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Investigations on the V(III) Reduction Process of All-Vanadium Redox Flow Battery

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The V(III) reduction process of all-vanadium redox flow battery was investigated by cyclic voltammetry, polarization curve and AC impedance. It was shown that V(III)/V(II) couple had undesired electrochemical activity and the V(III) reduction process was in mix controlling step. The probable reason was that the existence of complex of V(III), which had big ion radius, resulted in large diffusion resistance in the process of mass transfer. Therefore, the kinetics of V(III) reduction reaction was slow.

Keywords: All-vanadium redox flow battery; Reduction; Electrolyte; Polarization curve; Electrode process

1. INTRODUCTION

Redox flow battery (RFB) is a promising technology for large-scale storage of electrical energy [1], which stores energy using catholyte and anolyte separated by a membrane. This device could realize an independent scaling of the power part and electric energy storage part, leading to be well-suited for large electricity-storage. Among various RFB systems, vanadium redox flow battery (VRFB), initially proposed by Skyllas-Kazacos [2, 3], has aroused the most extensive attention due to its utilization of four different valence state of vanadium species that can significantly diminish the cross-contamination of active components. The VRFB has been exerted to have almost unlimited cycle life since the electrode reactions involve no phase change [4] and the battery can be theoretically overcharged and overdischarged. In recent years, VRFB has been commercialized by many companies such as Golden Energy Fuel Cell GEFC (China), Cellenium (Thailand), Prudent energy (China), and Gildemeister (Germany) [5]. The VRFB is comprised of the V(IV)/V(V) redox couple for the positive electrode and the V(II)/V(III) redox couple for the negative electrode, where the reactants are typically

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dissolved in sulfuric acid. Although the overall cell performance depends on various factors [6], the negative and positive electrode reactions are the most important ones to optimize the cell operation and to realize high energy efficiency. Up to now, the electrochemistry performance and electrode processes of positive redox couple in VRFB have been investigated extensively. Among them, Gattrell et al. [7] reported that the reduction of V(V) to V(IV) proceeds by CEC mechanisms at low overpotentials and by ECC mechanisms at high overpotentials. Oriji et al. [8, 9] studied the stokes radii of V(IV) and V(V) species in concentrated sulfuric acid solutions and further discussed the electrochemical behavior of positive electrolytes. Xu et al. [10] studied the electrochemical behavior of the V(IV)/V(V) couple on a graphite electrode at different temperatures and found the anodic oxidation of V(IV) is a mixed kinetic-diffusion controlled process at the anodic polarization ranged from 32 to 132 mV. Wen et al. [11] investigated the electrode process of concentrated V(IV)/V(V) species, and they found the electrode process was affected significantly by the sulfuric acid concentration. The electrode process of V(IV)/V(V) is controlled by the electrochemical polarization and diffusion in H_2SO_4 solution below 2 M while it turns to diffusion control in H_2SO_4 above 2 M. Our previous researches [12] confirmed that V(IV)/V(V) couple had good electrochemical activity and reversibility. Compared to V(IV)/V(V) species, the electrode process of V(II)/V(III) redox reaction are not well understood, which limits the development of VRFB with high power and efficient characteristics. So far, Skyllas-Kazacos [2] investigated the electrochemical performance of V(III)/V(II) redox couples based on grassy-carbon electrode. It was suggested that the system may be considered as irreversible. Zhao et al. [13] studied the solubility of V(III)-H_2SO_4 system and put forward that V(III)/V(II) couples exhibited irreversibility and elevated H_2SO_4 concentration benefited to its reversibility. Some organic or inorganic additives for the negative electrolyte can enhance the reversibility of the reaction and boosted the energy efficiency of the battery [14, 15]. Even so, the mechanism of V(III)/V(II) redox reaction is still unclear and the reasons of the undesired electrochemical behavior of negative reaction are uncertain. To explore the process of negative reaction and to well understand the electrochemical properties of negative electrolyte, in this study, the electrochemical behavior of V(III)/V(II) was investigated by cyclic voltammetry, polarization curve and AC impedance. The reductive reaction order and the controlling step of the reaction were determined from the polarization curve. Furthermore, the reason why V(III)/V(II) couple had worse electrochemical activity than V(IV)/V(V) couple was proposed.

2. EXPERIMENTAL

2.1 The preparation of VRFB negative electrolytes containing V(III)

The VRFB negative electrolytes were prepared by chemical method [16]. The mixture of industrial pure V_2O_5, V_2O_3 and oxalic acid (AR) with a mass ratio of 1 : 6 : 2 was added to the 9.2 $mol \cdot L^{-1}$ sulfuric acid at 80°C. Distilled water was added to dilute the solution after keeping reaction for 20 min at 80°C. The VRFB negative electrolyte was obtained by filtration after reacting for 10 minutes. By adding dilute sulfuric acid, electrolytes with the same acidity but various vanadium concentrations were obtained. Ammonium ferrous sulfate titration method [5] was used for the determination of the electrolyte concentration.

2.2 Electrochemical measurements

The cyclic voltammograms and polarization curves were measured using a three-electrode system comprised by a graphite plate (50 mm×30 mm×5 mm) as the auxiliary electrode, saturated calomel electrode (SCE, with a standard electrode potential of 0.2414V) as the reference electrode, platinum electrode (10mm×10mm) as the working electrode for we compared the electrochemical activity of V(III)/V(II) couple on platinum, glassy-carbon and graphite electrode, and found V(III)/V(II) couple exhibits better electrochemical activity on platinum electrode [12]. Data were recorded by the electrochemical station (CHI660D, ChenHua Instrument Co. Limited, Shanghai, China). The scan range was controlled from -0.25~1.60V, because the hydrogen evolution occurs when the electrode potential is less than -0.25V. The scan rates were (a) $50mVs^{-1}$, (b) $30mVs^{-1}$, (c) $10mVs^{-1}$, respectively. The polarization curves were determined by using controlled potential steps with slow linear sweep potential under stir condition (scan rate 1 mVs^{-1}, scan range 0.4 ~ -0.23V).

In the same cell with three electrodes, the AC impedance measurements of V(III)-H_2SO_4 solution were carried out with the electrochemical station under stir condition at frequency from 1×10^6 Hz to 1 Hz with an amplitude of ±5 mV. The electrodes were immersed in the electrolyte for a few minutes before the test in order to stabilize the open circuit voltage. The results of AC impedance were simulated by Zsimpwin with an equivalent circuit shown in Fig.1. It was suggested that the electrochemical behavior of V(III)-H_2SO_4 solution could be simulated accurately with an equivalent circuit of *Rs*(*Cp*(*RpW*)).

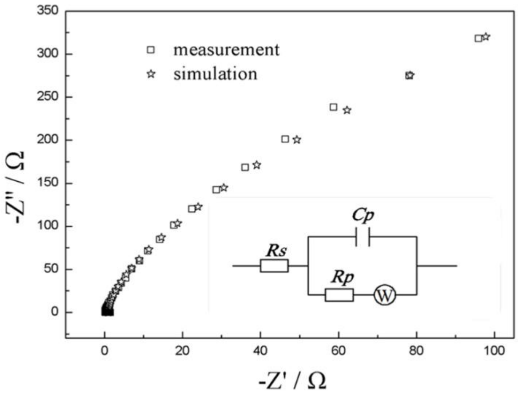

Figure 1. Measured and simulated AC impedance spectra of VRFB negative electrolyte using *Rs*(*Cp*(*RpW*)) as molder

2.3 UV-Vis spectra measurements

UV-Vis spectra of the electrolyte were recorded on a UV spectrophotometer (UV-1800PC, Shanghai Meipuda Instrument Co. LTD, Shanghai, China) with a scanning range from 1100 to 190 nm and scanning interval of 1 nm.

3. RESULTS AND DISCUSSION

3.1 Determination of basic kinetic parameters

A typical series of cyclic voltammograms of V(III)-H_2SO_4 solution containing V(III) 1.640 mol·L^{-1}, total vanadium (TV) 1.7425 mol·L^{-1} were conducted. The results are shown in Fig.2. From the Fig.2, the oxidation peaks O_1 of V(IV)/V(V) couple and its corresponding reduction peaks R_1 can be observed obviously. As for V(Ⅲ)/V(Ⅱ) couple, we can only observe the reduction peaks R_2 but no apparent corresponding oxidation peaks. This means that V(III)/V(II) couple is electrochemical irreversibility and has undesired electrochemical activity. The oxidation peak O_3 is caused by the adsorption reaction [17]. In order to study the mechanism of the reduction reaction, the polarization curves were conducted to determine the kinetic parameters of the reaction.

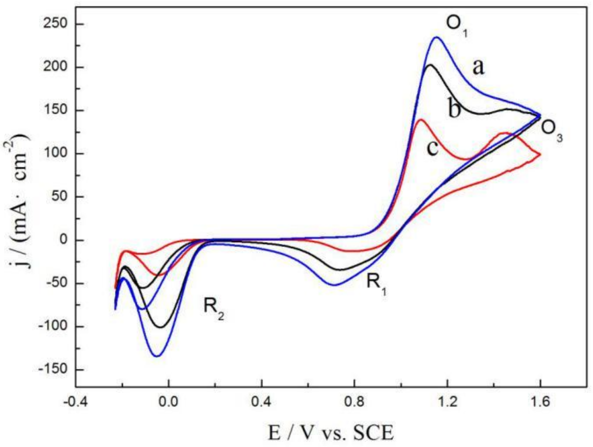

Figure 2. Cyclic voltammetry curves of the electrolyte (V(III) 1.640 mol·L^{-1}, total vanadium (TV) 1.7425 mol·L^{-1}) on platinum electrode at 25 °C with different sweep rates (a.50mVs^{-1}, b.30mVs^{-1}, c.10mVs^{-1})

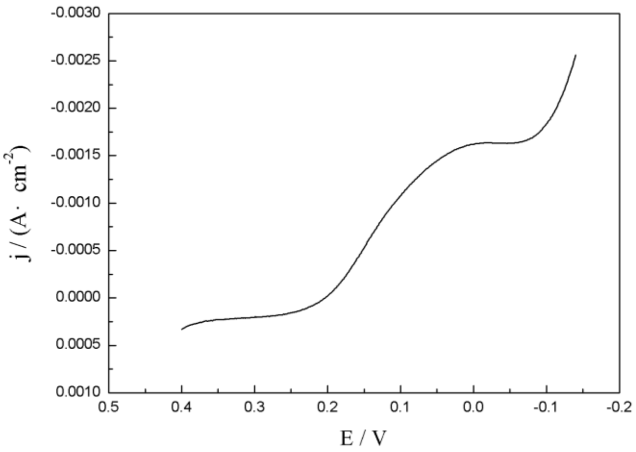

Figure 3. Polarization curve of V(III)-H_2SO_4 solution containing V(III) 1.640 M, TV 1.7425 M

The typical steady-state polarization curve of V(III)-H_2SO_4 solution (containing V(III) 1.640

mol·L^{-1}, TV 1.7425 mol·L^{-1}) is shown in Fig.3. There are two reduction reaction waves. The first one is the reduction of V(III) to V(II). The equilibrium potential is about 0.203V. The limiting current appears at an electrode potential of 0.0 V, and the limiting current density j_d is 1.825×10^{-3} A·cm^{-2}. The second reduction wave is associated with the hydrogen evolution reaction when electrode potential is less than about -0.10V.

If the electrochemical step is slow (low exchange current density), there may be a potential polarization as η>100/n (mV) without causing severe concentration polarization, and the opposite direction current can be ignored. In this case, it obeys Tafel equation [18]:

$$\eta_c = -\frac{2.3RT}{\alpha nF}\lg j^0 + \frac{2.3RT}{\alpha nF}\lg j \qquad (1)$$

Where, R is the ideal gas constant; T is absolute temperature; F is the Faraday constant; j is current density; $j°$ is exchange current density; η_c is overpotential; α is the charge transfer coefficient; n is the number of electrons involved in the rate-determining step.

Therefore, the Tafel line can be fitted from the curve of η_c vs. lg j. The fitting line equation and error estimation are shown in Tab.1. The small value of intercept of the regression equation indicated that the electrochemical polarization of reaction was weak. The slope of the Tafel line depends mainly on the number of electron transfer or valence of ions. As for the reaction that involves only in one electron transfer, the slope should be 0.118 mV. In the case of presented reaction, the calculated slope value (0.110 mV) can inferred that it was a one-electron reaction.

According to the regression equation and function (1), the charge transfer coefficient and exchange current density can be calculated as 0.536 and 1.7056×10^{-4} A·cm^{-2}, respectively. The small value of exchange current density indicated the poor reversibility of the reaction just as discussing in cyclic voltammetry curves before.

Table 1. The result of linear regression

Fitting extent	Regression equation	correlation coefficient
$40 \le \eta_c \le 80$mV	$\eta_c = 0.41502 + 0.11014\lg j$	0.98454

The AC impedance of the vanadium negative electrolytes with various concentrations were preformed and the spectra are shown in Fig.4. The results of AC impedance are simulated by Zsimpwin with an equivalent circuit shown in Fig.1. Components parameters of the equivalent circuit obtained by simulating the AC impedance spectra in Fig.4 are listed in Tab.2. It can be seen that as the concentration of V(III) is raised, the solution resistance, *Rs*, decreases, especially a remarkable decreasing for 1.5864mol·L^{-1} V(III). The *Rs* depends mainly on the conductivity of electrode materials, electrolyte and contact resistance, wherein the *Rs* directly reflects the differences of the conductivity of electrolytes in this experiment. Therefore, the increase in concentration of V(III) boosts the solution conductivity.

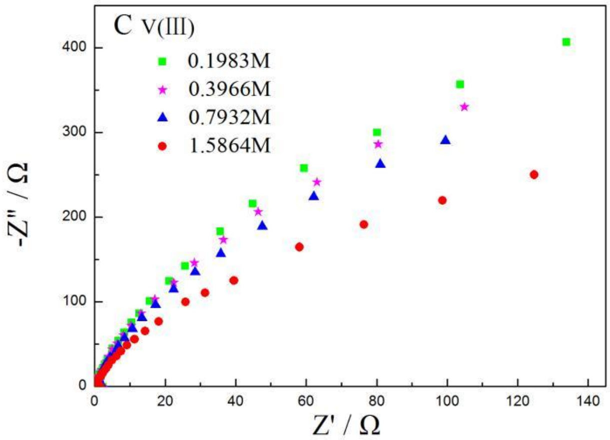

Figure 4. AC impedance spectra for 0.19~1.58 mol·L^{-1} V(III) in 3.4 mol·$L^{-1}H_2SO_4$

Table 2. Equivalent circuit parameters for the AC impedance spectra of 0.19~1.58 M V(III) in 3.4 M H_2SO_4

C(VIII)/mol·L^{-1}	Rs/Ω·cm^2	Rp/Ω·cm^2	$C\times10^{-5}$/F·cm^{-2}	$W\times10^{-4}$/S·$s^{0.5}$
0.1983	1.277	104.2	2.592	1.249
0.3966	1.262	177.1	3.401	1.509
0.7932	1.260	94.57	3.421	1.773
1.5864	1.023	63.05	3.677	2.632

3.2 The process of V(III) reduction reaction

In order to have a better understanding of the V(III) reduction reaction process, a deep discussion were conducted based on above studies. The reductive reaction order and the controlling step of the reaction were determined from the polarization curve.

Supposing the electrochemical step is the only control step of electrode reaction, the electrode potential keeps steady, and the component K is changeable only. In this condition, the reaction on electrode can be given as [18]:

$$\left(\frac{\partial \lg I}{\partial \lg c_k}\right)_{\phi,c_{i\neq k}} = Z_{O,K} \qquad (2)$$

Where, c_k is the concentration of component K; $C_{i\neq K}$ is concentration of the other components except K ; $Z_{O,K}$ is reductive reaction order.

Fig.5 represents the V(III) polarization curves of solutions which contain 0.19~1.58 mol·L^{-1} V(III) and 3.4 mol·L^{-1} H_2SO_4. With data of Fig.5, η_c vs. lg$j$ fits a straight line when overpotential is from 40 to 80 mV. According to the Tafel equation, the reduction reaction is controlled by electrochemical step in this overpotential range. Therefore, lg$j$ vs. lg$C$ graphs can be plotted in Fig.6 at an electrode overpotential of 40mV and 50mV, respectively. The following equation can be derived from linear regression of lg*j* vs. lg*C* graphs:

at η=40mV, $\lg j=0.63253\lg C-4.35637$ $R^2=0.9983$ (3)

at η=50mV, $\lg j=0.59819\lg C-4.42027$ $R^2=0.9968$ (4)

According to function (2), it can be calculated the $Z_{O,V(III)}$ is 0.63 at an electrode overpotential of 40mV, and 0.60 at 50mV. Generally, it is suggested that V(III) exist in sulfuric acid solution in form of V^{3+}. And the electrode reaction is as below:

$$V^{3+}+e^{-}\rightarrow V^{2+} \qquad (5)$$

According to the function (5), the reductive reaction order, $Z_{O,V(III)}$, should be 1, which differs from the results obtained from function(3) and function(4). There are two possible reasons. One is that the range of electrochemical controlling step of reduction reaction is quite narrow, which may be influenced by mix controlling step. Therefore, the calculation of reaction order may be affected. The second is that ions involving in reduction reaction are not simple ions like V^{3+} but complex, which may exist in different vanadium concentrations and H_2SO_4 concentrations.

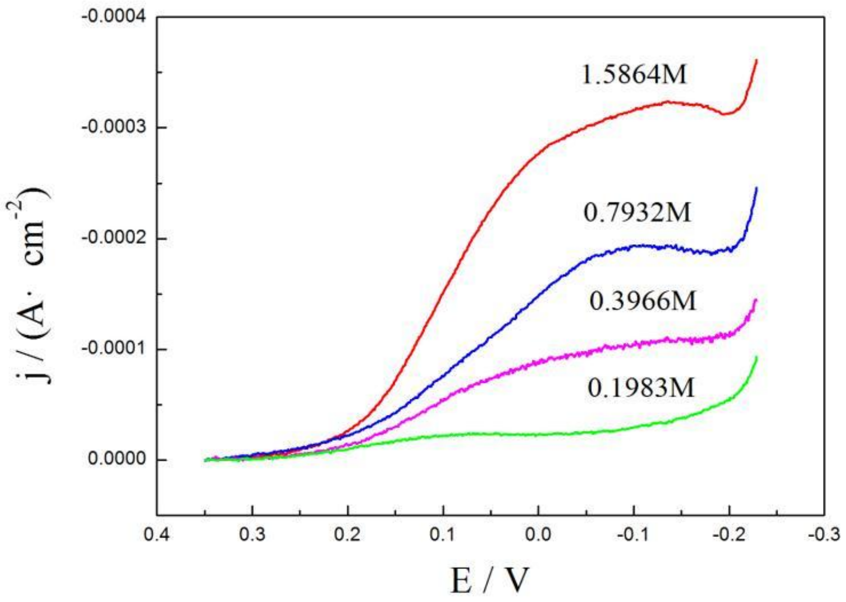

Figure 5. Polarization curves with various V(III) concentrations

The first possibility can be verified by polarization curve. When the reaction is in mixing control stage, the following equation can be deduced according to the current-overpotential function [18]:

$$\eta_c=\frac{RT}{\alpha nF}\ln\frac{1}{j^0}+\frac{RT}{\alpha nF}\ln\left(\frac{j\times j_d}{j_d-j}\right) \qquad (6)$$

Where, *R* is the ideal gas constant; *T* is absolute temperature; *F* is the Faraday constant; *j* is current density; j_d is limited current density; η_c is overpotential.; α is the charge transfer coefficient; *n* is the number of electrons involved in the rate-determining step.

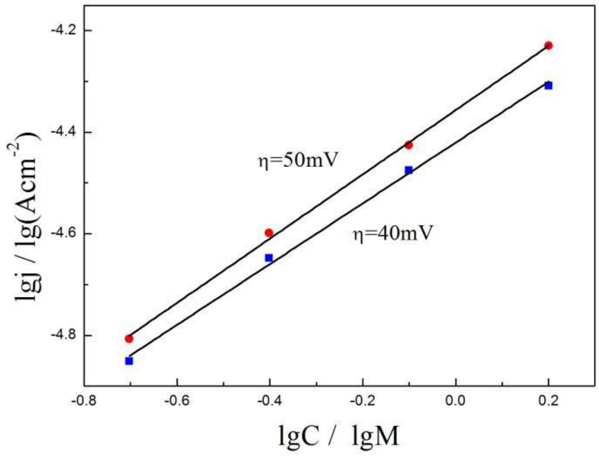

Figure 6. lg*j* vs lg*C* at overpotential 40mV and 50mV

The η_c-lg[($j_d \times j$)/(j_d-j)] relationship with a fitting line from the data in the linear segment of the polarization curve in Fig.5 is shown in Fig.7. It can be seen that η_c vs. lg[($j_d \times j$)/(j_d-j)] fits a straight line when overpotential is from 40 to 170 mV. That is to say the reduction reaction is controlled by mix step under low overpotential.

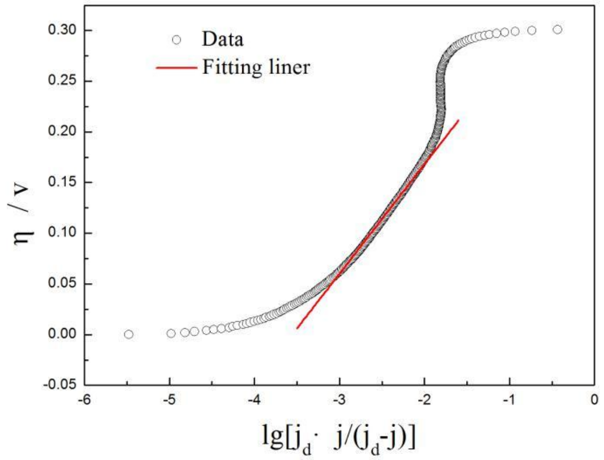

Figure 7. η vs lg[$j_d \times j$/(j_d-j)] for Polarization curve

Meanwhile, from the AC impedance spectra of Fig.4, the electrochemical controlled arc hardly be observed in the plot, nor a completely 45° linear controlling by diffusion. It is suggested that the electrode process is in mix controlling step, which is consistent with the consequence of polarization curve. However, the calculations of reductive reaction order, $Z_{O,K}$, were conducted when the overpotential are 40mV and 50mV, respectively. On this occasion, the reduction reaction is in the process of controlling by mix step. Hence, the calculation of reaction order may be affected.

The second possibility that the ions involving in reduction reaction are not simple ions like V^{3+} but complexes is proposed, and it can be verified by UV-Vis spectral analyses. The patterns of UV-Vis spectrophotometer of the solution obtained by dissolving V_2O_3 in sulfuric acid and the experimental electrolyte (containing V(III) 1.640 mol·L^{-1}, TV 1.7425 mol·L^{-1}) were shown in Fig.8. From the Fig.8, the absorption peaks with wavelength of 750nm~800nm and 600nm~620nm indicated the existence of VO^{2+} and V^{3+}, respectively [19]. The absorption peak of VO^{2+} can also be observed in the solution of V_2O_3 that is because the V_2O_3 has been oxidated partly. It's noted that an absorption peak with a wavelength of approximate 410 nm can be seen in the UV-Vis spectrogram, which might infer the existence of complex of V(III). The structure of V(III) complex may be a V-O-V bridge structure, coordination of sulfate or H_2O like $[V(III)(ox)_2(\mu\text{-}SO_4)]^{3-}$, $[V_3(SO_4)_2(OH)_6]^-$, $V(H_2O)_6^{3+}$ [20, 21] which have big ion radius. It is the big ion radius that causes the V(III) complex has large diffusion resistance during the process of mass transfer. Therefore the electrode reaction is in mixing controlling step. Large diffusion resistance also result in poor electrochemical activity of V(III)/V(II) couple.

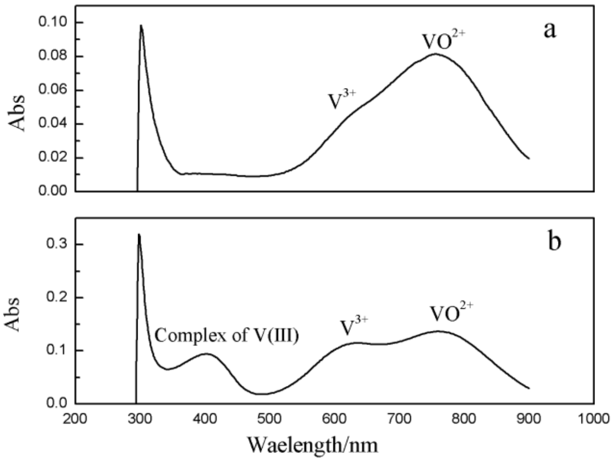

Figure 8. The UV-Vis spectrogram of different solution (a: V_2O_3 in sulfuric acid, b: the experimental electrolyte)

4. CONCLUSIONS

An investigation has been carried to try to explore the process of V(III) reduction reaction by applying the cyclic voltammetry, polarization curve and the AC impendence technique. It was found that the ions involving in reduction reaction are not simple ions like V^{3+} but complexes of V(III). The existence of complex which had complicated structure and big ion radius, resulted in large diffusion resistance in the process of mass transfer. Therefore, the electrode reaction was in mix controlling step and also for the existence of complex, V(III)/V(II) couple had worse electrochemical activity and reversibility than V(IV)/V(V) couple. In order to know more about the complex of V(III), a test on the formation of V(III) solutions is underway in our lab. The structures of vanadium ions need to be deeply explored.

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References

1. B.R. Chalamala, T. Soundappan, G.R. Fisher, M.R. Anstey, *Proceedings of the IEEE*, 102 (6) (2014) 976-999.
2. E. Sum, M. Skyllas-Kazacos, *J. Power Sources*, 15 (85) (1985) 179–190.
3. E. Sum, M. Rychcik, M. Skyllas-Kazacos, *J. Power Sources*, 16 (2) (1985) 85–95.
4. A.H. Whitehead, M. Harrer, *J. Power Sources*, 230 (10) (2013) 271-276.
5. M. Ulaganathan, A. Jain, V. Aravindan, S. Jayaraman, W.C. Ling, T.M. Lim, M.P. Srinivasan, Q. Yan, S. Madhavi, *J. Power Sources*, 274 (274) (2015) 846-850.
6. L. Semiz, N.D. Sankir, M. Sankir, *Int J Electrochem Sci.*, 9 (2014) 3060-3067.
7. M. Gattrell, J. Park, B. Macdougall, J. Apte, S. Mccarthy, C.W. Wu, *J. Electrochem. Soc*, 151 (1) (2004) A123-A130.
8. G. Oriji, Y. Katayama, T. Miura, *Electrochimica. Acta*, 49 (19) (2004) 3091-3095.
9. G. Oriji, Y. Katayama, T. Miura, *J. Power Sources*, 139 (1-2) (2005) 321–324.
10. H.J. Liu, Q. Xu, C.W. Yan, Y.Z. Cao, Y.L. Qiao, *Int J Electrochem Sci* , 6 (2011) 3483-3496.
11. Y. Wen, H. Zhang, P. Qian, P. Zhao, H. Zhou, B. Yi, *Acta Phys-Chim Sin*, 22 (4) (2006) 403-408.
12. W.Z. Liu, D.M. Luo, L.I. Dan, X.L. Meng, F.B. Zeng, *Materials Science Forum*, 809-810 (2014) 822-830.
13. J.X. Zhao, W.U. Zeng-Hua, X.I. Jing-Yu, X.P. Qiu, *J. Inorg. Mater*., 27 (5) (2012) 469-474.
14. J. Liu, S. Liu, Z.He, H.Han, Y.Chen, *Electrochimica. Acta*, 130 (4) (2014) 314–321.
15. L. Liu, X.J. Liu, L.I. Xiao-Bing, F. Chang, X.L. Feng, F.M. Meng, *Chinese Journal of Power Sources*, 34 (6) (2010) 552-555.
16. D.M. Luo, W.Z. Liu, D. Li, X.L. Meng, F.B. Zeng, *China Patent*, CN 103904343(2014).
17. Y. L. Qiao, Q. Xu, J. Zhang, Y. C. Zhai, *Chinese Electrochemistry*, 13 (3) (2007) 269-273.
18. Q. Cha, *Introduction to electrode kinetics*, Science Press, Beijing (2002).
19. X.W. Wu, S. Peng, B.J. Feng, T. Yamamura, Y. Takashi, S. Isamu, S.Q. Liu, K.L. Huang, *J. Inorg. Mater*, 26 (5) (2011) 535-539.
20. K. Kanamori, *Coordin. Chem. Rev.*, 237 (1) (2003) 147-161.
21. K. Kanamori, Y. Ookubo, K. Ino, K. Kawai, H. Michibata, *Inorg. Chem.*, 30 (20) (1991) 3832-3836.

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