

Proton conducting ionic liquid electrolytes for liquid and solid-state electrochemical pseudocapacitors



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ABSTRACT

Proton conducting polymer electrolytes employed in many electrochemical pseudocapacitors are typically based on aqueous systems, which limit the operating potential and temperature range of these energy storage devices. In this study, we developed non-aqueous polymer electrolytes based on protic ionic liquids (PIL). We relied on cationic substitution to obtain proton conducting yet environmentally benign non-fluorinated ionic liquids. By developing binary systems of PILs with different cations, eutectic compositions of PILs with drastically lowered melting points were demonstrated. Through thermal analyses of these binary systems, phase diagrams were constructed which allowed us to obtain eutectic binary PIL mixtures exhibiting a liquidus range from $-70\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$. These eutectic PIL mixtures were incorporated into polymer systems to develop non-aqueous thin film proton-conducting polymer electrolytes for solid pseudocapacitors. The proton conductivity of the eutectic ionic liquids was observed in the polymer electrolyte systems and promoted pseudocapacitive behavior in solid and liquid capacitor cells.

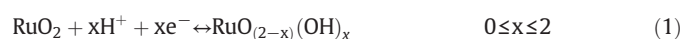
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1. Introduction

Polymer electrolytes are key enablers for solid, thin, flexible, and wearable electrochemical energy storage devices such as batteries and electrochemical capacitors (ECs). Acting as a separator and ionic conductor, they allow lightweight designs and prevent leakage of liquid electrolytes. Most current liquid electrolytes are limited either by their operating potential (around 1.2 V) and low thermal stability in aqueous media, or by the volatility and flammability of organic media. Ionic liquids (ILs) exhibit good ionic conductivity, low volatility, and a wide electrochemical potential window [1,2]. They can also be incorporated into polymer electrolytes as ionic conductors and plasticizers [3–5]. Protic ILs (PILs) are a class of ILs that contain protonated species and are proton conductive, while most ILs are aprotic and are not proton conducting.

Research on IL-based polymer electrolytes for ECs often focuses on electrochemical double-layer capacitors (EDLCs) using fluorinated aprotic ILs [6–9]. While EDLCs have limited charge storage capacity, fluorinated ILs can generate toxic and reactive products that are environmentally undesirable [10–12]. Two approaches that could mitigate these issues are leveraging pseudocapacitive materials to supplement or replace EDLCs, and developing environmentally benign non-fluorinated ILs to be implemented in polymer electrolytes.

Pseudocapacitors are attractive due to their higher specific capacitance over that of EDLCs, but many are only active in specific electrolytes. For example, RuO_2 , a well-known pseudocapacitive material, stores and releases charge via continuous change of oxidation states facilitated by proton exchange according to reaction (1) [13]:



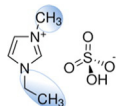
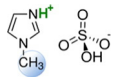
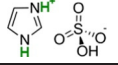
To enable reaction 1 in polymer–IL electrolytes, proton-conducting ILs or PILs are required. So far, there are limited studies demonstrating the pseudocapacitive electrodes such as RuO_2 [14,15], MnO_2 [16], and carbon electrodes containing surface functionalities [17] in PILs, and fewer on environmentally benign non-fluorinated PILs. Among reported PILs, 1-ethyl-3-methylimidazolium hydrogen sulfate (EMIHSO_4) appears to meet both requirements of being protic and environmentally benign. It has also been extensively studied in polymer electrolyte [18–22]. However, although EMIHSO_4 exhibits proton conducting characteristics [20,21], these protons are merely produced by the relatively weak dissociation of HSO_4^- and the EMI cation is inactive for proton production.

To obtain a non-fluorinated protic IL, we attempted to increase the proton conductivity of EMIHSO_4 by cationic substitution. The cations were tailored by varying the alkyl groups of the imidazolium ring and by introducing proton functionalities. The structures of the investigated ILs are depicted in Table 1, in which the alkyl chains of the EMI cation were substituted with hydrogen to increase the proton activity in 1-methylimidazolium hydrogen sulfate (MIHSO_4) and imidazolium

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Table 1
Structure and melting temperature of PILs with different cations.

| Ionic liquid | Structure | Melting point (°C) |
|--|---|--------------------|
| 1-Ethyl-3-methylimidazolium hydrogensulfate (EMIHSO ₄) |  | 24 |
| 1-Methylimidazolium hydrogensulfate (MIHSO ₄) |  | 47 |
| Imidazolium hydrogensulfate (ImHSO ₄) |  | 85 |

hydrogen sulfate (ImHSO₄). Imidazole (Im) is a self-dissociating compound with high proton conductivity in the liquid state [1,23]. While these PILs are promising, their high melting temperatures (Table 1) prevent their application at room temperature or below. One way to alleviate this problem is to introduce external ions to lower the melting point, e.g., by developing eutectic mixtures of ILs [24–29]. Extended operating temperatures from –50 °C to 100 °C for EDLCs were reported by Lin et al. [30] using a eutectic mixture comprised of piperidinium and pyrrolidinium-based ILs.

Therefore, it is our intention to leverage this method to develop PILs for non-aqueous non-fluorinated polymer–PIL electrolytes to enable solid-state pseudocapacitors. Our investigation proceeded in 2 steps:

- Reducing the melting point of these PILs by developing eutectic compositions of binary MIHSO₄–ImHSO₄ and EMIHSO₄–ImHSO₄ PIL systems and constructing phase diagrams to identify their respective operating temperatures.
- Confirming the relative proton activity of eutectic binary MIHSO₄–ImHSO₄ and EMIHSO₄–ImHSO₄ in comparison to EMIHSO₄ and demonstrating their proton conducting characteristics in both liquid and polymer electrolyte-enabled devices utilizing pseudocapacitive electrodes.

2. Experimental

2.1. Ionic liquids

Three ILs (shown in Table 1) were studied in this work: 1-ethyl-3-methylimidazolium hydrogen sulfate (EMIHSO₄, 95%), 1-methylimidazolium hydrogen sulfate (MIHSO₄, 95%), and imidazolium hydrogen sulfate (ImHSO₄). While EMIHSO₄ and MIHSO₄ were purchased from Sigma-Aldrich, ImHSO₄ was synthesized by the reaction of sulfuric acid with imidazole (99% Alfa Aesar) in the following steps:

- Dissolving imidazole (i.e., the base) (24.94 g, 0.37 mol) in water;
- Adding an equimolar amount of sulfuric acid (97–98% in water) (35.88 g, 0.37 mol) dropwise to the base solution under stirring for about 1 h at below 35 °C;
- Stirring the mixture for 4 h at room temperature, and then drying at 70 °C under vacuum for 48 h to obtain the final product of a crystalline powder (55.41 g, yield 91%).

EMIHSO₄ and MIHSO₄ were also vacuum dried at 70 °C for 48 h to remove any trace water and were stored in a nitrogen atmosphere glove box (H₂O < 1 ppm). No water signal was detected in the pure ILs according to FTIR.

2.2. Liquid electrolytes

Liquid binary IL mixtures were developed by combining two pure ILs at various weight ratios. These mixtures were then heated above their melting point while stirring until a homogeneous liquid was formed.

2.3. Polymer electrolytes

The polymer electrolytes used in this study and their compositions are summarized in Table 2. The polymer matrix was poly(ethylene oxide) (PEO, MW = 1,000,000 Alfa Aesar). The PEO-based electrolytes were prepared by solution casting following the procedure reported in [18,19]. PEO powder was dissolved with stirring and heating at 50 °C in a mixed solvent of PC and MeOH with weight ratio of 1.8:1. After the formation of a polymer gel, IL was added to reach a polymer–IL weight ratio of 1:3. This precursor solution was held at 50 °C with stirring for 2 h before being cast onto a glass petri dish. This was followed by heating and vacuum drying to form a free-standing film.

2.4. Electrode and cell assembly

Two types of electrodes were used in this work: RuO₂ as pseudocapacitive electrode and titanium (Ti) as double-layer electrode. RuO₂ is the best known pseudocapacitive material active in protic media. RuO₂ was coated on a 25 μm thin Ti foil processed similarly to a dimensionally stable anode with a loading of 1.5 mg cm^{–2}, resulting in a capacitance of ca. 170 mF cm^{–2} in 1 M H₂SO₄ electrolyte for a single electrode. The electrochemical behavior of these electrodes in aqueous electrolyte was reported elsewhere [31].

The performance of the pure ILs and the binary IL mixtures were characterized in a two-electrode cell configuration in which a filter paper (Whatman® cellulose filter paper, medium porosity, thickness 150 μm) separator was soaked with electrolyte, and then sandwiched between the electrodes. Solid-state cells were fabricated by sandwiching the polymer electrolytes between two electrodes. These cells were further protected with electroplating tape and then sealed by PET SelfSeal™ lamination.

2.5. Characterization of electrolytes

The electrochemical performance of the electrolytes and the cells was evaluated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using a Princeton Applied Research VersaSTAT 3 potentiostat. EIS was measured at a voltage amplitude of ± 10 mV and a frequency range from 0.01 Hz to 100 kHz. The conductivity of the electrolytes was measured using titanium electrodes in a two-electrode configuration using a beaker cell, and the resistivity values of the electrolytes were extracted from impedance analyses. The capacitance of the cells was obtained by integrating the charge from the CV measurements divided by voltage. The preparation of the liquid and the polymer electrolytes, assembly of the cells, and the electrochemical measurements were all performed inside a nitrogen atmosphere glove box.

Thermal characterization was performed using differential scanning calorimetry (DSC) on a TA Instruments Q20 DSC. 5–10 mg samples of the pure IL or the equilibrated binary mixtures were placed in

Table 2
Polymer electrolytes and their composition.

| Denotation | Type | Composition |
|---|---|---|
| PEO–MIHSO ₄ –ImHSO ₄ | Polymer electrolyte incorporating MIHSO ₄ –ImHSO ₄ eutectic liquid electrolyte | 1:3 weight ratio of polymer to total IL |
| PEO–EMIHSO ₄ –ImHSO ₄ | Polymer electrolyte incorporating EMIHSO ₄ –ImHSO ₄ eutectic liquid electrolyte | 1:3 weight ratio of polymer to total IL |

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