Vanadium species in HCL and H2SO4 mixed acid as the positive electrolyte for Vanadium Redox Flow Battery

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Keywords: Vanadium redox flow battery, HCL, Mixed acid solution, electrochemical reversibility, energy efficiency.

Abstract. This paper examined HCL and H2SO4 Mixed Acid as the Supporting Electrolyte for Vanadium Redox Flow Battery. The results of Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS) showed that the MAS sample had a better electrochemical activity than Pristine sample. At 20mAcm-2, VRFB with MAS sample exhibited a better discharge capacity than pristine sample. Moreover, the VFRB with MAS sample achieved higher average energy efficiency (81.26%) compared to the pristine cell (75.62%) and exhibited excellent cycling stability.

1. Introduction

As one of the most promising Redox flow battery (RFB) technologies for large-scale storage, vanadium redox flow battery (VRFB) initially proposed by Skyllas-Kazacos^[1-2], has high efficiency, long cycle life, low running cost and its independent tunability of power and capacity. VRFB store energy through the conversion between V^{2+}/V^{3+} and V^{4+}/V^{5+} redox couples, which are in aqueous sulfuric acid solution as the and negative half-cell respectively, So the energy density of VRFB is directly determined by the concentration of electrolytes^[3-7]. However, the limitations on vanadium solubility and the stability of the electrolyte solutions, especially the V(V) electrolyte, which can hardly be more than 1.8 M, and the temperature range is generally restricted between 10 and 40°C, so significantly affects the performance of VRFB^[8-9]. In the last decade, much work has been done to improve the solubility and stability of the positive electrolyte solutions, such as adding organics and inorganics ^[10-14]. Still, the concentration of stable vanadium species could not be exceeded 1.8M, overall improvement of the VRB systems in terms of energy capacity and stability has been quite limited ^[15]. Chloride and Chloride-sulfate mixed Acid had used as supporting electrolyte in VRFB ^[15-16].In this paper, we further researched the VRFB system that uses mixed sulfate and chloride electrolytes. Its electrochemical activity were evaluated by CV and EIS. Its performance in VRFB was investigated by charge-discharge technique.

2. Experimental

2.1. Preparation of electrolyte

The 2M V (IV) electrolyte solutions were prepared by dissolving vanadyl sulfate (VOSO₄·nH₂Os, Shanghai Dibo Chemical Co. Ltd., China, n = 4) in 2M HCL+2M H₂SO₄ and 4M H₂SO₄ supporting electrolyte, respectively. The resulted solution was then placed in the vanadium redox cell and charged with a current density of 20 mAcm⁻² until a bright yellow solution of V (V) was produced in the positive. The electrolyte solutions in the positive are the 2M V (IV)/ V (V) + 2M H₂SO₄+2M HCL and 2M V (IV)/ V (V) +4M H₂SO₄ test solutions.

2.2. Electrochemical measurements

Cyclic voltammetry (CV) tests were conducted in a three-electrode system on the CHI660 electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) at a scan rate of $10\text{mV}\cdot\text{s}^{-1}$ between 0.2 V and 1.4 V at room temperature. The system employed a 1cm^2 Pt sheet as working electrode, a 4cm^2 Pt sheet as counter electrode and an aqueous saturated calomel electrode

(SCE) as reference electrode. To avoid cross-contamination of different ions on the electrodes surface, the Pt sheets ware rinsed carefully after each test.

Electrochemical impedance spectroscopy (EIS) was also conducted on the CHI660 electrochemical workstation. The sinusoidal excitation voltage applied to the cells was 5 mV. The frequency range was from 0.01Hz to 100 KHz.

2.3. Charge-discharge test

The VRFB cell performance was tested using a single static cell system, which consisted of two graphite felt electrodes (thickness is 7 cm, Shenhe carbon fiber Materials Co., Ltd.), two conductive plastic current collectors and a Nafion 117 membrane. The effective reaction area of both electrode and membrane was about 10 cm². The porous graphite felt were filled with electrolytes on both sides. For cell performance evaluation and electrolyte solution preparation, The single cells were conducted on xinwei battery test system (xinweier electronics Co., Ltd.) between 0.7V and 1.7V at a range of constant current density of 20 mAcm⁻². Cell cycling tests were performed at a fixed charging and discharging current density of 20 mA cm⁻².

The bulk solution resistance and charge-transfer resistance of MAS (1.52Ω , 14.41Ω) are lower than that of Pristine (2.33Ω , 20.42Ω). Therefore, the MAS causes charge-transfer resistance to decline, reflecting a higher reactive velocity, which corresponds to CV testing ^[18].

2.4. Cell tests

The VRFB cell performance was tested using a single static cell system, which consisted of two graphite felt electrodes (thickness is 7 cm, Shenhe carbon fiber Materials Co., Ltd.), two conductive plastic current collectors and a Nafion 117 membrane. The effective reaction area of both electrode and membrane was about 10 cm². The porous graphite felt were filled with electrolytes on both sides. For cell performance evaluation and electrolyte solution preparation, the single cells were conducted on xinwei battery test system (xinweier electronics Co., Ltd.) between 0.7V and 1.7V at a range of constant current density of 20 mAcm⁻². Cell cycling tests were performed at a fixed charging and discharging current density of 20 mA cm⁻².

3. Results and discussion

3.1. Cyclic voltammetry

Fig.1. shows the CV cueves of MAS and Pristine samples at 10 mV/S. The oxidation and reduction peaks current corresponding to a V(V)/V(IV) couple appear at approximately 1.0V and 0.75 V(vs. SCE), respectively.

It can be seen that the potential gaps of the MAS solutions between oxidization and reduction peaks (Δ Ep) decrease, indicating better electrochemical reversibility^[17-18], and the peak currents greatly increase and become more symmetrical, implying improved redox kinetics ^{[17].}

3.2. EIS analysis

We carried out EIS measurement to further understand the effect of supporting electrolyte on the performance of the V(IV)/V(V) electrolyte. The Nyquist complex-plane impedance plots of MAS and Pristine are shown in Fig.2. Each Nyquist plot includes semi-circle in the high-frequency region and a sloping straight line in the low-frequency region, demonstrating that the V(IV)/V(V) redox reaction is mix-controlled by charge transfer and diffusion steps. The radius of the semicircle corresponds to the charge-transfer resistance, while the linear part is associated with the diffusion of vanadium species in the electrode ^[17-18]. The inset in Fig. 2 shows the equivalent circuit derived from the Nyquist plots. R1 is bulk solution resistance, R2 is Faradaic interfacial charge-transfer resistance, CPE1 is the constant phase element that accounts for double layer capacitance, and CPE2 is the constant-phase which represents the diffusion capacitance attributed by the diffusion process of V(IV) and V(V) ions in pore channel of the graphite electrodes^[18].

3.3. Charge-discharge test

The discharge tests were performed in static cells at the current density of 20 mA cm⁻². Fig.3 presents the typical discharge capacity of cells using positive with MAS and Pristine acid in 30 cycles.

As observed in Fig.3-(1), with the cycle increasing, discharge capacity of MAS sample and Pristine sample decay due to the self-discharge rates for the two samples. But the discharge capacity of MAS sample slowly during the whole operation, due to its better reversibility and electrochemical reaction reversibility verified by CV and EIS.

Fig.3-(2) gives its columbic and energy efficiency as a function of cycling number at 20mAcm⁻². In 30 cycles, the VRFB with MAS acid have a better stable coulombic efficiency and energy efficiency than pristine one. The average energy efficiency of the cell with MAS acid is 81.26%, 5.64% higher than that of the pristine one, demonstrating the enhancement of electrochemical performance. The excellent electrochemical performance of the cell with MAS acid should be ascribed to the good thermal stability.

4. Conclusion

A vanadium sulfate and chloride mixed electrolyte proved to be stable with a vanadium content of up to 2 M. CV and EIS techniques results showed the electrochemical activity of the electrolyte with MAS was significantly improved compared with that in sulfuric acid. Furthermore, charge and discharge data clearly exhibited higher discharge capacity, energy efficiency and coulombic efficiency compared with the pristine solution. The cycling data show that the VRFB with MAS system has a better stability.



Fig.1 Cyclic voltammograms of MAS and Pristine samples at a scan rate of 10mV/s for MAS and Pristine samples



Fig.2.Electrochemical impedance spectroscopy (EIS) of MAS and Pristine samples



Fig.3. Charge-discharge test of VRB with MAS and Pristine samples: (1) Discharge capacity (2) Coulombic efficiency and energy efficiency

Acknowledgment

This present research is funded by the Vanadium titanium material and compound technology laboratory (No. 13FTFH04-2014)

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