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Short Communication

Chloride Ion Conducting Polymer Electrolytes Based on Cross-linked PMMA-$PP_{14}Cl$-$PP_{14}TFSI$ Ion Gels for Chloride Ion Batteries

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Chloride ion conducting polymer electrolytes based on cross-linked ion gels for chloride ion batteries were prepared by in-situ photo induced copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate cross-linker (EGDMA) in the presence of ionic liquid mixture, 0.5 M 1-butyl-1-methylpiperidinium chloride ($PP_{14}Cl$) in 1-butyl-1-methylpiperidinium bis-(trifluoromethylsulfonyl)imide ($PP_{14}TFSI$). The as-prepared ion gel membranes with 80 wt% chloride containing ionic liquid mixture are self-standing, flexible and transparent with superior thermal (up to about 340 ºC) and electrochemical stability (5.0 V vs. SS/SS). The ionic conductivity of chloride ion conducting IL-based gel polymer electrolytes (IL-GPEs) reached 0.9×10^{-4} S cm^{-1} with 80 wt% ionic liquid mixture at 25 ºC. Preliminary charge and discharge testing has demonstrated the feasibility of using chloride ion conducting IL-GPEs for chloride ion batteries.

Keywords: Ion gel; polymer electrolyte; chloride ion battery; ionic liquid

1. INTRODUCTION

In spite of rechargeable batteries based on cation transfer such as Li^+, Na^+ [1,2], Chloride ion battery (CIB) and fluoride ion battery using anion such as F^- or Cl^- as the transfer ion were also developed [3,4]. The use of Cl^- as the transfer ion for constructing CIB is an interesting approach owing to the high theoretical energy density and abundant material resources [4]. A key challenge is the development of chloride ion conducting electrolytes with high ionic conductivity. Solid inorganic chloride conductors such as $PbCl_2$, $SnCl_2$, and LaOCl transfer chloride at very high temperature. Until now, aprotic chloride ionic liquids with cations of imidazolium, pyrrolidinium, piperdinium, pyridinium, and quaternary ammonium which supply chloride sources and some ionic liquids with similar cations but different anions such as BF_4^-, PF_6^-, and $[N(CF_3SO_2)_2]$ or propylene carbonate solvent as plasticizer were usually used together as liquid electrolytes in CIBs. Although the liquid electrolytes have high conductivity, they bear the high risk of leakage, volatility and flammability. Another big issue in CIB is Lewis acidic metal chloride (e.g., $FeCl_3$ or $CuCl_2$) cathodes can react with Lewis base electrolyte that contains chloride ions, resulting in dissolution of cathodes into the ionic liquid electrolyte [4-6].

To solve this problem, metal oxychlorides such as FeOCl and $VOCl_x$, which are more stable than metal chlorides, have been investigated to be new cathode materials for CIBs [7-11]. Besides the optimization on the cathodes, the development of polymer electrolyte is very promising to improve the performance of CIBs. Chloride conducting solid polymer electrolyte membranes prepared by mixing polyvinyl chloride, commercial gelatin, or polyvinyldifluoride-hexafluoropolymer with solid chloride-containing salts, such as tetrabutylammonium chloride, was used to construct solid state chloride ion batteries very recently [12]. However, the conductivity of the solid polymer electrolyte is rather low compared to chloride containing ionic liquid mixture and electrochemical reactions can only occur at the electrode-electrolyte interphase in solid-state chloride-ion batteries. Another approach can be the immobilization of the chloride containing ionic liquid mixture into polymer matrices to form IL-based gel polymer electrolytes (IL-GPEs). GPEs are widely studied for constructing highly safe lithium ion and Li-S batteries with high performance [13-14]. Despite the flexibility, leakage prevention, safety, and simple processing of GPEs, IL-GPEs endow the merits of ionic liquids such as high ionic conductivity, non-flammability, good thermal and electrochemical stability to batteries [14].Moreover, as an intermediate state between ionic liquid mixture and solid chloride IL salt, IL-GPEs have higher ionic conductivity at room temperature and better electrode-electrolyte compatibility than solid polymer electrolyte.

IL-based polymer electrolytes can be prepared through doping of polymers with ILs or in situ polymerization or cross-linking of monomers in ILs [15]. Cross-linking is an efficient approach for trapping large amount of ionic liquid to obtain high ionic conductivity as well as maintain good mechanical strength of IL-GPEs [14,18]. Ion gels synthesized by in situ cross-linking of a series of vinyl monomers with ILs in the presence of cross-linker were first developed by Watanabe group. The ionic conductivity of these cross-linked ion gels increased with an increasing ILs content and reached a value higher than 1 mS cm^{-1} at ambient temperature [16,17]. One issue needs to be considered is the carefully chosen of monomer in order to get ion gels with completely compatible of ionic liquid and polymer [19].

To the best of our knowledge, no work has been reported on chloride conducting IL-GPEs. The main objective of this study is to develop chloride ion conducting IL-based polymer electrolytes for CIBs. The IL-based polymer electrolytes were obtained by in situ photo induced chemical cross-linking of MMA and EGDMA in the presence of chloride containing ionic liquid mixture $PP_{14}Cl/PP_{14}TFSI$. Ionic liquid acts as a good plasticizer as well as a supplier of chloride ion. Then thermal property, ionic conductivity, and electrochemical properties of the as-prepared chloride ion conducting IL-based polymer electrolytes were investigated.

2. EXPERIMENTAL

2.1 Materials

MMA and EGDMA (Aladdin) were distilled under reduced pressure before use. Chloride containing ionic liquid mixture was made by dissolving 0.5M 1-Butyl-1-methylpiperidinium chloride ($PP_{14}Cl$) in 1-Butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide ($PP_{14}TFSI$) [7]. The chloride ion conducting IL-GPE membranes were prepared by in situ photo polymerization. First, MMA (100 mg, 1.00 mmol), EGDMA (50 mg, 0.25 mmol), 0.5M $PP_{14}Cl/PP_{14}TFSI$ (70 wt%, 80 wt%, 90 wt% of total components), and 2,2-diethoxyacetophenone (0.5 mol % to a total mole amount of the acrylate moiety) were mixed together until a transparent and homogenous solution was formed. The above solution was degased and poured into a mold. Self-standing cross-linked polymer membranes were obtained by UV-irradiation to the mixture using a mercury lamp (Maxima ML-3500C, SP) for 15 min.

2.2 Methods

A mold for synthesis of cross-linked polymer membrane by in-situ photo polymerization was prepared as follows. A silicone rubber spacer (0.3 mm in thickness) which has 55 mm×18 mm wide space was sandwiched between two pieces of slide glass (76mm×26 mm, 1.2-1.5 mm in thickness) covered with PTFE tape. The mold was fixed with two clips.

The morphology of IL-based polymer electrolytes membrane was observed by Field Emission Scanning Electron Microscopy (FESEM, Merlin Compact). FT-IR spectra were recorded on a NEXUS 670 spectrometer (Nicolet) equipped with an attenuated total reflectance (ATR) accessory. X-ray Powder Diffraction (XRD) was performed using a Rigaku SmartLab Diffractometer with Cu-Kα radiation. Differential Scanning Calorimetry (DSC) measurements were carried out in the temperature range from -80 ºC to 150 ºC at a scanning rate of 10 ºC min^{-1} by using a Q2000 DSC instrument. Thermogravimetric analysis (TGA) was performed from room temperature to 600 ºC at a heating rate of 10 ºC min^{-1} under nitrogen atmosphere with a NETZSCH instrument STA449C.

Ionic conductivity of pure $PP_{14}TFSI$, 0.5M $PP_{14}Cl/PP_{14}TFSI$ and IL-GPE ($\sigma_{IL\text{-}GPE}$) was measured in a Swagelok cell with two parallel stainless steel electrodes by the electrochemical impedance spectroscopy (EIS) method. Impedance data were obtained under an electrochemical working station CHI660Di in the frequency range of 1 Hz-100 kHz between 25 and 100 °C. Ionic conductivity of $PP_{14}TFSI$, 0.5M $PP_{14}Cl/PP_{14}TFSI$ was calculated based on Eq. (1). The conductivity of IL-GPEs can be calculated from Eq. (2) from the known area and thickness of the GPE membranes:

$$\sigma_{IL} = \frac{1}{R_b k} \tag{1}$$

$$\sigma_{ILGPE} = \frac{l}{R_b A} \tag{2}$$

Where k is the cell constant (cm^{-1}), l is the electrolyte thickness (cm), A is the activity area (cm^2) and R_b is the resistance of the electrolyte (Ω).

Electrochemical stability window (ESWs) of chloride containing ionic liquid mixture and IL-GPEs were evaluated on SS ||IL GPE||SS cell by linear sweep voltammetry (LSV) on biologic VMP-3

(Biologic, France) at 25 ºC at sweep rate of 5 mVs^{-1}. The coin cell was assembled by sandwiching the IL-GPE between the lithium anode and the FeOCl cathode. The preparation of FeOCl/carbon composite materials and the fabrication of the cathode electrodes were reported in the previous work [11]. All battery-assembly was conducted in a dry argon atmosphere glovebox. All the cell components were vacuum-dried before they were introduced to the glove box. Discharge and charge tests were carried out galvanostatically at 10 mA g^{-1} over a voltage range between 1.6 and 3.5 V by using biologic VMP-3 (Biologic, France) at 25 ºC.

3. RESULTS AND DISCUSSION

Fig.1a shows schematic illustration of preparation of chloride ion conducting IL-GPEs by in situ crosslinking polymerization. Highly transparent, freestanding, non-porous and extremely flexible IL-GPEs membranes were obtained (Fig.1a and 1b), indicating good compatibility between chloride containing ionic liquid mixture and the choosing PMMA polymer. The absence of absorption at 1640 cm^{-1} corresponding to C=C double bond stretching of EGDMA in FTIR spectroscopy demonstrated a well-cross-linked IL-GPEs (Fig.1c). XRD characterization confirmed increased amorphous phase of the IL-GPEs compared to PMMA matrix and thus the improvement in ionic conductivity of IL-GPEs could be expected [20] (Fig.1d).

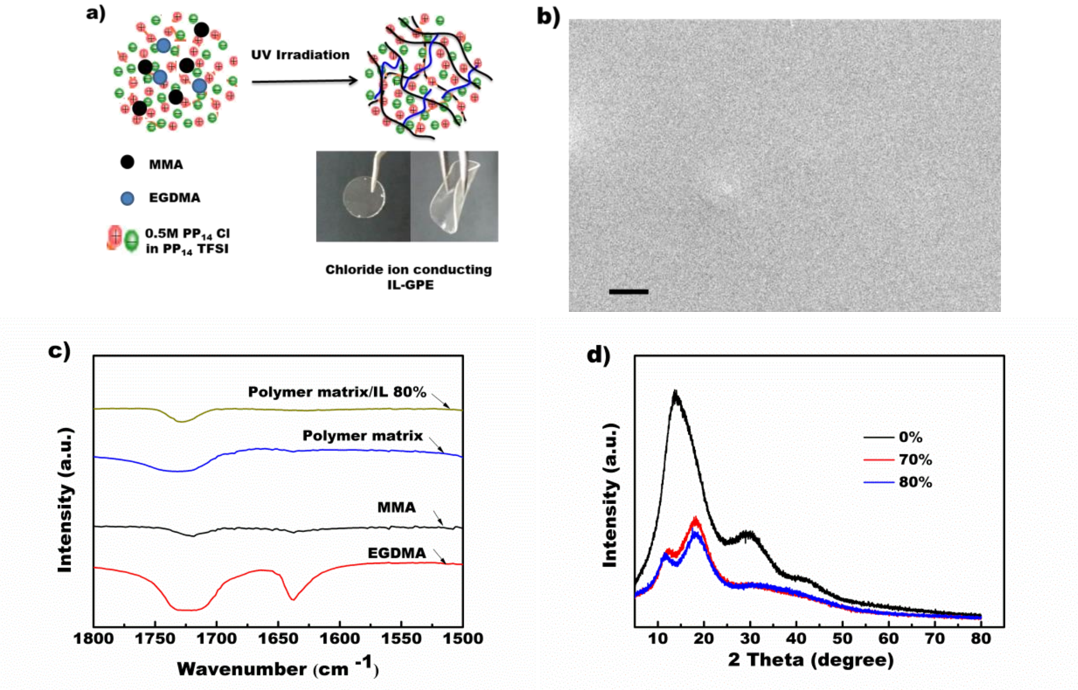

Figure 1. (a) Schematic illustration of preparation and photos for IL-GPEs membranes; (b) SEM image of IL-GPE membrane with 80 wt% ionic liquid; (c) FT-IR spectra of MMA and EGDMA before and after UV-crosslinking in IL-GPE; and (d) XRD pattern of the IL-GPEs.

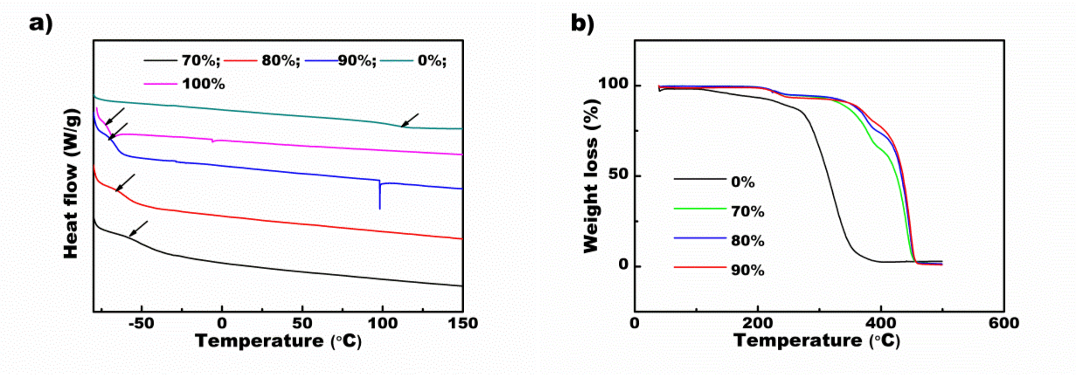

Figure 2. (a) DSC and (b) TGA curves of IL-GPEs. Scan rate: 10 ºC min^{-1}.

As evaluated by DSC (Fig.2a), the PMMA bulk exhibits glass transition temperature (T_g) at around 105.4 ºC. The chloride containing ionic liquid mixture (0.5M PP14Cl/PP14TFSI) shows T_g at -71.57 ºC. When the chloride containing ionic liquid mixture reaches 70 wt%, 80 wt% and 90 wt%, T_g of the IL-GPEs shifted to -57.2 ºC, -64.9 ºC and -69.3 ºC, respectively. This drop in T_g can be attributed to the plasticizing effect of the binary ionic liquid mixture in IL-GPE electrolytes which enhances the segmental motion of the PMMA chains. Chloride ion conducting IL-GPE membranes are thermally stable up to about 340 ºC as shown by TGA curves which is much higher than the previous solid polymer electrolyte [12] (Fig. 2b). The developed IL-GPEs were promising polymer electrolytes for very safe chloride ion batteries.

Ionic conductivity of chloride containing ionic liquid mixture and IL-GPEs were investigated by using electrochemical impedance spectroscopy (EIS). Chloride ion conducting IL-GPEs show similar Nyquist plots with the chloride containing ionic liquid mixture as shown in Fig.3a. The intercept on the real axis gives the bulk resistance of the electrolyte [21]. Ionic conductivities of the $PP_{14}TFSI$ and the chloride containing ionic liquid mixture are 1.2×10^{-3} S cm^{-1} and 5.4×10^{-4} S cm^{-1} at 25 ºC, respectively. The ionic conductivity reduction of chloride containing ionic liquid mixture is ascribed to the decrease of ion mobility resulted from an increase in viscosity of the system [22]. Ionic conductivity of IL-GPEs reach the value of 0.9×10^{-4} S cm^{-1} with 80 wt% and 3.99×10^{-4} S cm^{-1} with 90 wt% ionic liquid at 25 ºC (Fig.3b and Table 1), which are comparable to that of 0.5M $PP_{14}Cl/PP_{14}TFSI$ ionic liquid mixture (5.4×10^{-4} S cm^{-1}) and much higher than the previous solid polymer electrolyte (10^{-7} S cm^{-1}~10^{-4} S cm^{-1}) [12].

Ionic conductivity of chloride containing ionic liquid mixture and IL-GPEs increases with increasing temperature due to faster migration of carrier ions and easier motion of PMMA segments at higher temperature (Fig.3b). The temperature dependence of ionic conductivity follows Arrhenius equation in the temperature range of 25-100 ºC.

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{RT}\right) \qquad (3)$$

where σ is the conductivity, E_a is apparent activation energy, R is the gas constant. E_a can be calculated from Eq. (3) and the values are 9.74, 8.85, 6.84 kJ mol^{-1} with 70 wt%, 80 wt%, 90 wt% of the chloride-containing ionic liquid mixture, respectively (Table 1). The data are slightly lower than that of the reported lithium ion conducting ionic liquid polymer electrolyte [21]. The enhancement in conductivity and decrease of E_a by increasing the ionic liquid content was consistent with the decreased T_g derived from DSC analysis, which indicates easier ion transport due to increased ion carrier number and the plasticization effect of ionic liquid [20,24].

The electrochemical stability window of IL-GPE with 80 wt% ionic liquid has been found in the range of -2.5 to 2.5 V (vs. SS) at 25 ºC, which is wider than that of the liquid electrolyte (Fig.3c). It promises that the developed IL-GPEs have suitable electrochemical stability to be used in CIBs. Fig.3d shows the preliminary result of charge-discharge profiles of Li||FeOCl CIB cell assembled with chloride ion conducting IL-GPE containing 80 wt% ionic liquid. It should be noted that as the content of the chloride-containing ionic liquid mixture increased above 80 wt%, the IL-GPE membrane became sticky and fragile and is difficult to be handled in assembling battery. The FeOCl cathode delivers an initial discharge capacity of 60 mAh g^{-1} and 122 mA h g^{-1} after 7 cycles with chloride ion conducting IL-GPE at 80 wt% ionic liquid. Discharge capacities of the cells increased upon cycling, which can be ascribed to the crosslinking nature of the current ion gel electrolyte and the gradually optimization of the electrode-electrolyte interface [25]. Such preliminary charge and discharge results demonstrated chloride ion conducting IL-GPEs as feasible novel electrolyte in CIB systems. Further studies related to utilization of IL-GPEs in metal chloride cathode CIB systems are underway.

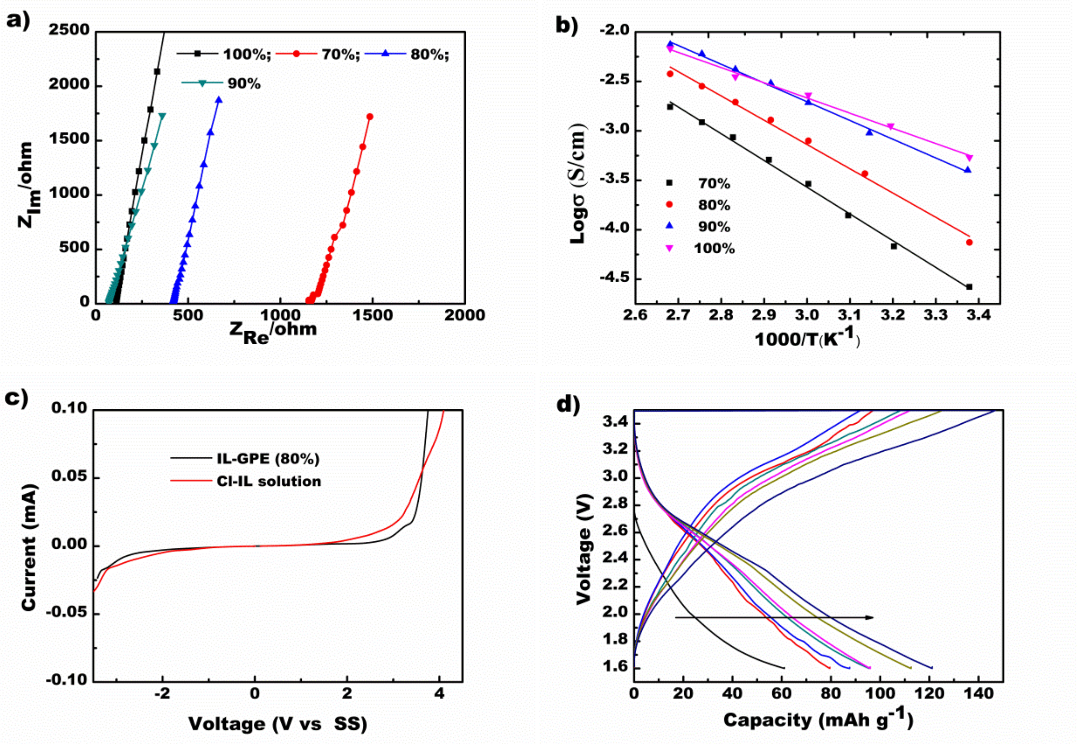

Figure 3. (a) Nyquist plots at 25 ºC, (b) the ionic conductivity determined from the Nyquist impedance data at different temperatures and (c) linear sweep voltammograms at 25 ºC (SS||IL-GPE||SS cells, scan rate: 5 mV s^{-1}) for chloride containing ionic liquid mixture and IL-GPEs; (d) Charge-discharge profiles for the Li||FeOCl Cell using IL-GPE with 80 wt% chloride containing ionic liquid mixture.

Table 1. Ionic conductivity and activation energy E_a of ionic liquids and IL-GPEs.

	σ (S cm^{-1}) at r.t.	E_a(kJ mol^{-1})
$PP_{14}TFSI$	1.2×10^{-3}	-
0.5M $PP_{14}Cl/PP_{14}TFSI$	5.4×10^{-4}	2.94
IL-GPEs 90 wt%	3.99×10^{-4}	6.84
IL-GPEs 80 wt%	0.9×10^{-4}	8.85
IL-GPEs 70 wt%	3.39×10^{-5}	9.74
Chloride conducting solid polymer electrolyte (PVC, gelatin or PVDF-HFP with solid chloride IL)	10^{-7}~10^{-4}	-

4. CONCLUSIONS

Chloride ion conducting IL-GPEs based on cross-linked PMMA-$PP_{14}Cl$-$PP_{14}TFSI$ ion gels were developed and investigated for using in CIBs. The obtained IL-GPEs membranes were free-standing, transparent and flexible with superior thermal and electrochemical stability. Chloride ion conducting IL-GPE membranes are thermally stable up to about 340 ºC as shown by TGA. Chloride ion conducting IL-GPE showed high ionic conductivity of 0.90×10^{-4} S cm^{-1} with 80 wt% chloride containing ionic liquid mixture and electrochemical stability up to 5.0 V vs. SS/SS at 25 °C. The assembled cell consisting of the Li||IL-GPE|| FeOCl exhibited high capacity above 122 mAh g^{-1} after 7 cycles at C/25 rate. The results demonstrated that it could be very promising for using chloride ion conducting IL-based gel polymer electrolytes in CIBs.

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