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Short communication

Tetrabutylammonium hexafluorophosphate and 1-ethyl-3-methyl imidazolium hexafluorophosphate ionic liquids as supporting electrolytes for non-aqueous vanadium redox flow batteries

Dapeng Zhang, Qinghua Liu, Xiaosong Shi, Yongdan Li*

Tianjin Key Laboratory of Catalysis Science and Technology and State Key Laboratory for Chemical Engineering (Tianjin University), School of Chemical Engineering, Tianjin University, Tianjin 300072, China

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ABSTRACT

Tetrabutylammonium hexafluorophosphate ($TEAPF_6$) and 1-ethyl-3-methyl imidazolium hexafluorophosphate ($EMIPF_6$) are synthesized and used as the supporting electrolytes of a non-aqueous redox flow battery using vanadium acetylacetonate ($V(acac)_3$) as the active species. The conductivity and cyclic voltammograms of the electrolytes of the two ionic liquids are measured. The cyclic voltammograms show that both of them are stable in an operating potential range (−2.5–1.5 V). The diffusion coefficients of $V(acac)_3$ in the electrolytes are determined as $0.92–1.47 \times 10^{-6}$ cm^2 s^{-1} in 0.5 mol l^{-1} $TEAPF_6$ and $2.35–3.79 \times 10^{-6}$ cm^2 s^{-1} in 0.5 mol $EMIPF_6$, respectively. The charge–discharge performances of the two non-aqueous $V(acac)_3$ containing electrolytes with $TEAPF_6$ and $EMIPF_6$ as the supporting electrolytes are evaluated in an H-type glass cell. The coulombic efficiencies are measured as in the range of 53.31–57.44% at 50% state of charge with an electrolyte containing 0.2 mol l^{-1} $TEAPF_6$, and as in the range of 46.04–43.46% for the electrolyte containing $EMIPF_6$ with the same concentrations of the components.

1. Introduction

A redox flow battery (RFB) is a kind of promising large scale energy storage device which utilizes oxidation and reduction reactions of two redox couples in the electrolytes for charge and discharge [1]. Electrical energy is stored in the electrolytes, which are reserved in two separate containers. The electrolytes are pumped into an electrochemical reactor where the reactions happen in two chambers separated by a membrane.

A number of RFBs classified with different active species have been developed, such as iron–chromium [2], all vanadium [3,4] and bromine–polysulfide RFBs [5]. Generally, most of the RFBs examined in literature employ aqueous electrolytes. Therefore, the operating potential of them is constrained by the electrochemical potential window of water (depending on pH, generally lower than 2.0 V) [6]. Organic solvents offer a much higher potential window, e.g. 5.0 V for acetonitrile (CH_3CN), with which, much higher power and energy output can be obtained [7–11].

Recently, vanadium acetylacetonate [$V(acac)_3$] was used as the active species in non-aqueous redox flow batteries. The open circuit voltage of this system is 2.2 V, much higher than that of all vanadium redox flow system with an aqueous electrolyte (1.26 V). While, the energy efficiency is still low mainly due to the low conductivity of the electrolyte and side reactions.

Ionic liquids have been explored extensively in recent years due to their unique properties, which facilitate applications with great potentials. They have been used in several electrochemical processes due to their high ionic conductivity, large electrochemical window and high stability [12–14].

In this work, ionic liquids tetrabutylammonium hexafluorophosphate ($TEAPF_6$) and 1-ethyl-3-methyl imidazolium hexafluorophosphate ($EMIPF_6$) were synthesized and used in the non-aqueous $V(acac)_3$ system as supporting electrolytes. The potential application of ionic liquids in non-aqueous RFBs was evaluated using cyclic voltammograms and the charge–discharge performance was determined using a static H-type cell.

2. Experimental

2.1. Electrolytes

Both $TEAPF_6$ and $EMIPF_6$ were synthesized using a two-step method. The corresponding bromide salts were prepared firstly and the hexafluorophosphate salts were added to exchange the bromonium ion to the aimed anion (PF_6^-). $TEAPF_6$ was prepared by the

* Corresponding author. Tel.: +86 22 27405613; fax: +86 22 27405243.
E-mail address: ydli@tju.edu.cn (Y. Li).

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Table 1
Conductivity of electrolytes with 0.01 mol l^{-1} V(acac)$_3$ and different concentration of ionic liquids.

Concentration of ionic liquid (mol l^{-1})	Conductivity (ms cm^{-1})	
	$TEAPF_6$	$EMIPF_6$
0.05	6.09	7.10
0.10	10.63	11.95
0.20	18.22	19.98
0.50	34.86	38.03

reaction of pure triethylamine and ethyl bromide at 55 °C for 48 h [15]. The bromide salt was dissolved in acetonitrile. Then acetate was added to recrystallize the crystallites. The bromide crystallites and hexafluorophosphate salt were dissolved in water and stirred for 3 h. At last the solution was dried in vacuum at 60 °C for 24 h. Similarly, $EMIPF_6$ was synthesized with 1-methylimidazole, ethyl bromide and the hexafluorophosphate salt.

The solvent acetonitrile (Guangfu, China) was pretreated in dried Zeolite 4A (Guangfu, China) to remove the trace amount of water to the extent of <0.05 wt.% [9].

The electrolytes were prepared with dissolving V(acac)$_3$ (Alfa, U.S.A.) and ionic liquids in CH_3CN (Guangfu, China). Prior to all measurements, the electrolytes were deoxygenated by bubbling with dry nitrogen (Liufang, China) for 15 min and all experiments were performed under the atmospheric pressure in nitrogen [9].

2.2. Conductivity and cyclic voltammetry

The conductivity of the electrolytes with 0.01 mol l^{-1} V(acac)$_3$ and different concentrations of ionic liquids were examined with electrochemical impedance spectroscopy (EIS) [16]. The experiments were carried out by using a single cuboid glass cell with two graphite plates as electrodes spaced by 3 cm. Cyclic voltammetry employed a three-electrode cell with a glassy-carbon electrode (Aidahengsheng, China) with 0.28 cm^2 surface area as the working electrode, a graphite plate (Aidahengsheng, China) as the counter electrode and a silver/silver ion (Ag/Ag^+ with CH_3CN as solvent) electrode (Aidahengsheng, China) as the reference electrode. The working electrode was polished with 1200 grit silicon carbide polishing paper [4], ultrasonically cleaned with deionized water and dried at 80 °C for 5 h. The experiments were performed with a Versa STAT 3 electrochemistry work station (Princeton Applied Research, U.S.A.) under room temperature.

2.3. Charge–discharge experiments

Charge–discharge tests were performed in an H-type glass cell using galvanostatic method. Each compartment contained 15 ml electrolyte with a magnetic stirrer. A graphite electrode, 80 mm × 15 mm × 5 mm was used in each chamber as anode and cathode, respectively. An UltrexTM AMI-7001 (Membranes-International Ltd., U.S.A.) anion exchange membrane was fixed between two chambers as a separator. The membrane was pretreated by soaking it into the test solution for more than 4 h before testing. All tests were performed under atmospheric pressure with the bubbling nitrogen.

3. Results and discussion

3.1. Conductivity and voltammetric behavior of the electrolytes

The conductivity of the electrolytes with 0.01 mol l^{-1} V(acac)$_3$ and different concentrations of ionic liquids are shown in Table 1. The conductivity of the electrolyte increased with the increase of the concentration of the ionic liquids and reached a reasonable value. It also can be seen that the conductivity of $TEAPF_6$ is lower than $EMIPF_6$ with a same concentration. Compared to the data of Morita et al. [17], the conductivity of $TEAPF_6$ is also a little lower than $TEABF_4$. However, $TEAPF_6$ has a wider electrochemical window and is more inexpensive than $TEABF_4$.

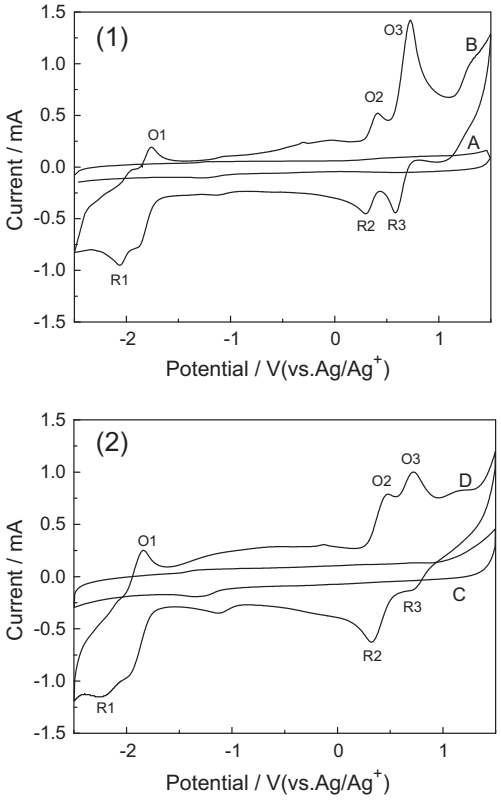

Fig. 1. Cyclic voltammograms in different electrolytes with the scan rate of 0.2 V s^{-1}: (A) 0.2 mol l^{-1} $TEAPF_6$ in CH_3CN, (B) 0.01 mol l^{-1} V(acac)$_3$ and 0.2 mol l^{-1} $TEAPF_6$ in CH_3CN, (C) 0.2 mol l^{-1} $EMIPF_6$ in CH_3CN, (D) 0.01 mol l^{-1} V(acac)$_3$ and 0.2 mol l^{-1} $EMIPF_6$ in CH_3CN.

Three cyclic voltammograms of $TEAPF_6$ and $EMIPF_6$ in CH_3CN with and without V(acac)$_3$ recorded with a scan rate of 0.2 V s^{-1} are shown in Fig. 1. The two electrolytes composed of ionic liquids and acetonitrile can reduce the background current with a great extent and do not have any important peaks in the potential window. Here three redox couples are observed in −2.5–1.5 V for the electrolyte with the active species V(acac)$_3$. According to previous studies [18], these current peaks were attributed to the following reactions:

$$R1/O1 : V(III)(acac)_3 + e^- \Leftrightarrow [V(II)(acac)_3]^- \quad (1)$$

$$R2/O2 : V(III)(acac)_3 \Leftrightarrow [V(IV)(acac)_3]^+ + e^- \quad (2)$$

While, the R3/O3 couples may form from the oxidation of V^{4+} to V^{5+} or oxidation of the V(acac)$_3$ species.

From the potentials of each half reaction, the cell potential for the $TEAPF_6$ system is 2.3 V and for $EMIPF_6$ is 2.4 V, both of them are higher than that of V(acac)$_3$ using $TEABF_4$ as the supporting electrolytes (2.2 V) [9]. The cyclic voltammograms show that $EMIPF_6$ and $TEAPF_6$ as supporting electrolytes can be regarded as electrochemically inert and are suitable for the V(acac)$_3$ non-aqueous RFB.

3.2. Kinetics of electrode reactions with ionic liquids

A series of cyclic voltammograms with different scan rates from 0.05 to 0.50 V s^{-1} for electrolyte containing 0.01 mol l^{-1} V(acac)$_3$