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RESEARCH PAPER

Investigations on the Electrode Process of Concentrated V(IV)/V(V) Species in a Vanadium Redox Flow Battery

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Abstract: The electrode process of concentrated V(IV)/V(V) species has been studied at a graphite electrode by using cyclic voltammetry, low speed linear polarization, and impedance techniques. The results have revealed that in H_2SO_4 solution below 2 mol·L^{-1} containing 2.0 mol·L^{-1} V(IV), the electrode process of V(IV)/V(V) is controlled by the electrochemical polarization and diffusion with poor reversibility. When the concentration of H_2SO_4 is above 2 mol·L^{-1}, the electrode process of V(IV)/V(V) turns to diffusion control with improvement of the reversibility. An increase in concentration of H_2SO_4 solution facilitates a decrease in impedance, whereas too high concentration of H_2SO_4 solution (>3 mol·L^{-1}) results in a remarkable increase in the viscosity of solution leading to a large mass transportation polarization, and thus the impedance starts to increase a little. In 3 mol·L^{-1} H_2SO_4 solution, the reversibility and kinetics of V(IV)/V(V) are improved gradually and the characteristics of impedance also improves with an increase in concentration of V(IV) solution. But, when the concentration of V(IV) solution exceeds 2.0 mol·L^{-1}, the viscosity of the solution is so high that the mass transportation polarization increases considerably, resulting in the deterioration of electrochemical performance of V(IV)/V(V) species and an increase in impedance. Therefore, by considering from the standpoint of increasing energy density and electrode kinetics comprehensively, the optimal concentration of H_2SO_4 is 3 mol·L^{-1} containing 1.5–2.0 mol·L^{-1} of V(IV).

Key Words: Vanadium redox flow battery; V(IV)/V(V); High concentration; Electrode process

Ever since Thaller[1] proposed the concept of the redox flow battery (RFB), researchers have been exploring possible redox couples. However, only recently, the sodium polysulfide/bromine and the vanadium redox battery have shown prospects of applications[2–3]. Effect of the cross-contamination of the positive electrolyte and negative electrolyte on performance of the RFB has been considerably diminished because of the use of a single element for both the negative and positive halves of the vanadium RFB. Therefore, the vanadium RFB is more superior to other systems.

Although performance of the vanadium RFB is influenced by many factors such as membranes and electrodes, investigations on the positive/negative electrode reaction kinetics are of the same importance for optimization of performance of the battery. So far, the V(IV)/V(V) electrode process kinetics have been described in a lot of literature, but concentration of the aqueous media used was limited to diluted vanadium solutions ranging from 0.1 to 0.5 mol·L^{-1}, which were far lower than that of practical electrolytes[4–6]. Based on spectroscopic and/or dynamic electrochemical data , the dissolved states of V(V) and V(IV) in concentrated sulfuric acid(H_2SO_4) solution were discussed in literatures[7–9], whereas the conclusions kept rather different from one report to another. Oriji *et al.*[10] studied the electrochemical behaviors of 2.0 mol·L^{-1} $VOSO_4$ in 1–9 mol·L^{-1} H_2SO_4 solution by applying a rotating disk electrode. Oriji *et al.*[11] determined the electrochemical parameters such as diffusion coefficients and Stokes radii of V(V) and V(IV) species with high concentrations, finding that the electrode reaction of V(IV)/V(V) may be accompanied by a certain chemical step. But then, Oriji *et al.*[10–11] had employed

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a platinum electrode and a glassy carbon electrode, while practical electrodes are graphite and porous carbon felts. In addition, the concentration of a vanadium aqueous solution and H_2SO_4 as a supporting electrolyte had not been optimized.

In the present study , the electrode process kinetics of concentrated V(IV)/V(V) at a graphitic electrode have been studied by cyclic voltammetry, linear sweep voltammetry at a low scan rate, and impedance measurements to obtain the optimal concentration of V(IV)-H_2SO_4 solution used in the vanadium RFB.

1 Experimental

1.1 Preparation of V(IV)-H_2SO_4 solution

$VOSO_4 \cdot nH_2O$ (Shanghai Lvyuan Chemicals, n=3.0 according to thermogravimetric analysis, the purity is ≥97.9%.) was dissolved in 1–4 mol· L^{-1} H_2SO_4 to give a V(IV) solution.

1.2 Pretreatment of electrodes

A graphitic rod (Shanghai Xinxia carbon Co Ltd) was employed as a working electrode. Prior to determination, the electrode surface was polished with a 1000-grit polishing paper, and then the electrode was sonicated for 10 min in water, followed by air-dry.

1.3 Apparatus and equipment

A Ubbelohde-type capillary viscometer; A model 600B electrochemical workstation (Shanghai CH Instruments Co.); An EG&G electrochemical workstation (Princeton Corporation, USA) including a 273A potentiostat and a 1025 frequency response analyzer.

1.4 Measurement procedures

The viscosity of the solution was obtained as follows: a volume of liquid was taken to flow through the capillary viscometer from a fixed height of the liquid surface in a thermostat bath of (20±2)℃, and the flowing time was recorded, multiplying with the correcting constant coefficient (0.04112 $mm^2 \cdot s^{-2}$) to give the viscosity .

A graphite rod (area=0.103 cm^2) and a saturated calomel reference electrode(SCE) were employed as the working and the reference electrodes, respectively. Subsequently, a three-system was built by using a graphite plate with a large surface area as the counter electrode. The cyclic voltammetry and linear polarization plots of V(IV)-H_2SO_4 solution with different concentrations were determined by applying the model 600B electrochemical workstation. In the same cell with three electrodes, the impedance measurements of V(IV)-H_2SO_4 solution with different concentrations were carried out with an EG&G electrochemical workstation at frequency from 1×10^5 Hz to 0.1 Hz with an amplitude of ±5 mV.

2 Results and discussion

2.1 Effect of H_2SO_4 concentration on the V(IV) / V(V) electrode reaction

The concentration of V(IV) solution commonly used in the vanadium flow battery is 2.0 mol·L^{-1} [5–6]. Fig.1 shows cyclic voltammograms of 2.0 mol· L^{-1} $VOSO_4$ in 1–4 mol·L^{-1} H_2SO_4 solution. The potential differences(ΔV_p) and the ratios (I_{pa}/ I_{pc}) of the anodic peak current to the cathodic peak current obtained from Fig.1 are listed in Table 1. As can be seen from Table 1, when applying 1 mol·L^{-1} H_2SO_4, the anodic peak current is far higher than the cathodic peak current, leading to the I_{pa}/I_{pc} beyond 1.8. It can be deduced from the electrode reaction expression (1) that 1.0 mol V(V) can not be reduced unless 2.0 mol H^+ exists in the solution. However, when 1 mol·L^{-1} H_2SO_4 is used, the $n(H^+)$ is just the theoretic value of H^+ needed for the reduction reaction of V(V). It suggests that practical requirements for the reduction reaction of V(V) would not be met. And hence the anodic peak current is much larger than the cathodic peak with a relatively larger potential difference and providing poor reversibility for the couple.

$$VO_2^+ + 2H^+ + e^- = VO^{2+} + H_2O \qquad (1)$$

As the concentration of H_2SO_4 increases, the peak potential difference as well as I_{pa}/ I_{pc} decreases and the I_{pa}/ I_{pc} is gradually close to 1 with an improvement in reversibility of the

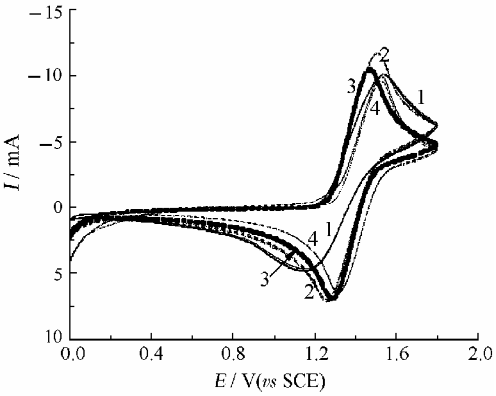

Fig.1 Cyclic voltammograms of a stationary graphite electrode in 1–4 mol·L^{-1} H_2SO_4 solution containing 2.0 mol·L^{-1} V(IV)
scan rate=50 mV·s^{-1}, $c(H_2SO_4)$/(mol·L^{-1}) : 1) 1; 2) 2 ; 3) 3 ; 4) 4

Table 1 Cyclic voltammogram data of 2.0 mol·L^{-1} $VOSO_4$ on a graphite electrode in 1– 4 mol·L^{-1} H_2SO_4 solution

$c(H_2SO_4)$/(mol·L^{-1})	ΔV_p[a] / V	I_{pa}/I_{pc}[b]
1	0.386	1.817
2	0.249	1.224
3	0.185	1.121
4	0.212	1.032

[a] ΔV_p means the difference between the anodic potential and the cathodic potential.

[b] I_{pa}/I_{pc} means the ratio of the anodic peak current to the cathodic peak current.