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"Water-in-ionic liquid" solutions towards wide electrochemical stability windows for aqueous rechargeable batteries

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ABSTRACT

Several hydrophilic ionic liquids dissolved in water with different molalities are studied as "water-in-ionic liquid" supporting electrolytes. They exhibit wide electrochemical stability window from 3 to 4.4 V, high ionic conductivities and good flowability, making them promising supporting electrolytes for aqueous high-voltage rechargeable batteries. In such supporting electrolytes, enhanced redox activities of lithium insertion/extraction in anodic TiO_2 film at low negative potential and Fe^{3+}/Fe^{2+} couple at moderate positive potential were observed. Cyclability of an aqueous TiO_2/Fe^{2+} hybrid battery is demonstrated with a voltage of 1.7 V.

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1. Introduction

Aqueous rechargeable batteries have drawn considerable attention with advantages of non-flammability, low cost and high ionic conductivity [1,2]. Commercial aqueous batteries typically use toxic heavy metal compounds and corrosive species, which are harmful to the environment. For instance, lead-acid batteries and vanadium redox flow batteries use sulfuric acid as supporting electrolytes [3], whereas nickel-cadmium batteries utilize an alkaline solution. Generally, aqueous rechargeable batteries have output voltages less than 1.5 V due to the limitation of the electrochemical stability window (ESW) of water (thermodynamically 1.23 V) [4—7]. By suppressing the hydrogen and oxygen evolution reactions, high operation voltages are accessible in specific cases. In lead-acid batteries, an electronically insulating dense $PbSO_4$ layer on the lead anode suppresses the hydrogen evolution to realize an output voltage of 2 V [8,9]. In nickel-cadmium batteries, a

passivated layer increases the overpotential of oxygen evolution [9]. Recently, Suo et al. reported an aqueous lithium-ion battery with a voltage of 2.3 V using a "water-in-lithium salt" electrolyte [10]. Yamada et al. developed aqueous batteries with voltage about 3.1 V using hydrate-melt electrolytes [11]. These work opens new avenues to develop aqueous high-voltage rechargeable batteries [12].

Ionic liquids are widely studied in electrochemical applications owing to their nonvolatility, ionic mobility, and thermal, chemical and electrochemical stability [13—16]. Room temperature ionic liquids have wide ESWs and are good alternatives as supporting electrolytes for electrodeposition [14,17], supercapacitors [18], fuel cells [14] and rechargeable batteries [13,19]. Interestingly, highly hydrophilic ionic liquids with high melting points beyond room temperature can be dissolved in water to form "water-in-ionic liquid" electrolytes [20]. In aqueous media, they permit higher ionic conductivity and lower viscosity for practical applications. It is unclear yet how the cationic and anionic groups of different ionic liquids can affect the ionic conductivities as well as ESWs. Moreover, it is highly desirable to find suitable redox couples for aqueous high-voltage lithium-ion batteries [13] and redox flow batteries [20,21].

Herein, we investigate the ESWs and ionic conductivities of "water-in-ionic liquid" solutions for several representative ionic

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liquids with different molalities. With LiCl as lithium source in the supporting electrolytes and a Cl^- conducting membrane, we demonstrate an aqueous TiO_2/Fe^{2+} hybrid battery in "water-in-ionic liquid" solutions with high voltage and areal capacity. It is well known that titanium oxide (TiO_2) with different polymorphs can work as anode materials for lithium insertion/extraction owing to their low cost and structural integrity [22]. Interestingly, low negative potential for lithiation reaction in anatase TiO_2 is accessible in our aqueous supporting electrolytes. Ferrum-based compounds attract extensive interests because they are cheap, non-toxic and electrochemically reversible [7,23]. The ionic liquid environment can also remarkably promote the redox kinetics for Fe^{3+}/Fe^{2+} couple reaction at a moderate positive potential in the catholyte.

2. Experimental

2.1. Chemicals

Ionic liquids including 1-ethyl-3-methylimidazolium chloride (EMImCl, Acros Organics, 97%), 1-butyl-3-methylimidazolium chloride (BMImCl, Aldrich, 98%), tetraethylammonium chloride (TEACl, Alfa Aesar, 98%), tetrabutylammonium chloride (TBACl, Aldrich, 98%), 1,2,3-trimethylimidazolium methyl sulfate (TriMImMeSO$_4$, Alfa Aesar, 95%) and 1-ethyl-2,3-dimethylimidazolium ethyl sulfate (EMMImEtSO$_4$, Fluka, 94.5%) were used as received. Ammonium fluoride (Sigma Aldrich, 98%), ethylene glycol (Alfa Aesar, 99%) and titanium foil (127 μm thick, Sigma Aldrich, 99.7%) were used to prepare anodic titanium dioxide. Lithium chloride (Sigma Aldrich, 99%), ferrous chloride tetrahydrate (Acros Organics, 97%) and hydrochloric acid (VWR, 37%) were used as additives for aqueous electrolytes. All chemicals were used without further purification.

2.2. Preparation and characterization of "water-in-ionic liquid" solutions

Ionic liquids were dissolved in deionized water at different molalities (from 5 m to 20 m, i.e., molality of 5 m means 5 mmol of ionic liquid dissolved in 1 mg of water.) as "water-in-ionic liquid" solutions. The ionic conductivities of "water-in-ionic liquid" solutions was measured by a WTW Cond 3110 conductivity meter equipped with TetraCon® 325 (Xylem, Germany). The ESWs were investigated by cyclic voltammetry (CV) with a Biologic VMP3 potentiostat in a three-electrode system. Glassy carbon rod, Pt foil and Ag/AgCl electrode were used as working electrode, counter electrode and reference electrode, respectively. CV measurements were conducted at a moderate scan rate of 20 mV s^{-1} to examine the ESWs and to minimize the influence of uncompensated ohmic drop.

2.3. Preparation and characterization of anodic titanium dioxide

Anodic titanium dioxide (ATO) was prepared in ethylene glycol containing 0.3 wt% NH$_4$F and 2 v% H$_2$O under 60 V for 6 h at room temperature, using titanium foil and graphite electrode as working electrode and counter electrode, respectively. Afterwards, the titanium foil was rinsed, dried and then calcined at 450 °C for 2 h in air. The resulted titanium foil was anodized again under 60 V for 10 min, and immersed in H$_2$O$_2$ (30 wt%) for 4 h to peel off the ATO film. X-ray diffraction (XRD) measurement was conducted with X'Pert Pro diffractometer (PANalytical) using Cu $K\alpha_{1,2}$ radiation. The morphology of ATO film was characterized by scanning electron microscopy (SEM, FEI Quanta FEG 250). CV were tested in a three-electrode cell, ATO film, Pt foil and Ag/AgCl electrode were used as

working electrode, counter electrode and reference electrode, respectively. The electrolytes were EMImCl/H$_2$O (10 m) or in BMImCl/H$_2$O (10 m) containing LiCl additives, respectively.

2.4. Test of an aqueous TiO_2/Fe^{2+} hybrid battery

ATO film was attached to a graphite rod with copper tape as anode and immersed in 1 mL of BMImCl/H$_2$O (10 m) containing 1 M LiCl. 1 mL of BMImCl/H$_2$O (10 m) containing 0.1 M Fe^{2+} ions and 1 M HCl was used as catholyte, with another graphite rod as cathode terminal. A piece of methylated and crosslinked polybenzimidazole anion exchange membrane (about 40 μm in thickness) in chloride form [19] was used to separate them. In a hybrid battery configuration, one half cell contains typically liquid active species, while the other compartment could be gas or solid active materials [24]. This hybrid TiO_2/Fe^{2+} battery was tested in a home-made static H-cell, and activated for two times before cycling, considering the sluggish diffusion of Li^+ ions in solid state TiO_2 (~10^{-13} cm^2 s^{-1}) [25].

3. Results and discussions

The ESWs of aqueous EMImCl and BMImCl solutions with different molalities ranging from 5 to 20 m were investigated in a three-electrode system by CV measurements. As shown in Fig. 1a and b, when the molality increases up to 20 m, the onset potential in the cathodic branch decreases gradually to −2.0 V vs. Ag/AgCl due to hydrogen evolution reaction [26], whereas in the anodic branch the onset potential shifts to 1.0 V vs. Ag/AgCl, demonstrating an overall ESW of about 3.0 V. Quaternary ammonium salt based ionic liquids are commonly used as conductive additives in electrolytes. In this work, TEACl and TBACl were selected to study the ESWs. A TEACl/H$_2$O solution at 5 m shows an onset potential of hydrogen evolution reaction of about −2.7 V vs. Ag/AgCl (Fig. 1c), which is much more negative than that of imidazolium chloride based ionic liquids in Fig. 1a and b, whereas the onset potential in the anodic process is almost identical with that of aqueous imidazolium chloride solutions. Therefore, aqueous quaternary ammonium chloride solutions possess a broader ESW than aqueous imidazolium chloride solutions, which is further confirmed in the CV curves of TEACl/H$_2$O and TBACl/H$_2$O at higher molalities (10 m and 15 m) in Fig. 1c and d. During the cathodic scan, the onset potential shifts to −2.8 V vs. Ag/AgCl in TBACl/H$_2$O (15 m), displaying an overall ESW of ~4.0 V (Fig. 1d). Notably, a TBACl/H$_2$O (15 m) solution is still flowable at room temperature, whereas TEACl/H$_2$O (15 m) gelatinized after resting for several days (Fig. S1).

Imidazolium based ionic liquids such as TriMImMeSO$_4$ and EMMImEtSO$_4$ with large alkyl sulphates as anions were selected. In contrast to the CV curves of imidazolium chloride solutions (Fig. 1a and b), in the cathodic scan, as expected, the onset potential of TriMImMeSO$_4$/H$_2$O solution shifts to −2.3 V vs. Ag/AgCl when the molality increases to 20 m (Fig. 1e). EMMImEtSO$_4$/H$_2$O solution (20 m) shows an even lower onset reduction potential of −2.4 V vs. Ag/AgCl (Fig. 1f). Unlike chloride anions, the alkyl sulfate anions based ionic liquids exhibit a higher onset potential of 2.0 V vs. Ag/AgCl in the anodic scan, leading to an overall ESW of 4.4 V in EMMImEtSO$_4$/H$_2$O solution (20 m).

The ESWs of the six different types of "water-in-ionic liquid" solutions are summarized in Fig. 2a. EMImCl/H$_2$O and BMImCl/H$_2$O solutions show wide ESWs similar to lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) [10], but the whole window shifts negatively by about 0.7 V. The difference of the ESWs in "water-in-ionic liquid" solutions can be associated with the molalities of solutions, the sizes of cationic and anionic groups of ionic liquids, as well as the