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Reaction Mechanism of $V(V) / V(IV)$ Redox Couple at Graphite Felt Composite Electrode Bonded with Conductive Carbon Plastic

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Abstract: The rate-determining step of $V(V) / V(IV)$ redox reaction was investigated at graphite felt (GF) composite electrode by various techniques: cyclic voltammetry, polarization curve and impedance spectroscopy. Cyclic voltammetry analysis indicated that $V(V) / V(IV)$ redox reaction at GF electrode is quasi reversible. A certain chemical reaction step is suspected to follow the electron transfer step of this reaction. The Tafel slope value (0.124) obtained from the polarization curve agrees well with theoretical value (0.12), which supposing the electron transfer step was the rate-determining step. Impedance Spectroscopies at various potentials were studied and simulated by equivalent circuits. The impedance value of the electron transfer step modified is greatly higher than the others, which shows that the electron transfer step is the rate-determining step. This further confirms the conclusion obtained by polarization curve test.

Key words: graphite felt; rate-determining step; vanadium redox battery; $V(V) / V(IV)$

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1 Introduction

The all vanadium redox flow battery (VRB) has become the research focus, and it has received more and more attentions after it was first reported by Skylas-Kazacos M. et al.^[1-2] in 1985 due to its unique technical advantage. The VRB has been tested in the application for the power of wind and solar as well as peak shaving in electric-network for a long time, and now the technology is coming into commerce^[3-4].

The vanadium redox battery employs the $V(V) / V(IV)$ and $V(V) / V(IV)$ redox couples in H_2SO_4 in the negative and positive half-cell electrolytes, respectively. The integral performance is restricted by such reason as the complexity and instability of vanadium species of different value in electrolyte solutions, and the indefinite relationship between ion

species and its electrochemistry. So far, Sum E. et al.^[2, 5] studied the electrochemical behavior of $V(V) / V(IV)$ redox couple at glassy carbon and gold electrode as well as graphite electrode using cyclic voltammetry and rotating disk electrode. The diffusion coefficient and the dynamic parameter of $V(V) / V(IV)$ redox couple on graphite electrode were obtained. Recently, Oriji Gaku^[6] pointed out that the redox process of $V(V) / V(IV)$ couple at glassy carbon electrode involves the post chemical transforming process with the transfer of oxygen atom. Gattrell M.^[7] also reported that the reaction mechanism of $V(V) / V(IV)$ redox couple agreed to the models of CEC and ECC in the low and high overpotential ranges, respectively. In spite of these research, there is much less research on the controlling

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step and alternating current (AC) impedance of $V(V)/V(IV)$ redox reaction

We have investigated the electrochemistry activity and kinetics of $V(V)/V(IV)$ redox couple at various electrodes previously^[8]. In the present study, the reaction mechanism and controlling step of $V(V)/V(IV)$ redox couple at graphite felt composite electrode were studied by the methods of cyclic voltammetry, polarization curve and impedance spectroscopy.

2 Experimental Details

2.1 Preparation of Electrode

Polyacrylonitrile-based GF (A. R., provided by Shanghai Energy Carbon Limited Co.) was cut into a suitable size of 10 cm × 4 cm. The electrochemical oxidation for the GF was carried out in 1 mol/L H_2SO_4 solution for 8 minutes under the constant current density of 30 mA/cm² and a voltage ranging from 5 to 15 V, the oxidized GF served as anode and Ti plate as cathode, respectively. The treated GF was soaked in deionized water and washed thoroughly to remove the adsorbed H_2SO_4 . Finally, the treated GF was kept in a vacuum drying oven under 120 °C for 5 hours. The one side of dried sample was bonded with conductive plastic under 175 °C for 15 minutes^[9], and let the other side area of 1.5 cm² for the electrochemical reaction.

2.2 Preparation of Electrolyte Solution

The analytic grade V_2O_5 and V_2O_3 (provided by Tianjin Kemei Chemical Reagent Development Center) with the ratio of 1.05 : 1.0 were mixed with 3.5 mol/L H_2SO_4 simultaneously, and then the mixture was heated and filtered. The clear filtrate was collected to give a $V(V)$ solution containing 2.0 mol/L $V(V) + 3.0$ mol/L H_2SO_4 . The solution of $V(IV)$ was prepared by electrolyzing VO_2 solution using an electrolyzing device which was made up of graphite felt electrode, and ion exchange membrane was used to separate the electrolyte near anode from cathode. The purity solution of $V(IV)$ was obtained at anode after electrolysis. The electrolyte solution of $V(V)/V(IV)$ was obtained by mixing and diluting the above two solutions at a certain ratio. The concentration of

vanadium species in electrolyte solution was measured by ZDJ-4A automatic coulometric titrimer (Shanghai Precision & Scientific Instrument Co. Ltd, China)^[10].

2.3 Electrochemical Measurements

The cyclic voltammetry, polarization curve and AC impedance were carried out with CH 1660 electrochemical workstation (CH Instruments, Inc. American) in a three electrode system using Pt as counter electrode, SCE with Luggin Capillary as reference electrode. The scan rates in cyclic voltammetry and polarization curve were 10 ~ 0.2 mV/s and 1 mV/s, respectively. The sensitivity was set as 10⁻⁶. The measurement of AC impedance was processed after five scans of cyclic voltammetry, and the data was fitted by Zsimp Win 3.20 Demo software on CH 1660B workstation.

3 Results and Discussion

3.1 Analysis of Cyclic Voltammetry

The curves of cyclic voltammetry for $V(V)/V(IV)$ reaction at graphite felt electrode under different scan rate were displayed in Fig 1. As can be seen, the electrode reaction is a partial reversible reaction because the peak redox potential separation ($E_{pa} - E_{pc}$) exceeds 60 mV. The peak redox potential separation ($E_{pa} - E_{pc}$) reaches 100 mV under the minimum scan rate (0.2 mV/s). The peaks of redox potential exhibit symmetry at a certain extent, which indicated that the reaction is not absolutely irreversible.

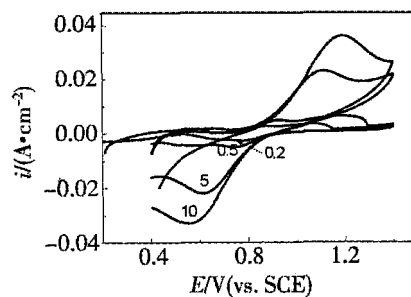


Fig 1 Cyclic voltammograms for $V(V)/V(IV)$ reaction at GF electrode in 0.0087 mol/L $V(IV) + 0.0087$ mol/L $V(V) + 1$ mol/L H_2SO_4 solution with various scan rates

The peak current density as a function of the square root of a scan rate ($v^{1/2}$) for $V(III)$ oxidation is shown in Figure 2. The peak current density increases with the augment in scan rate. However, the peak current density is not strictly proportion to $v^{1/2}$. The reaction approaches reversible process at a lower scan rate, but approaches irreversible process at a higher scan rate. The results indicate the reaction of $V(III)/V(IV)$ redox couple at graphite felt electrode is quasi-reversible.

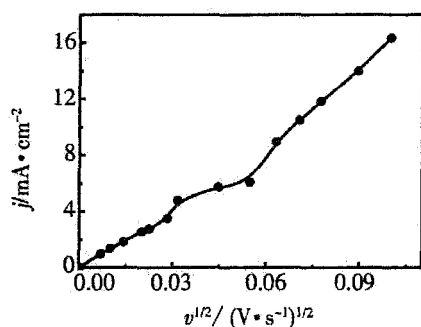


Fig 2 Peak current density as a function of the square root of scan rate for $V(III)$ oxidation

The half wave potential density ($E_{1/2}$) as a function of the scan rate ($\log v$) for $V(III)$ reaction is shown in Figure 3. As can be seen, the half wave potential density tends to increase as the scan rate increases. This indicates that the electrode reaction is a reaction of EC and including post-transition according to the classification of electrode reaction that accompanied chemical transition.

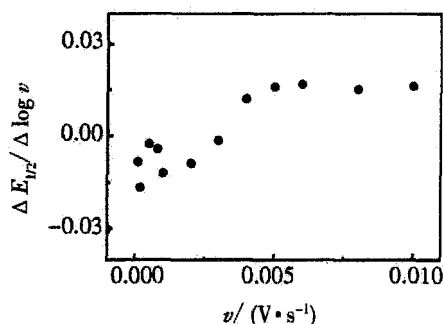
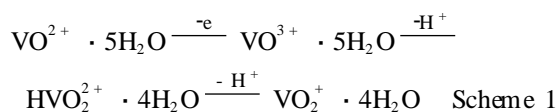


Fig 3 Half wave potential density as a function of the scan rate for $V(III)$ reaction

3.2 Analysis of Polarization Curve

According to the above analysis of cyclic voltammetry, the schematic diagram on the oxidation process of

$V(III)/V(IV)$ is shown in scheme 1.



If the reaction is assumed as the rate controlling step during the oxidation of $V(III)$, the steady-state polarization curve of electrochemical polarization on porous graphite felt electrode can be formulated as Eq 1:

$$I_a = i^0 \exp\left(\frac{-nF}{RT} \eta\right) \quad (1)$$

And the kinetic equation of polarization can be expressed as Eq 2:

$$\eta = -\frac{2.3RT}{F} \lg i^0 + \frac{2.3RT}{F} \lg I_a \quad (I_a \gg i^0) \quad (2)$$

It denotes transferring coefficient and varies with different electrode reaction, but is about equal to 0.5 commonly. The slope of polarization curve of the oxidation of $V(III)$ deduced from above equations:

$$\frac{\partial \eta}{\partial \lg I_a} = \frac{2.3RT}{0.5F} = 0.124 \quad (3)$$

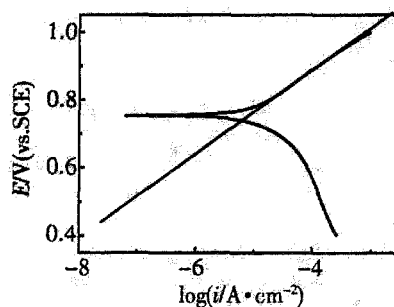


Fig 4 Polarization curve at graphite felt electrode in 0.03 mol/L $V(III)$ + 0.03 mol/L $V(IV)$ + 3 mol/L H_2SO_4 scan rate: 1 mV/s

The polarization curve at GF electrode in solution with 0.03 mol/L $V(III)$ + 0.03 mol/L $V(IV)$ in 3 mol/L H_2SO_4 is shown in Figure 4. The Tafel slope of anode regressed from the curve is 0.124. The experimental result is agreed with the theoretic value.

If the process of post chemical transition is assumed as the rate controlling step, and the balance of electrochemical reaction doesn't change, the function of electric potential of electrode vs concentration in solution can be expressed by the equation of Nernst

before or after polarization. There is no difference between the two chemical transition steps. The Tafel slope derived from revised Nernst equation as below Eq 4:

$$a = a + \frac{2.3RT}{F} \lg I_a \quad (4)$$

The Tafel slope is calculated as 0.06. And there is much difference between the theoretic value and the value obtained from experiment.

The above analytic results indicate that the electrochemistry reaction of the oxidation of V() is the rate controlling step at the porous graphite felt electrode.

3.3 Analysis of AC Impedance

The impedance spectra of GF electrode at different potentials are shown in Figure 5. There exist two semi-arcs with different size and a beeline. The semi-arc at high frequency region changes little with the change of polarization potential. And the impedance at this region is caused by the polarization of ohm. The semi-arc at low frequency region increases with

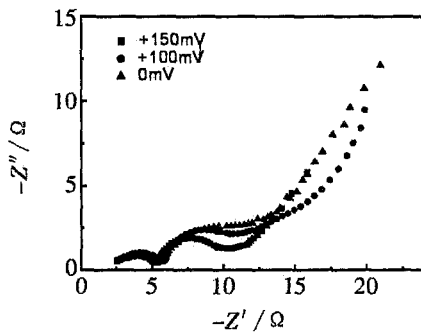


Fig 5 Impedance spectra of the graphite felt electrode at potential of 0, 100, 150 mV, respectively

the decreasing of polarization potential. The impedance at this region is caused by electrochemical polarization of the oxidation of V(). The diameter of semi-arc increases at lower polarization potential is due to the relative small AC current density (i^0) of oxidation.

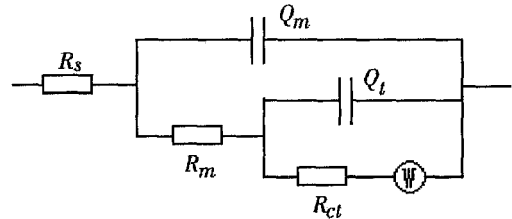


Fig 6 The equivalent circuits of graphite felt electrodes

The impedance spectra were fitted using the least-square procedure, and the results are listed in Table 1. The equivalent circuits of graphite felt electrodes at some potential are shown in Figure 6. R_s , R_m and R_{ct} denote the solution resistance between working electrode surface and reference electrode, the ohm polarization resistance at graphite felt, and the redox electrochemistry impedance, respectively. Q_m and Q_i denote constant phase element (CPE), which related to adsorbed intermediate and Faraday reaction, respectively. And the special physical implication of CPE is still unclear. It is only an experimental parameter introduced to fit the impedance data. Generally, the value of CPE is related to the roughness of electrode surface. The electrode surface resistance and capacity increase with the augment in surface roughness due to the increase of surface area. At the

Tab 1 Electrode kinetic parameters modified by equivalent circuit at open potential

Polarization potential / mV	R_s / cm^2	CPE		R_m / cm^2	CPE		R_{ct} / cm^2	$W / \text{S} \cdot \text{s}^{0.5}$
		$Y / \text{S} \cdot \text{s}^{-n}$	$n(0 < n < 1)$		$Y_1 / \text{S} \cdot \text{s}^{-n}$	$n(0 < n < 1)$		
0	2.686	0.0771	0.2142	202.30	0.0184	0.782	1.82e4	2.659e-10
100	1.798	0.0247	0.3688	42.78	0.0559	0.468	2292	1.522e-5
150	2.168	0.1423	0.2926	0.02	0.0209	0.294	271	2.751e-8

same time, the current density becomes inhomogenous when the surface roughness increases, which results in the occurrence of dispersion. W stands for Warburg impedance, i_e impedance caused by concentration polarization. As can be seen from Table 1, R_{ct} is the maximum impedance under three potential, which indicated the electrochemistry is the controlling step.

4 Conclusions

Cyclic voltammetry analysis indicates that $V(V)/V(IV)$ redox reaction at graphite felt composite electrode is quasi-reversible, and a certain chemical reaction step is suspected to follow the electron transfer step of this reaction. The study of polarization curve indicates the electrochemistry reaction of $V(V)/V(IV)$ (VO^{2+}) is the rate-controlling step during oxidation process. Impedance spectroscopy study also verified the conclusion obtained by polarization curve test.

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V(V)/V(IV)电对在石墨毡与导电塑料复合电极上的反应机理

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摘要: 应用循环伏安、极化曲线和交流阻抗等电化学方法研究了 $V(V)/V(IV)$ 电对在石墨毡复合电极上反应的速控步骤。结果表明, $V(V)/V(IV)$ 电对在石墨毡电极上的反应属准可逆过程, 且氧化过程包含有后置化学转化步骤; 该过程 Tafel 斜率的实验值为 0.124, 而理论计算的, 以电化学步骤作为控制步骤的 Tafel 斜率约 0.12, 两者吻合很好, 表明该氧化过程受电化学步骤控制; 以等效电路拟合不同极化电位下的交流阻抗, 得出该电化学反应阻抗远大于其他阻抗, 意味着电化学过程可能是电极反应的控制步骤, 与实验得到的极化曲线分析结果相一致。

关键词: 石墨毡; 控制步骤; 钒电池; $V(V)/V(IV)$