



Ionic liquid-mediated aqueous redox flow batteries for high voltage applications



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ABSTRACT

Aqueous redox flow batteries with high cell voltages represent a promising approach for low-cost, high safety and high energy density applications. However, water breakdown is a major concern because it limits cell voltage. For the first time, we report the use of a highly concentrated aqueous ionic liquid electrolyte, 1-butyl-3-methylimidazolium chloride (BMImCl)-H₂O, in an aqueous flow battery operating with a broad electrochemical stability window of 3 V. The proof-of-concept was demonstrated using 2 V redox couples of metal acetylacetonates and a hybrid Zn/Ce flow battery.

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1. Introduction

High performance, low cost and safe energy storage systems are essential for sustainable energy strategies [1–3]. Traditional lead-acid batteries cannot provide high energy density and today's Li-ion batteries, although offering higher energy density, are expensive to scale up. In contrast, redox flow batteries (RFBs) offer a promising approach due to their economy and scalability, especially for large-scale stationary applications [2]. In general, aqueous electrolyte systems have advantages such as safe operation, low cost and fast ionic mobility compared with non-aqueous systems. However, the electrochemical window of water (generally <1.5 V) seriously limits the application of redox couples with a large potential difference in aqueous systems. To solve this problem, organic solvents [4,5] or ionic liquid electrolytes [6,7] are commonly chosen for high voltage RFBs. Nevertheless, the flammability and toxicity of organic solvents and their low solubility for active species could hinder their practical use. Ionic liquids typically have higher viscosities than conventional solvents and the sluggish mass transport of active species in ionic liquid electrolytes remains an issue [8]. Hence, it is important to develop aqueous RFBs that can sustain a large potential difference in the redox couples of the positive and negative electrodes. With respect to the electrochemical window of aqueous electrolytes, the potentials of H₂ and O₂ evolution reactions from water decomposition must be drifted towards more negative and more positive potentials, respectively. This may be achieved by adjusting the pH values of the catholyte and anolyte individually in an RFB [9]. In addition, the

electrochemical stability limit can be slightly expanded by kinetic effects. However, there may be a conflict between the experimental conditions required to suppress the side reactions of H₂ and O₂ evolution and the parameters (e.g. temperature, concentration of acid, electrode materials) needed to optimize the reaction kinetics and the solubility of the active species.

Herein we report that a widened electrochemical window of 3 V can be achieved in an aqueous ionic liquid electrolyte with high molality, which is promising for safe and high voltage applications. The highly water-soluble and nonelectroactive ionic liquid 1-butyl-3-methylimidazolium chloride (BMImCl) was used and offers high stability against hydrolysis. Moreover, Cl⁻ ions can act as charge carriers in a flow battery system using an anion exchange membrane. By reducing the concentration of free water in the proposed electrolyte, H₂ and O₂ evolution reactions can be significantly suppressed and thus the electrochemical window can be expanded. The proof-of-concept is demonstrated by using two typical redox systems. Firstly, metal acetylacetonate complexes of V(acac)₃ and VO(acac)₂ exhibiting a 2 V cell voltage are selected as examples [4], which to date have only been investigated as high-voltage redox species in nonaqueous electrolytes such as acetonitrile [10] and ionic liquids [7]. Secondly, an electroactive redox pair consisting of Ce⁴⁺/Ce³⁺ and Zn²⁺/Zn couples has been chosen to demonstrate free selection of other redox species with a high cell voltage and good compatibility with the supporting electrolyte. A commercial anion exchange membrane is used to avoid crossover of active cations.

2. Experimental

BMImCl ionic liquid (≥98.0%), V(acac)₃ (97%), VO(acac)₂, ZnSO₄·7H₂O (≥99.0%) and Ce(SO₄)₂ were used as received without further

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purification. All chemicals were supplied by Sigma Aldrich. Cyclic voltammetry (CV) measurements were performed using a three-electrode cell, consisting of a glassy carbon working electrode, a Pt foil counter electrode, and a Ag wire quasi-reference electrode, with a BioLogic SP-150 potentiostat controlled via EC-lab software. Prior to CV measurements, the supporting electrolytes were deoxygenated for 10 min. A ferricinium⁺/ferrocene reference redox system (a half-wave potential of 0.148 V vs. Ag) was used to calibrate the potential of the Ag wire reference electrode.

For hybrid Zn/Ce RFB tests, a home-made flow cell with an active area of 4 cm² and a commercial FumaSep (FAA-3-30, about 30 μm thickness, FumaTech, Germany) anion exchange membrane were used. The membrane was soaked in a ZnCl₂ solution for 24 h and washed with distilled water before being incorporated into a flow battery. Graphite felt (GFD4.6 EA, SGL) with uncompressed thickness of 5 mm and an electrode compression of 20% was used as a positive electrode. Graphite felts were treated in a concentrated H₂SO₄ solution and then thermally processed at 500 °C for 30 h in static air. Zn/Ce flow battery experiments were carried out using Ce(SO₄)₂ (0.1 M Ce⁴⁺ in 10 m BMImCl-H₂O) and Zn metal sheet (Sigma Aldrich, 99.99%, 1 mm in thickness, polished and then immersed in 0.05 M Zn²⁺ in 10 m BMImCl-H₂O) as positive and negative redox active species, respectively. Zn sheet was sandwiched between two sheets of graphite felts (2 mm in thickness) and used as a negative electrode. During charge, Zn²⁺/Zn reduction occurred on the surface of the Zn sheet and graphite felts. Catholyte and anolyte (12 mL for each, flow rate: 20 mL min⁻¹) were delivered to each compartment using a peristaltic pump.

3. Results and discussion

3.1. Electrochemical stability window

Fig. 1a shows the chemical structure of BMImCl ionic liquid. In order to examine the electrochemical stability window of BMImCl-mediated aqueous electrolytes, mixtures of BMImCl-H₂O with different molalities and neutral pH value were obtained. When BMImCl was added to water, a clear colourless BMImCl-H₂O solution with water-like flowability was observed. When a molality of 10 m was reached, the volume increased by about three times and accordingly BMImCl accounts for about 60% of total volume. Fig. 1b shows the CV curves of 5 m and 10 m BMImCl-H₂O electrolytes at glassy carbon working electrodes measured in a potential range between -2 and 1.5 V vs. Ag at room temperature. The electrochemical stability window shows a dependence on the molality. The H₂ and O₂ gas evolution onset potentials are -1.75 and 1.3 V vs. Ag, respectively, in 10 m BMImCl-H₂O. Thus a potential window of about 3 V has been achieved for this aqueous electrolyte. No evolution of gas bubbles was observed within the 3 V electrochemical window. On reducing the molality to 5 m, the anodic breakdown potential of water shifts by 0.2 V towards a lower potential. Thus, the increase in water content narrows the electrochemical window of the BMImCl-H₂O electrolyte [11]. In highly concentrated BMImCl aqueous electrolytes, H₂O and Cl⁻ together build up the primary hydration sheath surrounding the [BMIm]⁺ cations. It is thought that the chemical environment of the [BMIm]⁺ and Cl⁻ is transformed into a state similar to that of a solid BMImCl crystal and the proportion of free water in the electrolytes is significantly reduced [12]. The decomposition of water is thus largely suppressed. Thermodynamically, the oxygen evolution reaction due to water oxidation is favoured over the chlorine evolution reaction arising from Cl⁻ oxidation [13]. When a more positive cutoff potential of 1.8 V was applied (Fig. 1c), the chlorine oxidation reaction occurred and a chlorine reduction peak located at about 1 V was observed. For comparison, 15 m LiCl-H₂O electrolyte was also tested between -2 and 1.5 V vs. Ag (Fig. 1c). There was negligible change in the volume of the aqueous solution when LiCl was added and H₂ evolution began at -1.4 V for the LiCl-based electrolyte.

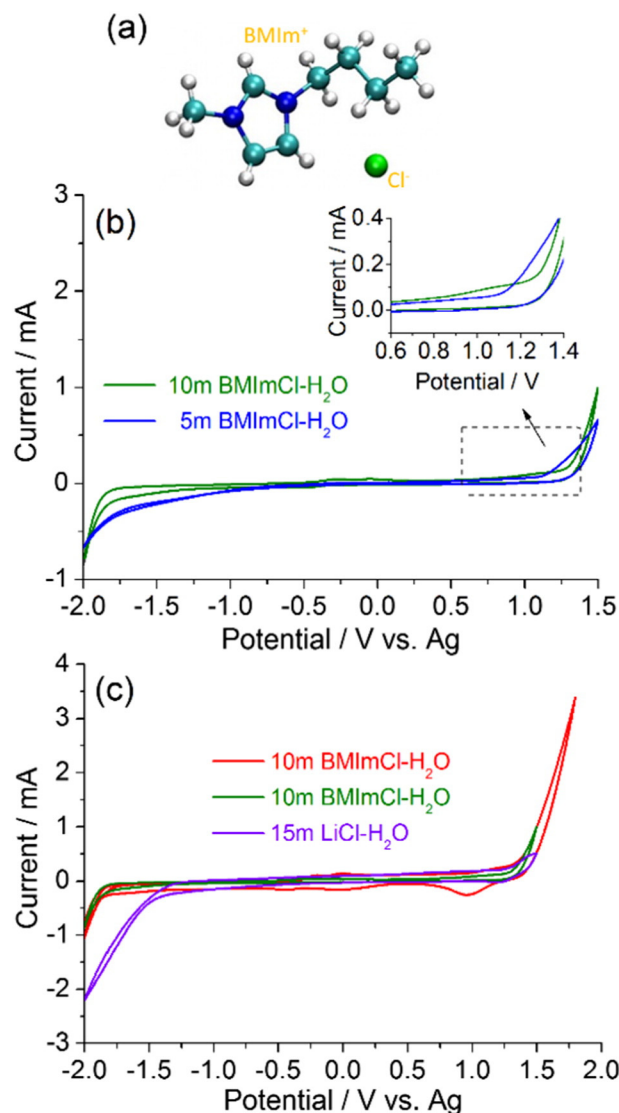


Fig. 1. (a) Chemical structure of BMImCl, (b) CV curves of varied molality of BMImCl in H₂O, (c) CV curves of 10 m BMImCl-H₂O and 15 m LiCl-H₂O electrolytes. Potential sweep rate: 50 mV s⁻¹.

3.2. Model redox reactions in BMImCl-H₂O electrolytes

To test our BMImCl-H₂O electrolytes, model compounds of V(acac)₃ and VO(acac)₂ were chosen as redox active species in CV experiments. These have shown voltages of about 2 V in acetonitrile electrolyte [4] and their redox reactions in aqueous electrolytes have never been investigated. The CV measurements for 0.01 M V(acac)₃ were performed at 50 and 100 mV s⁻¹ and within slightly different potential ranges. Fig. 2a shows the characteristic V³⁺/V²⁺ (O1/R1, at -1.1 V) and V⁴⁺/V³⁺ (O2/R2, at +0.9 V) redox peaks of V(acac)₃ within the electrochemical stability window of the BMImCl-H₂O supporting electrolyte. The CV curves observed are similar to those measured in [BMIm]⁺-bis(trifluoromethanesulfonyl)imide ([NTf₂)⁻ ionic liquid [6]. Note that the chemical conversion of V(acac)₃ to VO(acac)₂ has been observed due to the presence of trace amounts of water in the acetonitrile solvent [14]. As a comparison, VO(acac)₂, having a relatively high solubility of 0.2 M in the supporting electrolyte, clearly shows dominant multiple redox peaks of vanadium species spanning a potential range of about 2 V (Fig. 2b). It is thought that water molecules may coordinate to VO(acac)₂, leading to the formation of a new complex [4] which might be responsible for the presence of additional shoulder peaks. Upon

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