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Electrochemical Performance of VO^{2+}/VO_2^+ Redox Couple in the H_2SO_4-CH_3SO_3H Solutions

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The mixed acids with different ratio of H_2SO_4 to CH_3SO_3H were prepared, and their application in the vanadium redox flow battery (VRFB) as supporting electrolytes had been examined. It was found the solubility and stability of vanadium ions can be significantly enhanced by the increasing of CH_3SO_3H content in the mixed acid system. The electrochemical behaviors of VO^{2+}/VO_2^+ couple in different mixed acids were further studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results showed that the electrochemical activities, including the reversibility of electrode reaction, the reaction resistance for VO^{2+}/VO_2^+ couple were closely related to the CH_3SO_3H content in the mixed acid system, and reached the best value in the solution using 2.75 mol/L H_2SO_4+0.25 mol/L CH_3SO_3H mixed acid as supporting electrolyte. The VRFB with the optimized mixed acid electrolyte exhibits higher energy efficiency and the similar current efficiency compared with those of H_2SO_4 system.

Keywords: vanadium redox flow battery; electrochemical performance; methane sulfonic acid; mixed acid solution

1. INTRODUCTION

Recently, vanadium redox flow battery (VRFB) has received remarkable attentions as a promising energy storage technology for intermittently renewable energy because of its advanced characteristics such as long cyclic life, flexible design and high reliability [1–5]. The VRFBs utilize the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ redox couples to act as the negative and positive electrolytes, respectively. During battery discharge, VO_2^+ is reduced to VO^{2+} at the positive, accompanied by a concomitant oxidation of V^{2+} to V^{3+} at the negative; charging a VRFB reverses this process. Therefore, the energy density of VRFB is directly determined by the concentrations of vanadium ions in the electrolyte.

Sulfuric acid is a commonly used supporting electrolyte in the VRFB. Unfortunately, in sulfuric acid solution, hydrated penta co-ordinated vanadate ion $[VO_2(H_2O)_3]^+$ is apt to form V_2O_5 precipitation [6]. The poor stability of electrolytes, especially positive electrolyte, greatly limits the concentration of vanadium ions in the electrolyte, which limits the energy density of VRFB in turn.

For the purpose of developing stable electrolytes with high concentration of vanadium ions, many tactics have been proposed to inhibit the precipitate formation in the positive electrolyte of VRFB [7–13], such as adding additives, increasing the concentration of supporting electrolyte, using the mixed acid (H_2SO_4-HCl, H_2SO_4-CH_3SO_3H) system, *etc.* Among them, Li *et al.* [12] reported a very attractive result that a 2.5 mol/L vanadium electrolyte in a mixture of sulfuric acid and hydrochloric acid shows excellent electrochemical performance and thermal stability. But accompanying with the introduction of Cl^-, the evolution of chlorine may occur at the electrode in the anode process due to the inconsistency of the cells. Peng *et al.* [13] evaluated the electrochemical behaviors of 2 mol/L positive electrolyte for VRFB in 1.5 mol/L H_2SO_4+1.5 mol/L CH_3SO_3H mixed acids, which exhibited good electrochemical activity and charge-discharge performance. This preliminary exploration shows that the H_2SO_4-CH_3SO_3H mixed acid is a promising supporting electrolyte for VRFB. However, only the performance of 2 mol/L VO^{2+} electrolyte in 1.5 mol/L H_2SO_4+1.5 mol/L CH_3SO_3H and in 3.0 mol/L H_2SO_4 was reported in the literature, the influences of the ratio of CH_3SO_3H to H_2SO_4 on the electrochemical activity and stability of the electrolytes are worthy of further study.

To elucidate the effects of composition of H_2SO_4-CH_3SO_3H mixed acid, the solubility, stability, electrochemical properties of vanadium ions in the solutions with different ratio of CH_3SO_3H to H_2SO_4 were studied in the present paper. And the cyclic performance of VRFBs using H_2SO_4-CH_3SO_3H mixed acid as supporting electrolytes was also studied by a galvanostatic charging/discharging method.

2. EXPERIMENTAL

2.1 Solubility of $VOSO_4$

Table 1 Composition of H_2SO_4-CH_3SO_3H mixed acids

No.	C(H_2SO_4)/mol/L	C(CH_3SO_3H) /mol/L
1	0	3.0
2	0.5	2.5
3	1.0	2.0
4	1.5	1.5
5	2.0	1.0
6	2.25	0.75
7	2.5	0.5
8	2.75	0.25
9	3.0	0

The compositions of H_2SO_4-CH_3SO_3H mixed acids studied in this work are listed in Table 1. To determine the solubility of $VOSO_4$ in the mixed acids, excess amount of $VOSO_4 \cdot nH_2O$ （Shanghai Huating Chemical Co. Ltd., China, n=3.5) was added into 30 mL of each mixed acid, then sonicated for 30 min, after that the solutions were kept in sealed bottles at 25 ℃ for 30 days. Then the concentration of vanadium ions in the upper clear liquid was analyzed by an inductively coupled plasma mass spectrometry (ICP-MS).

2.2 Electrochemical study

An IviumStat potentiostat (Ivium Technologies, the Netherlands) was employed for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. Electrochemical experiments were carried out in a 3-electrode electrochemical cell with a graphite disk electrode with a surface area of 0.785 cm^2 as the working electrode, a large graphite plate as the counter electrode and a saturated calomel electrode (SCE) along with a salt bridge as the reference electrode. The CV curves were obtained between 0 V and 1.6 V. And the EIS tests were performed with an excitation signal of 5 mV in the frequency range of 0.01 Hz and 100 kHz. Prior to each measurement, the working electrode was manually polished with 0.3 and 0.5 μm α-Al_2O_3 powder and then washed by ultrasonic cleaning in doubly distilled water for 10 min. All electrochemical experiments were conducted at room temperature.

2.3 Stability of VO_2^+

To investigate the stability of VO_2^+, three typical solutions (No.1, 8 and 9 mixed acids listed in Table 1) containing *ca.* 2 mol/L VO_2^+ were prepared by electrooxidation of $VOSO_4$. 100 mL of tested solution was added into a sealed bottle, then placed in 40 ℃ water bath. The concentrations of VO_2^+ in these solutions were periodically measured by redox titration using an automatic potentiometric titrator (ZDJ-4A, Shanghai ray magnetic).

2.4 Charge-discharge test

A VRFB single cell was fabricated by sandwiching a piece of N115 perfluorinated ion-exchange membrane (Best Co., China) between two pieces of polyacrylonitrile (PAN)-based graphite felts with an area of 3×3 cm^2 and thickness of 5 mm (Shenhe Carbon Fiber Materials Co., China), two piece of graphite plates were used as the current collectors. The graphite felts were treated in air at 500 ℃ for 2 h to improve electrocatalytic activity and hydrophilicity. Two 40 mL vanadium solutions serving as negative and positive electrolytes were cyclically pumped into the corresponding half-cell by two peristaltic pumps (BT100-1L, Baoding Longer Precision Pump Co., China) with a flow rate of 20 mL/min. The performance of VRFBs was evaluated at room temperature by a BT2000 battery test system (Arbin, USA). The VRFBs were charged with 20 mA/cm^2 for 3 h (0.54 Ah), and then discharged to the cut-off voltage of 0.8 V with the same current density.

3. RESULTS AND DISCUSSION

3.1 Solubility of mixed acids

Table 2 shows the solubility of $VOSO_4$ in the mixed acids determined by ICP-MS. It can be seen that the saturated concentration of V^{4+} in the solutions decreases from 125 g/L to *ca.* 74 g/L with the decreasing of CH_3SO_3H concentration from 3 mol/L to 0 and the increasing of H_2SO_4 concentration from 0 to 3 mol/L. This indicates that CH_3SO_3H can dissolve more $VOSO_4$ than H_2SO_4, and all mixed acids, besides CH_3SO_3H solution, have higher solubility of $VOSO_4$ than H_2SO_4 solution[14]. Due to the energy density of VRFB depends on the concentration of vanadium ions, compared with H_2SO_4 solution, CH_3SO_3H solution and mixed acids may have higher specific energy when used as supporting electrolytes in VRFBs. However, for the application in VRFB, further research is needed to examine the electrochemical activity and stability of vanadium ions in the mixed acids.

Table 2 Concentration of V^{4+} in the mixed acids

Mixed acid	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9
V^{4+}(g/L)	125.005	106.123	96.037	92.181	90.168	89.527	87.095	81.365	73.817

3.2 Cyclic voltammetry

The cyclic voltammograms of mixed acids containing 1.5 mol/L $VOSO_4$ on the graphite disk electrode are shown in Fig. 1. The CV curves of these solutions are similar to each other in peak shape and exhibit evidently only one couple of redox peaks which corresponds to the redox reaction between VO^{2+} and VO_2^+. However, the oxidative and reductive peak currents increase with the increasing of H_2SO_4 and decreasing of CH_3SO_3H in the electrolyte, and reach the biggest value in the No.8 mixed acid (2.75 mol/L H_2SO_4+0.25 mol/L CH_3SO_3H). This may be associated with the higher conductivity of H_2SO_4 than that of CH_3SO_3H, whereas the addition of a certain amount of CH_3SO_3H in the solution is beneficial to the electrochemical reaction of VO^{2+}/VO_2^+ couple on the graphite electrode. The biggest redox peak currents and the smallest separation between the oxidation and reduction peak potentials (ΔE_p) are obtained in the electrolyte using No.8 mixed acid as supporting electrolyte. This implies that the vanadium ions in this solution have the best electrochemical reaction kinetics, which may be ascribed to the variation of existential states of vanadium ions after the addition of CH_3SO_3H[15].

To further study the reversibility of VO^{2+}/VO_2^+ couple in the No.8 mixed acid, CV curves at various potential scan rate were measured, as well as those in the CH_3SO_3H (No.1 in Table 1) and H_2SO_4 (No.9 in Table 1). It can be seen from Fig.2(a-c) that the oxidation and reduction peak currents increase with the increasing of potential scan rate in all three electrolytes.

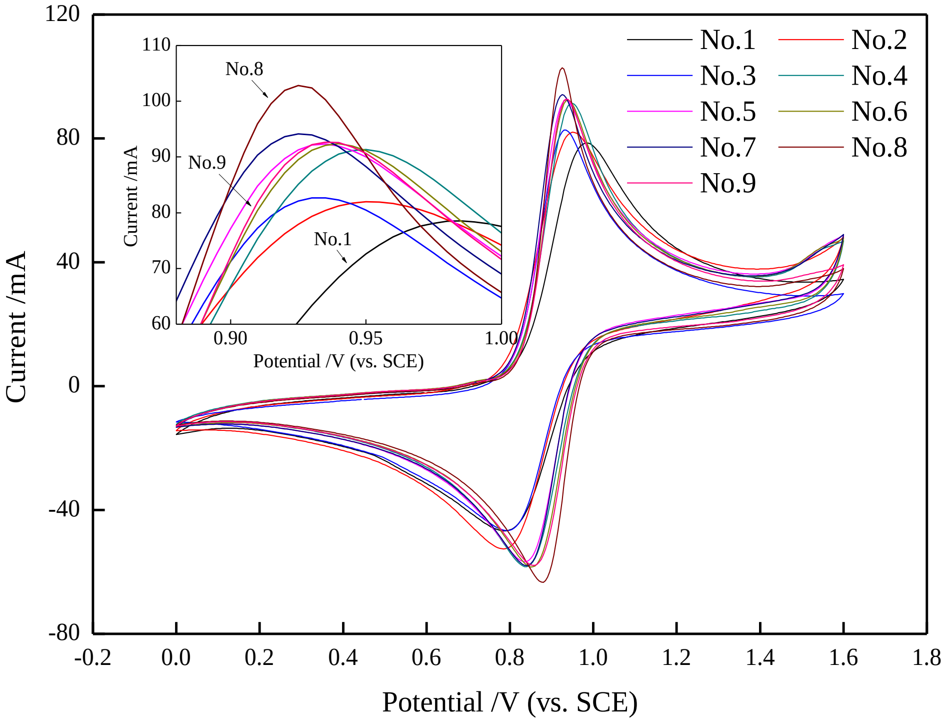
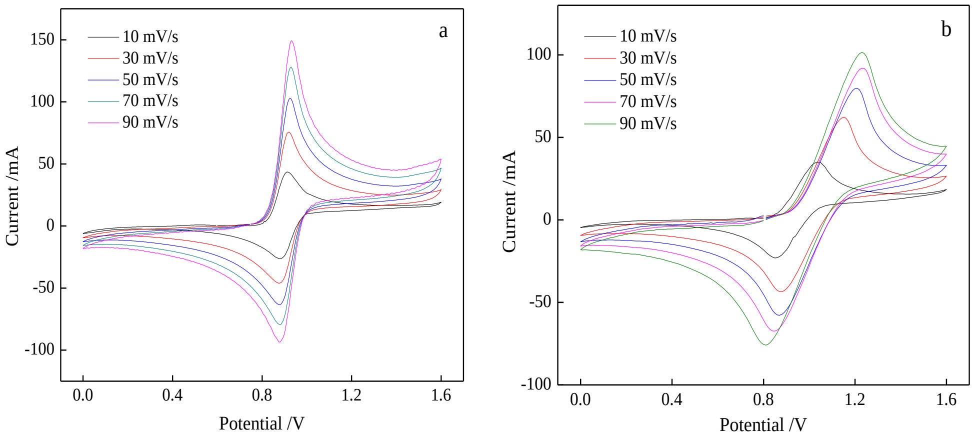


Figure 1. Cyclic voltammograms of mixed acids with different ratio of H_2SO_4 to CH_3SO_3H. Electrolytes: 1.5 mol/L $VOSO_4$ contained in the mixed acids listed in Table 1; Scan rate: 50mV/s

And the oxidation/reduction peak currents (i_p) have a good linear relationship with the square root of the scan rates ($\upsilon^{1/2}$) (Fig.2d), confirming that the oxidation of VO^{2+} and reduction of VO_2^+ in all three electrolytes are controlled by mass transport process[16]. The potential differences between oxidation and reduction peaks (ΔE_p) in the No.8 mixed acid (Fig.2a) keep around *ca.* 50 mV when the potential scan rate varies from 10 mV/s to 90 mV/s, while significant increasing of ΔE_p can be found in the other two electrolytes (CH_3SO_3H and H_2SO_4) (Fig.2b and c). This further proves that electrochemical reversibility of VO^{2+}/VO_2^+ couple in the No.8 mixed acid is better than those in the other two electrolytes (No.1 and No.9). According to the Randles-Sevcik equation[17], the above results may be ascribed to the higher diffusion rate of VO^{2+}/VO_2^+ couple in the No.8 mixed acid.



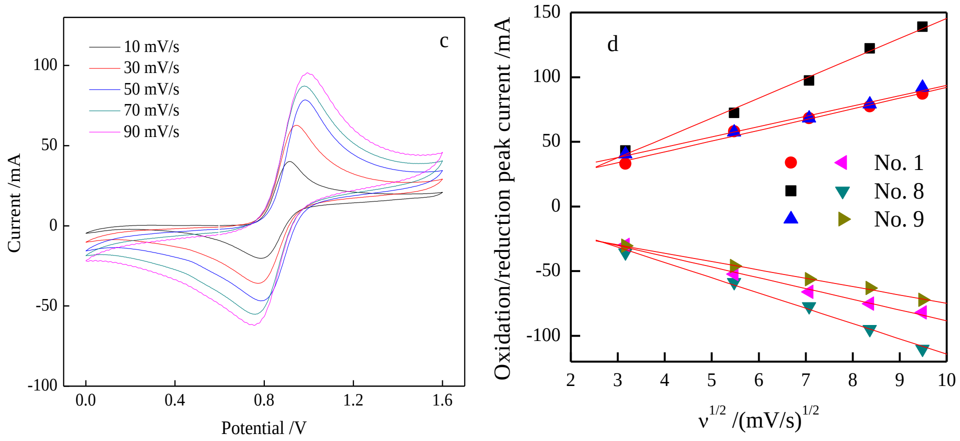


Figure 2. Cyclic voltammetric characteristics of mixed acid (a), CH_3SO_3H (b) and H_2SO_4 (c) at various potential scan rate. Electrolytes: 1.5 mol/L $VOSO_4$ contained in the mixed acids No.1, 8 and 9 listed in Table 1

3.3 Electrochemical impedance spectroscopy

To better understanding the influence of solution composition on electrochemical behavior of VO^{2+}/VO_2^+ couple, electrochemical impedance spectra were measured at the formal potential (φ_f). The formal potential is calculated according to the following equation[18], $\varphi_f = \frac{\varphi_{pc} + \varphi_{pa}}{2}$, in which φ_{pa} and φ_{pc} are oxidation peak potential and reduction peak potential, respectively, obtained from the CV curves shown in Fig.1.

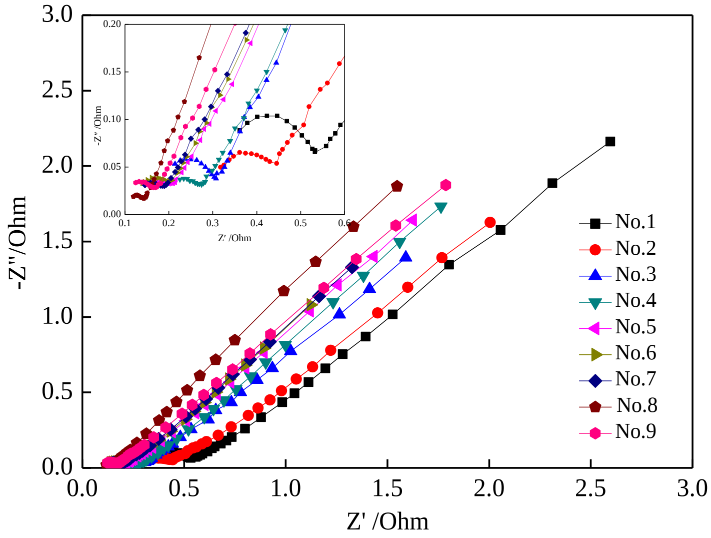


Figure 3. Nyquist plots of electrochemical impedance spectra. Electrolytes: 1.5 mol/L $VOSO_4$ contained in the mixed acids listed in Table 1

It can be seen from Fig. 3 that each plot consists of a semicircle in the high frequency region and a sloped line in the low frequency region, indicating that the redox reaction of VO^{2+}/VO_2^+ couple at the graphite electrode is simultaneously controlled by the charge transfer process and the diffusion process[19]. From the partial enlargement of the Nyquist plots in high frequency (the inset of Fig. 3), it can also be observed that the semicircles have different starting point and radius in different electrolytes, corresponding to different ohmic resistance (composed of solution resistance, electrode resistance and the contact resistance) and charge transfer resistance. In all nine electrolytes, the plot obtained in the solution containing 1.5 mol/L $VOSO_4$+2.75 mol/L H_2SO_4+0.25 mol/L CH_3SO_3H has the smallest ohmic resistance and charge transfer resistance, implying that the best conductivity and electrochemical activity of VO^{2+}/VO_2^+ couple can be achieved in this solution. This may be the reason for the cyclic voltammetric behaviors shown in Fig.1 and Fig.2.

3.4 Stability of the VO_2^+ solution

As mentioned in the Introduction, the stability of VO_2^+ in the positive electrolyte of VRFB is poor at an elevated temperature. To evaluate the influence of solution composition on the stability of VO_2^+, three typical solutions (No.1, No.8 and No.9 mixed acids) containing *ca.* 2.0 mol/L VO_2^+ were prepared by electrooxidation of $VOSO_4$, and the initial concentrations of VO_2^+ determined by redox titration were 2.02, 1.99 and 1.98 mol/L, respectively. Fig. 4 shows the change of VO_2^+ concentration in the as-prepared three solutions as a function of time at 40 ℃. In all three solutions the VO_2^+ concentration decreases with the prolonging of time, which may be ascribed to the formation of V_2O_5 precipitate[6]. After 120 h, the VO_2^+ concentration in 3 mol/L H_2SO_4 decreases to 1.12 mol/L, about 56.6% of the initial value (1.98 mol/L), while the concentration changes in the other two solutions are relatively smaller, 69.3% and 73.3% of the initial values in No.8 mixed acid and 3 mol/L CH_3SO_3H, respectively. This demonstrates the existence of CH_3SO_3H in the solution can improve the stability of VO_2^+, which may be ascribed to the high solubility of vanadium ions in CH_3SO_3H[14]. Therefore, better performance can be expected for the VRFB using mixed acid containing CH_3SO_3H as electrolyte.

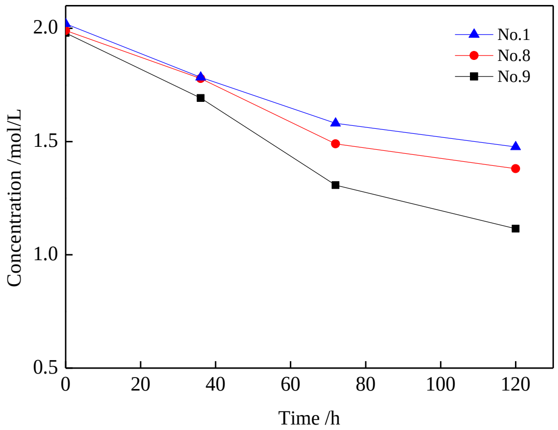
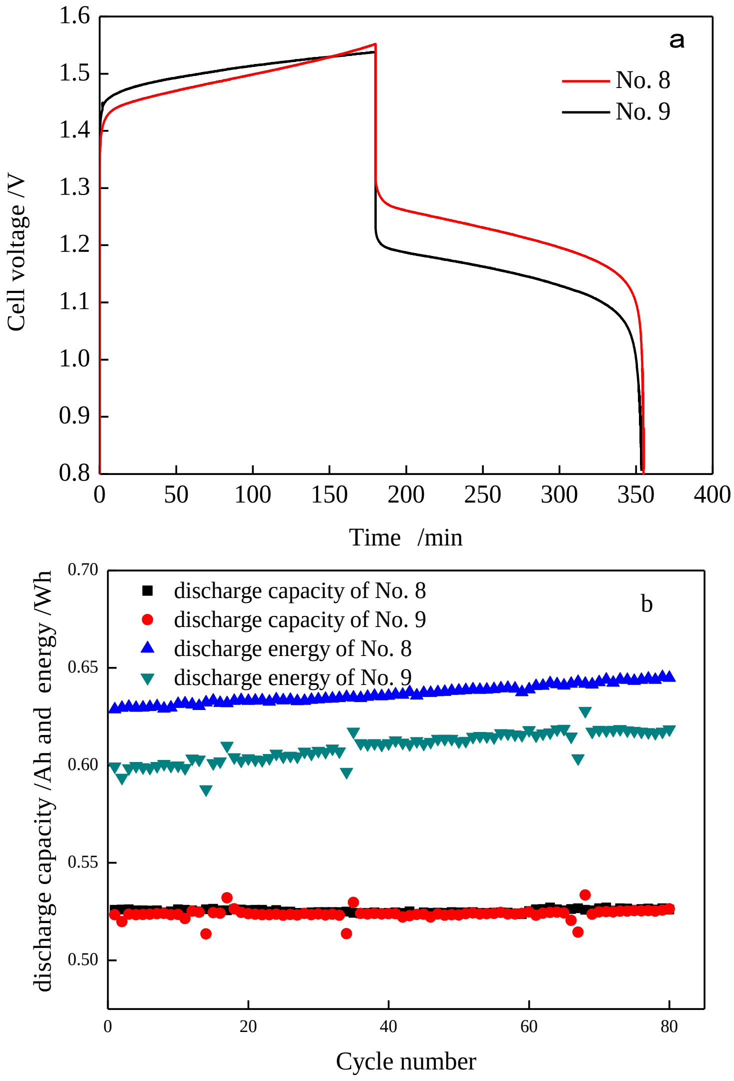


Figure 4. VO_2^+ concentration changes with time in different solutions. Electrolytes: *ca.* 2 mol/L VO_2^+ contained in the mixed acids listed in Table 1

3.5 Charge-discharge curves

The above-mentioned experimental results show that the increasing of CH_3SO_3H content in the supporting solution is beneficial to enhance the solubility and stability of vanadium ions in the electrolyte, but goes against the electrolyte conductivity and electrochemical activity of vanadium ions. Taking into consideration of various factors, the No.8 mixed acid exhibits the best performance compared to the others listed in Table 1. For further evaluation, the performance of a VRFB using No.8 mixed acid as supporting electrolyte was investigated, and that in 3 mol/L H_2SO_4 was also measured for comparison. Fig. 5a shows the typical charge-discharge curves of No.8 and No.9 mixed acids containing 1.5 mol/L vanadium ions, respectively. It can be seen that the VRFB using No.8 mixed acid as supporting electrolyte has lower charge voltage and higher discharge voltage. This may result from the higher conductivity and better electrochemical activity of vanadium ions in No.8 mixed acid[14]. Fig. 5b and 5c show the cyclic performance of two VRFBs using No.8 and No.9 mixed acids as supporting electrolyte, respectively.



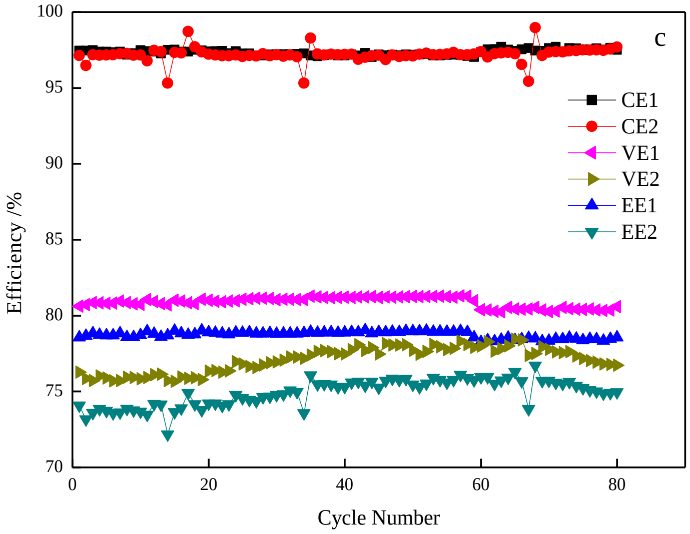


Figure 5. Electrochemical behavior of VRFBs with different electrolytes**.** Electrolyte: 1.5 mol/L vanadium ions contained in the No. 8 and No.9 mixed acids; a) Typical charge-discharge curves; b) Discharge capacities and energies; c) Performance of VRFBs

For both VRFBs in 80 cycles, almost the same discharge capacities (Fig. 5b) and current efficiencies (CE, Fig. 5c) can be achieved. This implies both VRFBs show good cyclic stability and reversibility in 80 cycles. In addition, VRFB using No.8 mixed acid as support electrolyte has higher voltage efficiency (VE, *ca*.81%) than that in 3 mol/L H_2SO_4 (*ca*.76%), which results in the higher discharge energy and energy efficiency in No.8 mixed acid compared with those in No.9 system.

4. CONCLUSIONS

The solubility and stability of vanadium ions can be significantly enhanced by the increasing of CH_3SO_3H content in the H_2SO_4-CH_3SO_3H mixed acid system. On the contrary, the negative effects are observed on solution resistance and electrochemical kinetics of VO^{2+}/VO_2^+ couple with the increasing of CH_3SO_3H. This may be related to the high viscosity of CH_3SO_3H and different complexation of $CH_3SO_3^-$ with vanadium ions compared with H_2SO_4. Within the scope of this work, the best electrochemical reversibility of VO^{2+}/VO_2^+ couple can be obtained in the solution using 2.75 mol/L H_2SO_4+0.25 mol/L CH_3SO_3H mixed acid as supporting electrolyte. At this point, the advantages and disadvantages factors resulting from the addition of CH_3SO_3H may reach a compromise. The VRFB with the optimized mixed acid electrolyte exhibits higher energy efficiency and the same high current efficiency compared with those of H_2SO_4 system. With the further evaluation and optimization, H_2SO_4-CH_3SO_3H mixed acid is of great potential for the practical application in the VRFBs with excellent properties.

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