



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

## ARTICLE INFO

## Article history:

Received 29 January 2011  
 Received in revised form 19 August 2011  
 Accepted 18 October 2011  
 Available online 12 November 2011

## Keywords:

Redox flow battery  
 Vanadium acetylacetonate  
 Ionic liquids  
 Tetrabutylammonium  
 hexafluorophosphate  
 1-Ethyl-3-methyl imidazolium  
 hexafluorophosphate

## ABSTRACT

Tetrabutylammonium hexafluorophosphate (TEAPF<sub>6</sub>) and 1-ethyl-3-methyl imidazolium hexafluorophosphate (EMIPF<sub>6</sub>) are synthesized and used as the supporting electrolytes of a non-aqueous redox flow battery using vanadium acetylacetonate (V(acac)<sub>3</sub>) 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)<sub>3</sub> in the electrolytes are determined as  $0.92\text{--}1.47 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  in  $0.5 \text{ mol l}^{-1}$  TEAPF<sub>6</sub> and  $2.35\text{--}3.79 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  in  $0.5 \text{ mol l}^{-1}$  EMIPF<sub>6</sub>, respectively. The charge–discharge performances of the two non-aqueous V(acac)<sub>3</sub> containing electrolytes with TEAPF<sub>6</sub> and EMIPF<sub>6</sub> 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  $0.2 \text{ mol l}^{-1}$  TEAPF<sub>6</sub>, and as in the range of 46.04–43.46% for the electrolyte containing EMIPF<sub>6</sub> with the same concentrations of the components.

© 2011 Elsevier B.V. All rights reserved.

## 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<sub>3</sub>CN), with which, much higher power and energy output can be obtained [7–11].

Recently, vanadium acetylacetonate [V(acac)<sub>3</sub>] 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<sub>6</sub>) and 1-ethyl-3-methyl imidazolium hexafluorophosphate (EMIPF<sub>6</sub>) were synthesized and used in the non-aqueous V(acac)<sub>3</sub> 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<sub>6</sub> and EMIPF<sub>6</sub> 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<sub>6</sub><sup>−</sup>). TEAPF<sub>6</sub> was prepared by the

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

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

Concentration of ionic liquid ( $\text{mol l}^{-1}$ )	Conductivity ( $\text{ms cm}^{-1}$ )	
	TEAPF <sub>6</sub>	EMIPF <sub>6</sub>
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  $55^\circ\text{C}$  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  $60^\circ\text{C}$  for 24 h. Similarly, EMIPF<sub>6</sub> 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  $<0.05 \text{ wt.}\%$  [9].

The electrolytes were prepared with dissolving  $\text{V}(\text{acac})_3$  (Alfa, U.S.A.) and ionic liquids in  $\text{CH}_3\text{CN}$  (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  $0.01 \text{ mol l}^{-1} \text{ V}(\text{acac})_3$  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  $0.28 \text{ cm}^2$  surface area as the working electrode, a graphite plate (Aidahengsheng, China) as the counter electrode and a silver/silver ion ( $\text{Ag}/\text{Ag}^+$  with  $\text{CH}_3\text{CN}$  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  $80^\circ\text{C}$  for 5 h. The experiments were performed with a Versa STAT 3 electrochemistry work station (Princeton Applied Research, U.S.A.) under room temperature.

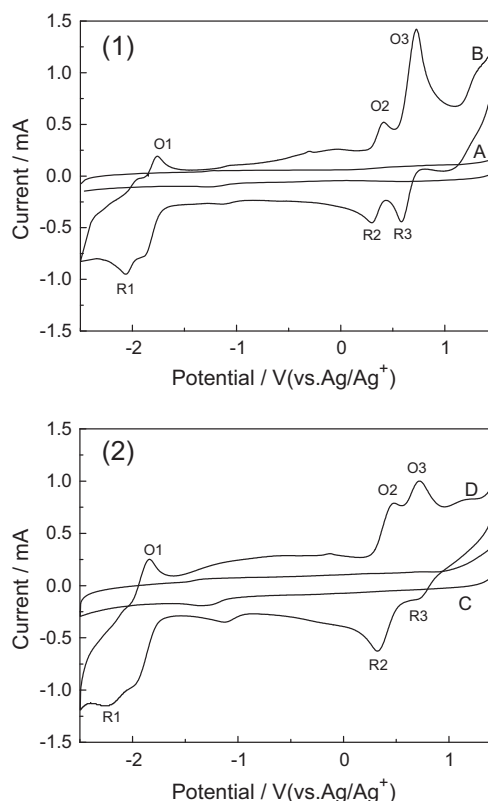
## 2.3. Charge–discharge experiments

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,  $80 \text{ mm} \times 15 \text{ mm} \times 5 \text{ mm}$  was used in each chamber as anode and cathode, respectively. An Ultrex<sup>TM</sup> 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

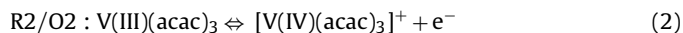
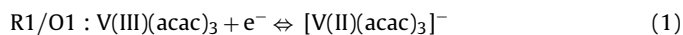
The conductivity of the electrolytes with  $0.01 \text{ mol l}^{-1} \text{ V}(\text{acac})_3$  and different concentrations of ionic liquids are shown in Table 1. The conductivity of the electrolyte increased with the increase of



**Fig. 1.** Cyclic voltammograms in different electrolytes with the scan rate of  $0.2 \text{ V s}^{-1}$ : (A)  $0.2 \text{ mol l}^{-1}$  TEAPF<sub>6</sub> in  $\text{CH}_3\text{CN}$ , (B)  $0.01 \text{ mol l}^{-1} \text{ V}(\text{acac})_3$  and  $0.2 \text{ mol l}^{-1}$  TEAPF<sub>6</sub> in  $\text{CH}_3\text{CN}$ , (C)  $0.2 \text{ mol l}^{-1}$  EMIPF<sub>6</sub> in  $\text{CH}_3\text{CN}$ , (D)  $0.01 \text{ mol l}^{-1} \text{ V}(\text{acac})_3$  and  $0.2 \text{ mol l}^{-1}$  EMIPF<sub>6</sub> in  $\text{CH}_3\text{CN}$ .

the concentration of the ionic liquids and reached a reasonable value. It also can be seen that the conductivity of TEAPF<sub>6</sub> is lower than EMIPF<sub>6</sub> with a same concentration. Compared to the data of Morita et al. [17], the conductivity of TEAPF<sub>6</sub> is also a little lower than TEABF<sub>4</sub>. However, TEAPF<sub>6</sub> has a wider electrochemical window and is more inexpensive than TEABF<sub>4</sub>.

Three cyclic voltammograms of TEAPF<sub>6</sub> and EMIPF<sub>6</sub> in  $\text{CH}_3\text{CN}$  with and without  $\text{V}(\text{acac})_3$  recorded with a scan rate of  $0.2 \text{ V s}^{-1}$  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  $-2.5$ – $1.5 \text{ V}$  for the electrolyte with the active species  $\text{V}(\text{acac})_3$ . According to previous studies [18], these current peaks were attributed to the following reactions:

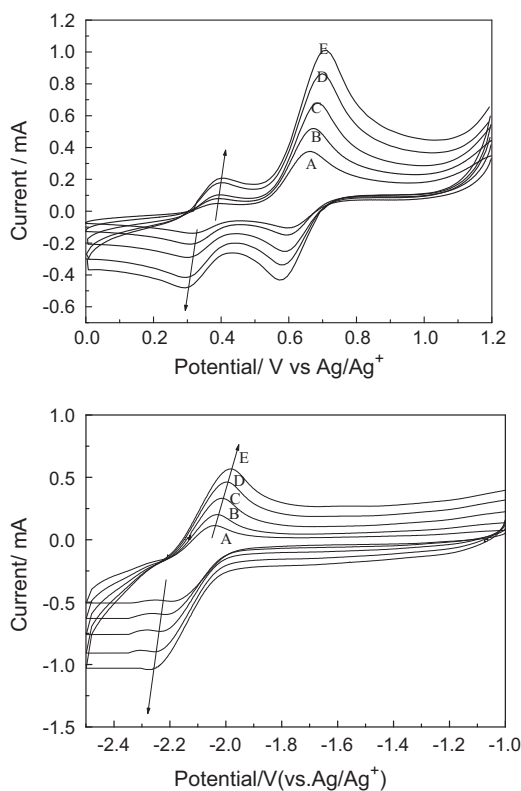


While, the R3/O3 couples may form from the oxidation of  $\text{V}^{4+}$  to  $\text{V}^{5+}$  or oxidation of the  $\text{V}(\text{acac})_3$  species.

From the potentials of each half reaction, the cell potential for the TEAPF<sub>6</sub> system is  $2.3 \text{ V}$  and for EMIPF<sub>6</sub> is  $2.4 \text{ V}$ , both of them are higher than that of  $\text{V}(\text{acac})_3$  using TEABF<sub>4</sub> as the supporting electrolytes ( $2.2 \text{ V}$ ) [9]. The cyclic voltammograms show that EMIPF<sub>6</sub> and TEAPF<sub>6</sub> as supporting electrolytes can be regarded as electrochemically inert and are suitable for the  $\text{V}(\text{acac})_3$  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  $0.50 \text{ V s}^{-1}$  for electrolyte containing  $0.01 \text{ mol l}^{-1} \text{ V}(\text{acac})_3$



**Fig. 2.** Cyclic voltammograms in  $0.01 \text{ mol l}^{-1} \text{ V(acac)}_3$  and  $0.5 \text{ mol l}^{-1} \text{ TEAPF}_6$  in  $\text{CH}_3\text{CN}$  with different scan rates: (A) 0.05, (B) 0.10, (C) 0.2, (D) 0.35, and (E)  $0.50 \text{ V s}^{-1}$ .

and  $0.5 \text{ mol l}^{-1} \text{ TEAPF}_6$  in  $\text{CH}_3\text{CN}$  are shown in Fig. 2. For the V(II)/V(III) redox couple, the peak separation ( $\Delta E_p$ ) increased from 171 to 314 mV and the ratio of anodic to cathodic peak currents ( $i_{pa}/i_{pc}$ ) increased from 0.20 to 0.55 as the scan rate is increased from 0.05 to  $0.50 \text{ V s}^{-1}$ . Similarly, for the V(III)/V(IV) redox couple,  $\Delta E_p$  increased from 67 to 118 mV and  $i_{pa}/i_{pc}$  increased from 0.35 to 0.43 as the scan rate increased. The ratio of anodic to cathodic peak currents is far from unity, indicating complexity in the electrode process. Although the R3/O3 couple is not clear, it is presented that TEAPF<sub>6</sub> supporting electrolyte has a positive effect on the reduction reaction R3 with a visible reduction peak in Fig. 2. This unique characteristic of TEAPF<sub>6</sub> makes it different from TEABF<sub>4</sub> and EMIPF<sub>6</sub> for potential application in RFBs with high efficiency due to the better reversibility of R3/O3 couple.

Fig. 3 shows the cyclic voltammograms for electrolyte containing  $0.01 \text{ mol l}^{-1} \text{ V(acac)}_3$  and  $0.5 \text{ mol l}^{-1} \text{ EMIPF}_6$  in  $\text{CH}_3\text{CN}$ . For the V(II)/V(III) redox couple, the peak separation ( $\Delta E_p$ ) increased from 85 to 135 mV and the ratio of anodic to cathodic peak currents ( $i_{pa}/i_{pc}$ ) increased from 0.22 to 0.52 as the scan rate is increased from 0.05 to  $0.50 \text{ V s}^{-1}$ . For the V(III)/V(IV) redox couple,  $\Delta E_p$  increased from 80 to 130 mV but  $i_{pa}/i_{pc}$  decreased from 0.83 to 0.45 as the scan rate increased.

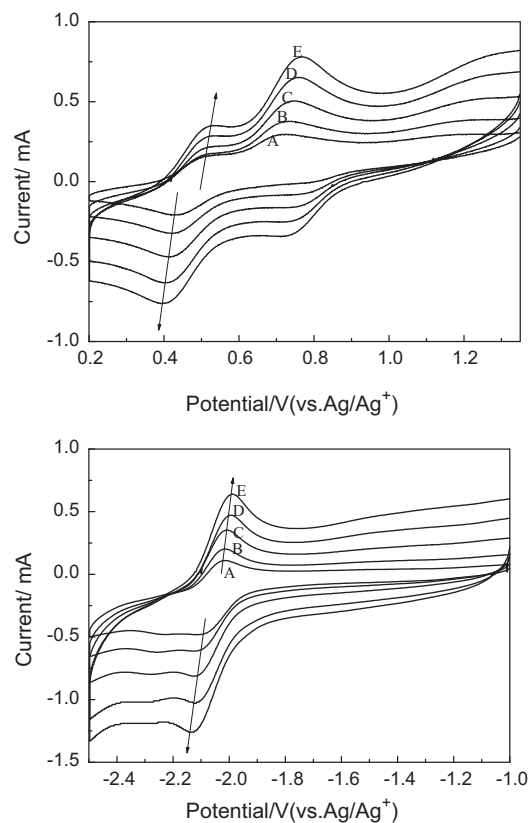
From Figs. 2 and 3, it can be concluded that both reactions (1) and (2) are quasi-reversible in both TEAPF<sub>6</sub> and EMIPF<sub>6</sub> supporting electrolytes. For a reversible redox couple, the peak current  $i_p$  is given by [19]:

$$i_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} \nu^{1/2} \quad (3)$$

For a totally irreversible redox couple, the peak current is given by [19]:

$$i_p = 2.99 \times 10^5 n^{3/2} A C \alpha^{1/2} D^{1/2} \nu^{1/2} \quad (4)$$

where  $n$  is the number of electrons transferred in the electrode reaction ( $n = 1$ ),  $A$  the electrode area ( $\text{cm}^2$ ),  $C$  the bulk concentration



**Fig. 3.** Cyclic voltammograms in  $0.01 \text{ mol l}^{-1} \text{ V(acac)}_3$  and  $0.5 \text{ mol l}^{-1} \text{ EMIPF}_6$  in  $\text{CH}_3\text{CN}$  with different scan rates: (A) 0.05, (B) 0.10, (C) 0.2, (D) 0.35, and (E)  $0.50 \text{ V s}^{-1}$ .

of primary reactant ( $\text{mol l}^{-1}$ ),  $D$  the diffusion coefficient of primary reactant and  $\nu$  the scan rate ( $\text{V s}^{-1}$ ). Since  $i_p$  is a function of  $\nu^{1/2}$ , a plot of  $i_p$  vs.  $\nu^{1/2}$  gives a straight line with a slope proportional to the diffusion coefficient of the active species.

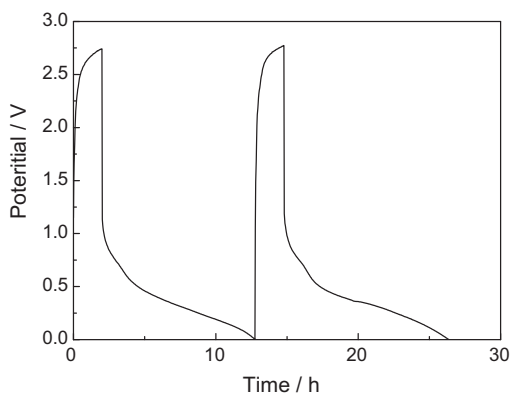
Because the electrode reactions appear to be quasi-reversible, the value for the diffusion coefficient of  $\text{V(acac)}_3$  would be located in between the results calculated from Eqs. (3) and (4). As listed in Table 2, the diffusion coefficients of  $\text{V(acac)}_3$  based on the cathodic peak currents for the V(III)/V(IV) redox couple both increase slightly along with the increase of the concentrations of the ionic liquids. For TEAPF<sub>6</sub>, the largest diffusion coefficient  $0.92\text{--}1.47 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  is obtained with the concentration of  $0.5 \text{ mol l}^{-1}$  at room temperature. When EMIPF<sub>6</sub> is used as the supporting electrolyte, the largest diffusion coefficient is in the range of  $2.35\text{--}3.79 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . This value is even higher than that when TEABF<sub>4</sub> was used as the supporting electrolyte, i.e.  $1.8\text{--}2.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [9].

### 3.3. Charge–discharge performance

The charge–discharge performances of the batteries with TEAPF<sub>6</sub> and EMIPF<sub>6</sub> used as the supporting electrolytes for non-aqueous  $\text{V(acac)}_3$  RFBs were evaluated in a H-type glass cell. The coulombic and energy efficiencies reached relatively constant values after 2 cycles, with similar charge–discharge curves were recorded. However, after 6 cycles, the shapes of the curves change due to the bubbling of the nitrogen which leads to the evaporation of the volatile components. Figs. 4 and 5 illustrate the charge–discharge cycles 3 and 4 of TEAPF<sub>6</sub> and EMIPF<sub>6</sub> as the supporting electrolytes, respectively. Galvanostatic method was used with charging current  $I_c = 1 \text{ mA}$  and discharging current  $I_d = 0.1 \text{ mA}$  with the cutoff voltage set as 0 V.

**Table 2**  
Diffusion coefficient of  $V(acac)_3$  with  $0.01 \text{ mol l}^{-1} V(acac)_3$  and with different concentrations of ionic liquids.

Concentrations of ionic liquids ( $\text{mol l}^{-1}$ )	TEAPF <sub>6</sub> $D (\text{cm}^2 \text{s}^{-1} \times 10^{-6})$		EMIPF <sub>6</sub> $D (\text{cm}^2 \text{s}^{-1} \times 10^{-6})$	
	Reversible	Irreversible	Reversible	Irreversible
0.05	0.58	0.93	1.51	2.42
0.10	0.65	1.04	1.731	2.79
0.20	0.83	1.34	2.02	3.25
0.50	0.92	1.47	2.35	3.79



**Fig. 4.** Charge–discharge curves of the electrolytes with  $0.01 \text{ mol l}^{-1} V(acac)_3$ ,  $0.2 \text{ mol l}^{-1}$  TEAPF<sub>6</sub> and  $I_d = 0.1 \text{ mA}$ ,  $I_c = 1 \text{ mA}$ , 50% state of charge.

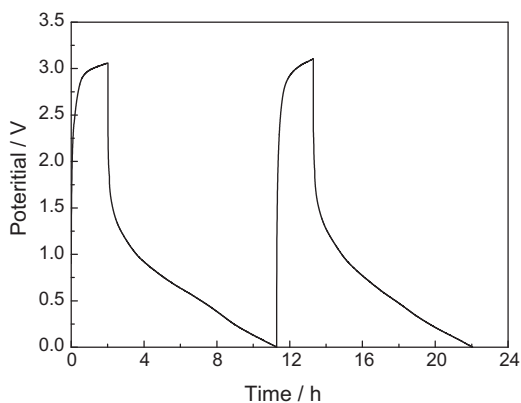
As shown in Figs. 4 and 5, the charge voltage was as high as 2.75 V for the system using TEAPF<sub>6</sub> and 3.0 V for that of EMIPF<sub>6</sub>. There is both a small discharge voltage plateau in these two systems, around 0.4 V and 0.6 V for TEAPF<sub>6</sub> and EMIPF<sub>6</sub>, respectively. The low discharge voltage may be due to the large ohmic drop and polarization in the H-type cell.

The ohmic overpotential in the H-type cell was measured by using the EIS method. The resistance for TEAPF<sub>6</sub> is 318 Ω. For EMIPF<sub>6</sub>, the resistance is 288 Ω. This suggests that the H-cell configuration led to overpotentials of 318 and 288 mV, respectively for the two electrolytes during charge. These values were 31.8 and 28.8 mV, respectively, during discharge for the two electrolytes.

Coulombic efficiency  $\eta_c$ , i.e. the ratio of electrical charge used during discharge compared to that used during charge, is calculated as

$$\eta_c = \text{Coulombic efficiency} = \frac{I_D t_D}{I_C t_C} \times 100\% \quad (5)$$

where  $I_D$  and  $I_C$  are discharge and charge cell currents,  $t_D$  and  $t_C$  are discharge and charge times.



**Fig. 5.** Charge–discharge curves of the electrolytes with  $0.01 \text{ mol l}^{-1} V(acac)_3$ ,  $0.2 \text{ mol l}^{-1}$  EMIPF<sub>6</sub> and  $I_d = 0.1 \text{ mA}$ ,  $I_c = 1 \text{ mA}$ , 50% state of charge.

The coulombic efficiency for TEAPF<sub>6</sub> is 53.31% and 57.44% in cycle 3 and cycle 4. For EMIPF<sub>6</sub>, the coulombic efficiency is 46.04% and 43.46%. It can be seen that the coulombic efficiency of TEAPF<sub>6</sub> is higher than EMIPF<sub>6</sub> by 7–14%. The reason may be due to the promotion effect of TEAPF<sub>6</sub> on R3/O3 couple as mentioned above.

It should be noted that the coulombic efficiency is low here and the data reported can only be used to compare the two electrolytes. This may be caused by the side reactions and/or the crossover of the active species through the anion-exchange membrane. As shown in Figs. 2 and 3, the electrode reaction processes are complex and some active species were oxidized to V(V). Due to the long time-scale of the discharge experiment, the crossover of the active species through the membrane is also important. Further investigation is needed to modify the membrane to fit the need of the non-aqueous system.

#### 4. Conclusions

TEAPF<sub>6</sub> and EMIPF<sub>6</sub> were synthesized and applied in a non-aqueous  $V(acac)_3$  redox flow battery as the supporting electrolytes.

The conductivity of the electrolytes increased obviously with the increase of the concentration of the ionic liquids in the electrolytes. The cyclic voltammograms indicate that both of the two ionic liquids are stable in  $V(acac)_3$  and  $CH_3CN$  electrolytes in  $-2.5$ – $1.5$  V. Kinetics of electrode reactions shows that both of V(II)/V(III) and V(III)/V(IV) reactions are quasi-reversible in both TEAPF<sub>6</sub> and EMIPF<sub>6</sub> supporting electrolytes. In both of the two electrolytes, the diffusion coefficient of the active species increased slightly with the increase of the concentration of the ionic liquids. The largest diffusion coefficient for TEAPF<sub>6</sub> is in the range of  $0.92$ – $1.47 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  at room temperature with  $0.5 \text{ mol l}^{-1}$  TEAPF<sub>6</sub>. For EMIPF<sub>6</sub>, the value is in the range of  $2.35$ – $3.79 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  with the same concentration.

The coulombic efficiency of the electrolyte containing  $0.2 \text{ mol l}^{-1}$  TEAPF<sub>6</sub> is measured as 53.31% and 57.44% for cycle 3 and cycle 4, respectively at 50% state of charge, while, for the EMIPF<sub>6</sub> system, the coulombic efficiency is 46.04% and 43.46% with the same concentrations of the components for cycle 3 and cycle 4.

#### Acknowledgements

The financial support of NSF of China under contract number 20736007 is gratefully acknowledged. The work has been also supported by the Program of Introducing Talents to the University Disciplines under file number B06006, and the Program for Changjiang Scholars and Innovative Research Teams in Universities under file number IRT 0641.

#### References

- [1] L.H. Thaller, US Patent 3,996,064 (1976).
- [2] N.H. Hagedorn, L.H. Thaller, J. Power Sources 8 (1981) 227.
- [3] E. Sum, M. Skyllas-Kazacos, J. Power Sources 15 (1985) 179.
- [4] E. Sum, M. Rychcik, M. Skyllas-Kazacos, J. Power Sources 16 (1985) 85.
- [5] A. Price, S. Bartley, S. Male, G. Cooley, Power Eng. J. 13 (3) (1999) 122.
- [6] C.H. Bae, Ph.D. Thesis, University of Manchester, Institute of Science and Technology, UK, 2001.

- [7] M.H. Chakrabarti, R.A.W. Dryfe, E.P.L. Roberts, *Electrochim. Acta* 52 (2007) 2189.
- [8] Y. Matstuda, K. Tanaka, M. Okada, Y. Takasu, M. Morita, T. Mastsumura-Inoue, *J. Appl. Electrochem.* 18 (1988) 909.
- [9] Q.H. Liu, A.E.S. Sleightholme, A.A. Shinkle, Y.D. Li, L.T. Thompson, *Electrochem. Commun.* 11 (12) (2009) 2312.
- [10] Q.H. Liu, A.A. Shinkle, Y.D. Li, C.W. Monroe, L.T. Thompson, A.E.S. Sleightholme, *Electrochem. Commun.* 12 (2010) 1634–1637.
- [11] A.E.S. Sleightholme, A.A. Shinkle, Q.H. Liu, Y.D. Li, C.W. Monroe, L.T. Thompson, *J. Power Sources* 196 (2011) 5742–5745.
- [12] H. Ohno, M. Yoshizawa, *Solid State Ionics* 154–155 (2002) 303.
- [13] C. Nanjundiah, S.F. McDevitt, V.R. Koch, *J. Electrochem. Soc.* 144 (10) (1997) 3392.
- [14] B. Garcia, S. Lavalleje, G. Perron, C. Michot, M. Armand, *Electrochim. Acta* 49 (2004) 4583.
- [15] S.V. Dzyuba, R.A. Bartsch, *J. Heterocycl. Chem.* 38 (2001) 265.
- [16] S. Ferrari, E. Quartarone, P. Mustarelli, A. Magistris, M. Fagnoni, S. Protti, C. Gerbaldi, A. Spinella, *J. Power Sources* 195 (2010) 559.
- [17] M. Morita, M. Goto, Y. Matsuda, *J. Appl. Electrochem.* 22 (1992) 901.
- [18] M.A. Nawi, T.L. Riechel, *Inorg. Chem.* 20 (7) (1981) 1974–1978.
- [19] A.J. Bard, L.R. Faulkner, *Electrochemical Methods – Fundamentals and Applications*, second ed., Wiley, 2001.