 equimolar (eq.) amounts with respect to the charge of PMA-S/P-H. In the case of P$_{14}$FSA, the ionic conductivity improved dramatically from 7.13×10^{-4} to 1.98 mS cm^{-1} at 25°C, while the activation energy (E_a) was halved (11.0 kJ mol^{-1}) (Table 1). CCD was also significantly improved, flowing up to 2.1 mA cm^{-2} (Figure 1a). Similarly, the ionic conductivity (σ) (1.23 mS cm^{-1}) and activation energy (10.6 kJ mol^{-1}) also improved significantly as P$_{14}$TFSA IL was added (Table 1), though the CCD was slightly lower the case with P$_{14}$FSA (1.7 mA cm^{-2}). Thus, the dissociation of lithium ions from the polymer chain is promoted by complexing the SIC polymer with IL, which greatly improves the electrochemical properties.

Figure 1b represents the cycle test at 1 mA cm^{-2} (the initial five and three cycles were performed at 0.01, 0.1, and 0.5 mA cm^{-2}, respectively, for cell activation) using Li/Li symmetric cells. Stable cycle performance was obtained at 1 mA cm^{-2} without capacity fading up to the 200th cycle. From this, it became clear that it has a stable long cycle without dendrite formation.

Table 1. Ionic conductivity, activation energy, and critical current density of pure PMA-S/P-H and PMA-S/P-H complexed with ILs.

Samples	IL	σ (mS cm^{-1})	E_a (kJ mol^{-1})	Critical current density	
				mA cm^{-2}	V
1	–	7.13×10^{-4}	24.0	0.1	2.00
2	P$_{14}$FSA	1.98	11.0	2.1	0.40
3	P$_{14}$TFSA	1.23	10.6	1.7	0.23

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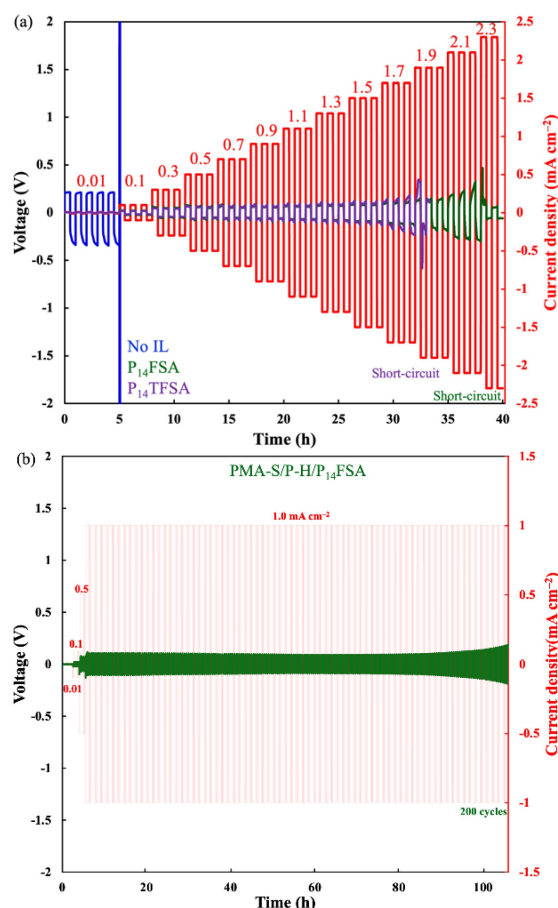European Chemical
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Figure 1. (a) Voltage profile and applied current density during the Li plating/stripping cycle test of pure PMA-S/P-H and PMA-S/P-H complexed with P_{14}FSA and P_{14}TFSA. (b) Long-term cycle performance of the Li/Li symmetric cell with PMA-S/P-H complexed with P_{14}FSA at 1 mA cm^{-2} and 25 °C.

Effects of the Amount of Ionic Liquids

Effects of the amount of ILs on the properties of PMA-S/P-H were investigated for ionic conductivity, activation energy, and CCD at the ratio of 0.5, 1, and 2 eq. against PMA-S. In the case of P_{14}FSA IL, even with the addition of 0.5 eq., there was a significant decrease and increase in activation energy (14.5 kJ mol^{-1}) and ionic conductivity (0.18 mS cm^{-1} at 25 °C), respectively (Figure 2a). Even with a small quantity of IL, a notable effect was observed in dissociating lithium ions from the anionic part of the polymer chain through the weakened interaction between the PMA-S and lithium ions (Figure 2c, 0.5 eq.). Meanwhile, lithium ions at non-interacting sites are still tightly interacting with the anionic part of the polymer chain, hindering their movement. For the PMA-S and IL at 1 eq., the activation energy further decreased to 13.0 kJ mol^{-1} and an ionic conductivity increased to 0.58 mS cm^{-1}. Additionally, improvement was observed in CCD (from 0.1 at 0 eq. and 0.1 at 0.5 eq. to 0.5 mA cm^{-2} at 1 eq.) (refer to Figure 2b). Subsequently, with an increase in the IL quantity to 2 eq., there is significant enhancement in physicochemical and electrochem-

ical properties ($\sigma = 1.98$ mS cm^{-1}, $E_a = 11.0$ kJ mol^{-1}, and CCD = 2.1 mA cm^{-2}).

A similar behavior was observed in the case of P_{14}TFSA IL. As the amount of the IL increased (0, 0.5, 1, and 2 eq.), the activation energy decreased ($E_a = 24.0 \rightarrow 14.9 \rightarrow 12.9 \rightarrow 10.6$ kJ mol^{-1}), and the ionic conductivity ($\sigma = 7.13 \times 10^{-4} \rightarrow 0.18 \rightarrow 0.69 \rightarrow 1.23$ mS cm^{-1}), and CCD ($0.1 \rightarrow 0.3 \rightarrow 0.9 \rightarrow 1.7$ mA cm^{-2}) improved significantly (Figure 2b). This observation highlights that the carboxylate group in PMA-S with high basicity diminishes its interaction with lithium ions by interacting with the organic cations.[41] Facilitating the dissociation of lithium ions from the PMA-S, the degree of enhancement is directly related to the quantity of ILs.

Effects of Ionic Species of Ionic Liquids

The influence of anionic species of the ILs on the Li plating/stripping behavior is summarized in Figure 3a. The cation of the IL was fixed to P_{14}^+, and five different anions (PF_6^-, TFSA$^-$, FSA$^-$, OTf$^-$, and $N(CN)_2^-$) were incorporated with the PMA-S/P-H. (See Table S1 for donor number (DN) of anion,[42,43] ionic conductivity, activation energy, and critical current density of the PMA-S/P-H complexed with ILs of different anions). Complexing the PMA-S/P-H with the ILs resulted in similar ionic conductivities (1.18~1.98 mS cm^{-1}) and activation energies (10.6~12.9 kJ mol^{-1}) regardless of anion species. On the other hand, CCD showed a significant dependence on the DN of anions (DN: $PF_6^- <$ TFSA$^- <$ FSA$^- <$ (EC/PC) $<$ OTf$^- <$ $N(CN)_2^-$). The CCD improved from 1.3 to 2.1 mA cm^{-2} with the increase of DN anions (from PF_6^- to FSA$^-$) but steeply decreased with OTf$^-$ and $N(CN)_2^-$ anions (0.4 and 0.1 mA cm^{-2}, respectively) which more strongly interact with Li$^+$ than the other three.[44,45]

The effect of the cationic species of the IL was examined in the same way (Figure 3b and Table S2), by incorporating six different cationic species (P_{12} (1-ethyl-1methylpyrrolidinium), P_{14}, PP_{14} (1-butyl-1-methylpiperidinium), EMI (1-ethyl-3-methyl-imidazolium), N_{4111} (butyltrimethylbutylammonium), and Phos$_{2225}$ (triethylpentylphosphonium)) with TFSA$^-$. Complexing the PMA-S/P-H with these ILs enhanced ionic conductivity (1.02~1.72 mS cm^{-1}) and lowered activation energy (10.6~12.8 kJ mol^{-1}) regardless of the cation species of the IL. Interestingly, the impact of cationic species on CCD is minimal because the organic cations interact with the anionic part of the SIC polymer, whereas the anionic species has a significant impact as they directly interact with lithium ions.[44,45]

Interaction between PMA-S/P-H and Ionic Liquids

IR and Raman spectra were recorded to verify the interaction of PMA-S/P-H and ILs in complex polymer electrolytes, using five ILs with varying anionic species. Firstly, in the case of $P_{14}PF_6$ (DN = −6.2 for PF_6^-), the band corresponding to the C=O stretching mode in PMA-S/P-H at 1572 cm^{-1} experienced a notable decrease in intensity upon complexation with the IL (Figure 4a) with the red-shift to 1564 cm^{-1}. This indicates that

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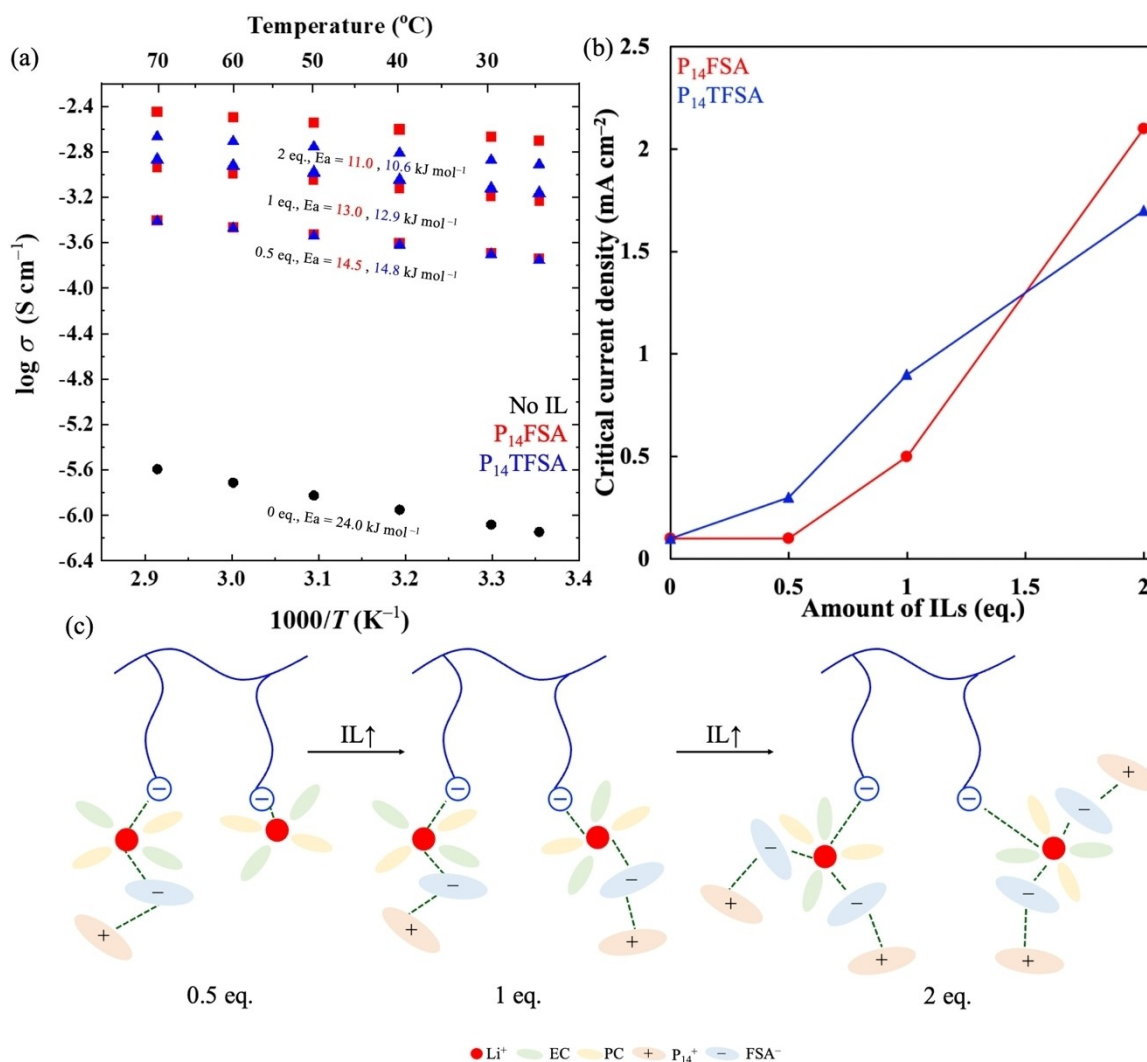Chemistry
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Figure 2. Effects of the amount of IL on (a) ionic conductivity and activation energy of PMA-S/P-H complexed with IL, (b) the relation of CCD against the amount of IL added to PMA-S/P-H, and (c) schematic diagram of the interaction between PMA-S and $P_{14}FSA$ IL.

the lithium ions from the SIC polymer interacted with the anions from ILs and pulled lithium ions out from the polymer chain. The complex polymer of other anions also showed the same trend except for $N(CN)_2^-$ (Figure S1). Moreover, the peak shift of anionic species was investigated by monitoring the peaks of key vibrational modes in Raman spectra. No significant peak shifts were observed for the PMA-S/P-H/IL electrolytes with PF_6^- and $TFSA^-$ anions according to the comparison of the Raman spectra of PMA-S/P-H/IL and IL (from 742 to 741 cm^- for the symmetric stretching mode of PF_6^- and from 741 to 740 cm^- for the S–N-S bending mode of $TFSA^-$) (Figure 4c,d). Although the overlap of the S–N-S bending mode of FSA^- (DN = 10.5) with the polymer peak makes the detailed dis-cussion difficult (Figure 4d), the absence of blue shift suggests FSA^- does not interact with Li^+.[46,47] In the complex polymer electrolyte preparation step, as the DN of the anion in the ILs increases, the anion more strongly attracts lithium ions, weakening the interaction between the PMA-S/P-H and lithium ions. Subsequently, when EC/PC (plasticizer) is added at the cell

stage, EC/PC (DN = 15.8) with the higher DN than PF_6^-, $TFSA^-$, and FSA^- of the IL preferentially coordinates with lithium ions, facilitating lithium ion conduction (Figure 5). Therefore, no peak shifts of these three anions were observed by forming the complex polymer.

In contrast, when using $P_{14}OTf$ IL, the peak corresponding to OTf^- anion (DN = 20.4) partly exhibits a blue-shift from 754 to 761 cm^{-1} for the CF_3 bending mode of OTf^- (Figure 4e). The OTf^- anion, which has a higher DN than EC/PC and effectively facilitates the release of lithium ions from the polymer chain, interacts too strongly with lithium ions and hinder lithium ion conduction.[44,45,48] As a consequence, the performance of CCD deteriorated with OTf^-. A blue shift from 664 to 668 cm^{-1} for the N-C-N bending mode of $N(CN)_2^-$ was observed in the case of $N(CN)_2^-$ (DN = 37.8), which even has the higher DN than OTf^- (Figure 4f). The $N(CN)_2^-$ anion exhibited even stronger inter-action with lithium ions than OTf^-, resulting in a lower CCD (Figure 5). These results suggest that using ILs with the lower DN than that of EC/PC is desirable to improve electrochemical
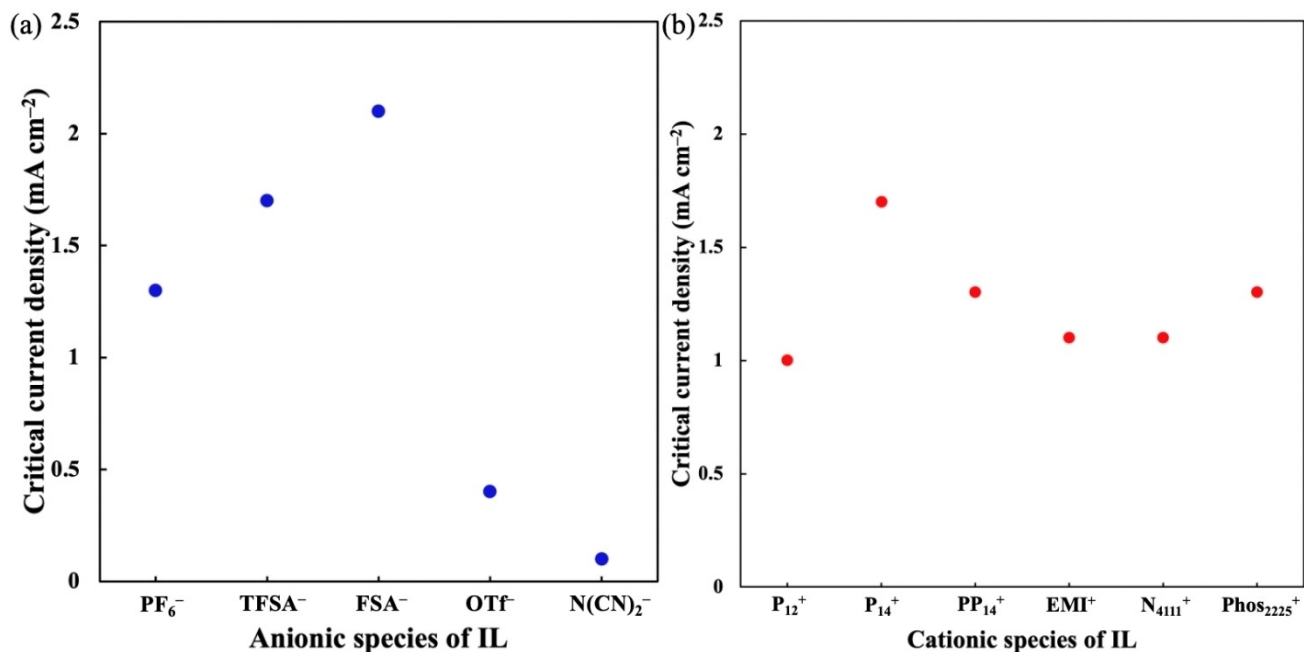
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Figure 3. Effect of ionic species of IL on the result of CCD measurements: (a) anionic and (b) cationic species.
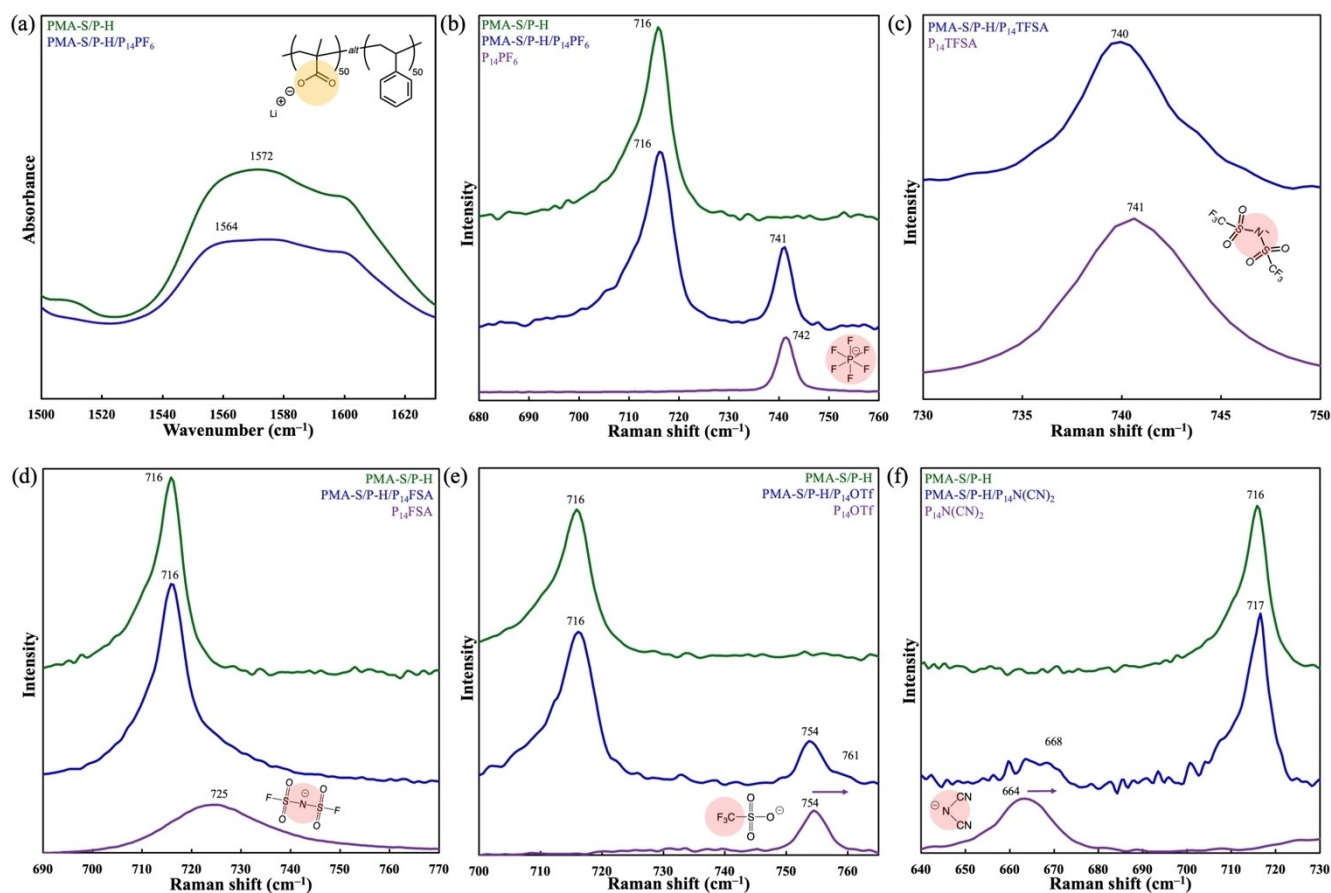

Figure 4. (a) IR spectra of PMA-S/P-H and PMA-S/P-H/IL for the C=O stretching mode of the carbonyl group in PMA-S/P-H. Raman spectra of the PMA-S/P-H/IL samples in the region for the peaks of (b) PF_6^-, (c) $TFSA^-$, (d) FSA^-, (e) OTf^-, and (f) $N(CN)_2^-$ anions.
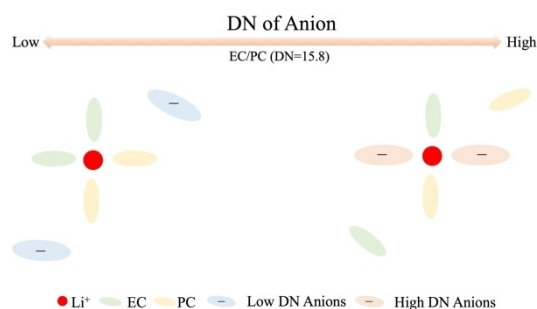
Figure 5. Schematic diagram illustrating the interaction between lithium ions and the donor number (DN) of the ILs.

properties. Among them, higher DN ($FSA^- > TFSA^- > PF_6^-$) was advantageous for improving CCD characteristics because they could strongly pull lithium ions from the anionic part of the polymer.[44,45,48] It should be noted that addition of only EC/PC does not lead to the increase of ionic conductivity or CCD. Existence of ILs is necessary to improve such performance.

Electrochemical Characterization of the Half-Cell

In order to demonstrate the performance of the present polymer complex electrolyte, the $Li|PMA\text{-}S/P\text{-}H/P_{14}FSA|LFP$ ($LFP = LiFePO_4$) half-cell was tested in the C-rate range from 0.1 to 6 C (voltage range of 2.41 and 4.01 V and temperature at
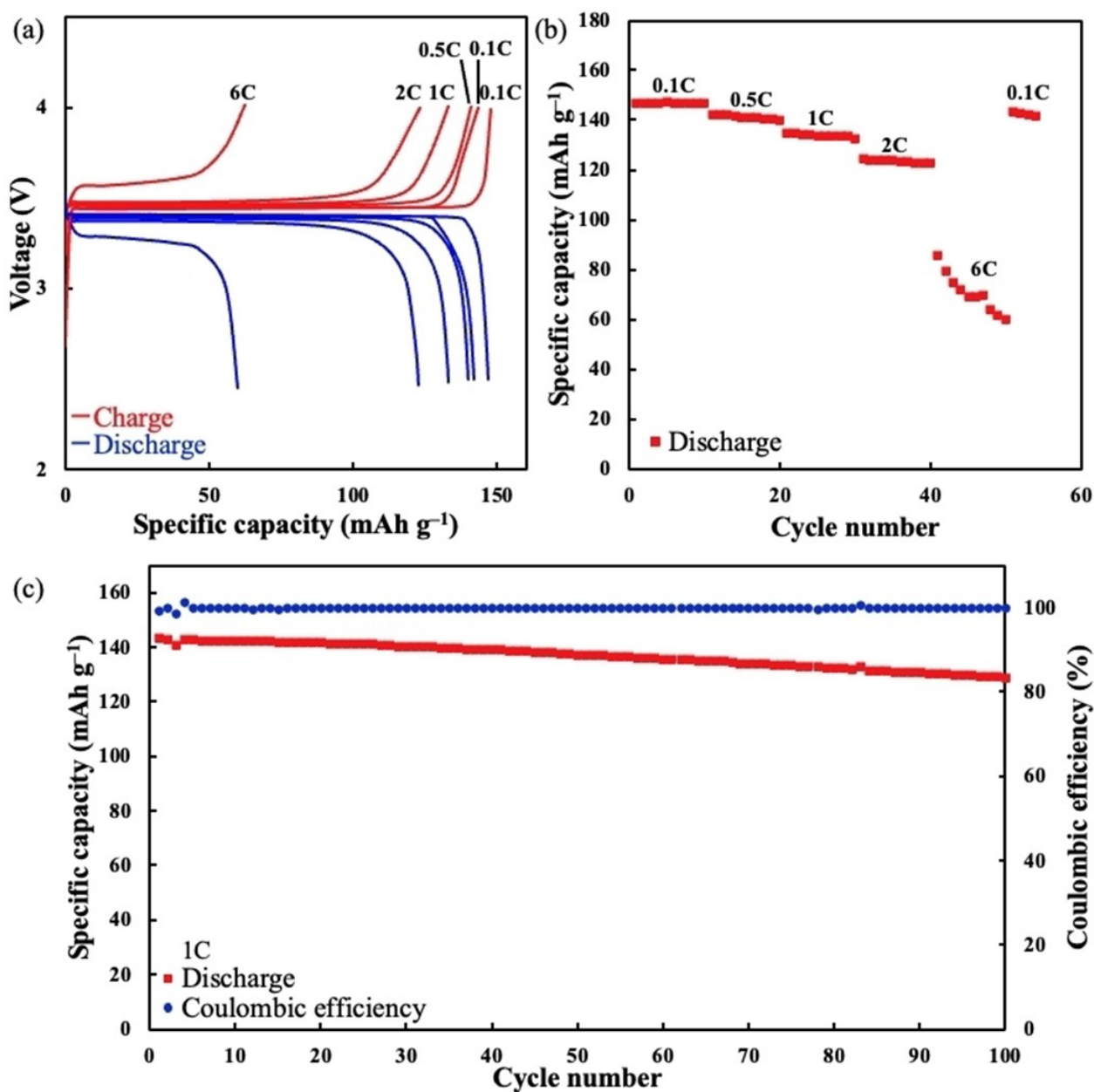

Figure 6. (a) Charge-discharge voltage profiles at different rates, (b) rate capability plot, and (c) long-term cycle performance at 1 C, 60 °C of $LFP|PMA\text{-}S/P\text{-}H/P_{14}FSA|Li$ metal half-cell.

60 °C). The resulting charge-discharge profiles are shown in Figure 6a and b. The cell exhibits an initial charge capacity of 150 mAh g^{-1} at 0.1 C. The stable charge-discharge cycles with minimal polarization in the polymer electrolyte was maintained until 2 C and high reversible capacities of 148, 141, 133, and 123 mAh g^{-1} are obtained after 10 cycles at 0.1, 0.5, 1, and 2 C, respectively. Although the cell shows some unstable behavior during charge-discharge at 6 C, high recuperation at 0.1 C after 6 C cycle is observed, exhibiting almost the same capacity as the initial one.

Figure 6c represents the cycle test at 1 C (the initial two and five cycles were performed at 0.1 C and 0.5 C, respectively, for cell activation). The initial discharge of 143 mAh g^{-1} maintained 89.9 % after 100 cycles with a high coulombic efficiency of 99.8 %. These results indicate that the composite polymer electrolyte composed of carboxylate-type SIC polymer and IL has a sufficient electrochemical performance and durability as electrolyte for LIBs.

Conclusions

In summary, a carboxylate-type SIC polymer, which faced limitations in dissociating lithium ions due to its strong basicity, showed enhanced conductivity by incorporating ILs with carbonate plasticizer. The electrochemical properties of the polymer electrolyte was substantially improved in proportion to the IL content. The SIC polymer exhibited markedly a low ionic conductivity and a CCD (0.1 mA cm^{-2}) without IL, whereas even with the addition of 0.5 eq. of IL (P$_{14}$FSA), the ionic conductivity was significantly enhanced from 7.13×10^{-4} to 0.18 mS cm^{-1}. Furthermore, when 2 eq. of IL was utilized, the ionic conductivity reached 2 mS cm^{-1} at room temperature and CCD current of 2.1 mA cm^{-2} was obtained. Additionally, the CCD of the composite electrolytes significantly depended on the DN of the anionic species of the utilized ILs; CCD was enhanced with increasing DN of the anions. However, there was a sudden decrease in CCD when anions with a higher DN than EC/PC (plasticizer) were employed due to the too strong interaction with lithium cation. Finally, the composite electrolytes demonstrated outstanding cycle stability (128.6 mAh g^{-1} at 1 C after 100 cycles) and excellent recuperation even after 6 C cycles in the Li/LFP cell. The complexation of the SIC polymer and IL allowed the promotion of lithium-ion dissociation and improvement of electrochemical properties as well as safety issues is expected to be a promising strategy of polymer electrolyte for lithium-ion batteries.

Experimental Section

Materials, preparation of polymer electrolytes and electrochemical measurements details are given in the Supporting Information.

Additional references cited within the Supporting Information.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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