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Unusual phenomena in the reduction process of vanadium (V) on a graphite electrode at high overpotentials

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An abrupt increase in the Tafel slope and the charge transfer resistance (R_{ct}) of V (V) ions on a graphite electrode are both observed at a transition potential (E_K). The possible vanadium complex $V_2O_3^{3+}$ might result in the change of reduction mechanism and the unusual phenomena.

As a promising electrochemical energy storage system for the stabilization and smooth output of renewable energy like solar and wind power, all-vanadium redox flow battery (VRFB) uses the VO_2^+/VO^{2+} and V^{2+}/V^{3+} couples in concentrated sulfuric acid solutions as positive and negative electrolytes, with the advantages of quick charging-discharging, simple structure, low cross-contamination and capability to withstand fluctuating power supply.[1-2] It is of great significance to understand the mechanism of the redox reactions of VRFB for developing electrode materials and optimizing the VRFB structure.

Compared with the negative V^{2+}/V^{3+} couple, the redox reaction for the positive VO_2^+/VO^{2+} couple is more complicated, with a multistep reaction process involving an oxygen transfer reaction before or after an electron-transfer step.[2-7] A probable chemical step (C) with the breaking/formation of the V-O chemical bond follows the electron transfer step (E) occurred in the reaction process for VO_2^+/VO^{2+} in both directions.[6] In contrast with the oxidation mechanism of VO^{2+}, the reduction mechanism of VO_2^+ in acidic solutions is generally thought to be more complicated.[5, 7-8] Skyllas-Kazacos et al. revealed that the abnormal two waves observed in the cathodic voltammgrams of VO_2^+/VO^{2+} are in relation to the reduction of the main VO_2^+ ions together with some other species such as V (V)-SO_4^{2-} complexes or carbon-oxygen surface complexes.[5] Moreover, Gattrel et al. observed an unusually high Tafel slope (350-450 mV·dec^{-1}) for the reduction of VO_2^+ at high overpotentials on a graphite electrode, and a model involving electron transfer through an adsorbed layer of possible vanadium intermediates such as VO_2^0 was established to explain the abnormality.[7-8] However, there has been little evidence for the presence of the adsorbed intermediates such as V (V)-SO_4^{2-} complexes or VO_2^0 during the reduction process of VO_2^+. Furthermore, the above-mentioned conjecture is obtained on the premise of a series of assumptions such as the mechanistic pathways for the reduction of V (V) ions at either low or high cathodic overpotentials involve both the same initial V (V) reactants and final V (IV) products, [7-8] and the related data is stuffless and lack of the cross-validation with different testing techniques. Therefore, it is essential to have more investigations on the unusual phenomena for fully understanding the reduction reaction mechanism of V (V) in acidic solutions.

Recently, a new CEC oxidation reaction mechanism has been proposed by us to describe the oxidation of VO^{2+}, the theoretic reaction orders of VO^{2+} and H^+ based on the new mechanism are well consistent with the experimental results, and the corresponding kinetic equation has been established.[3] Herein, the reduction reaction of V (V) ions has been examined on a rotating pyrolytic graphite disk electrode in sulfuric acid solutions with various pH and vanadium concentrations by steady-state potentiodynamic polarization and impedance spectroscopy measurements.

All chemicals used in the experiments were analytically pure agents and all solutions were prepared with de-ionized water. V (IV) solutions were made by dissolving $VOSO_4 \cdot nH_2O$ (n=2.82, according to the chemical precipitation method) in sulfuric acid solutions and then applied as initial electrolytes at both the positive and negative sides of a single VRFB cell. At the positive side of the cell 1.2 M V (V) + 3.0 M H_2SO_4 solutions were obtained by charging and then diluted to produce the solutions with various vanadium concentrations and varying pH. The 0.3 M V (V) + 3.0 M H_2SO_4 solutions with different pH were obtained by adding different concentrations of H_2SO_4 solution into the 1.2 M V (V) + 3.0 M H_2SO_4 solutions, the volumes of addition were pre-calculated, then the measurements of pH were carried out with a pHS-25 pH meter (Shanghai Precision Instrument Co. Ltd, China). The acidities of all solutions were no more than 3.0 M H_2SO_4.

Potentiodynamic polarization measurements were performed in V (V) acidic solutions at room temperature with a CHI730C Electrochemical Analysis Instrument (Shanghai Chenhua Instrument Co. Ltd, China) coupled with a rotating disk system (Pine Instruments) composed of a basal plane pyrolytic graphite disk working electrode (GB, diameter: 5 mm), an AFMSRCE electrode rotator and an AFE6MB shaft, with a potential scan rate of 1mV s^{-1} and a rotating rate of 2000 rpm. And the impedance spectroscopy (EIS, frequency range: 0.01-10^5 Hz, AC amplitude: 5mV) measurements were performed in a conventional three-electrode cell with a Princeton Applied Research EG&G potentiostat model 273 and EG&G 5210 lock-in amplifier. The ZView2 software was used to fit the EIS plots with an assumed equivalent circuit. A platinum plate and a saturated calomel electrode (SCE, 0.244 V) were used as the counter electrode and the reference electrode, respectively. A salt bridge was applied to decrease the liquid junction potential between the Luggin capillary and the GB working electrode. The GB electrode was initially polished with aqueous slurries with alumina powders (average particle diameter: 0.6 µm) on a piece of chamois cloth and then ultrasonically cleaned for 5 min in ethanol and de-ionized water in turn.

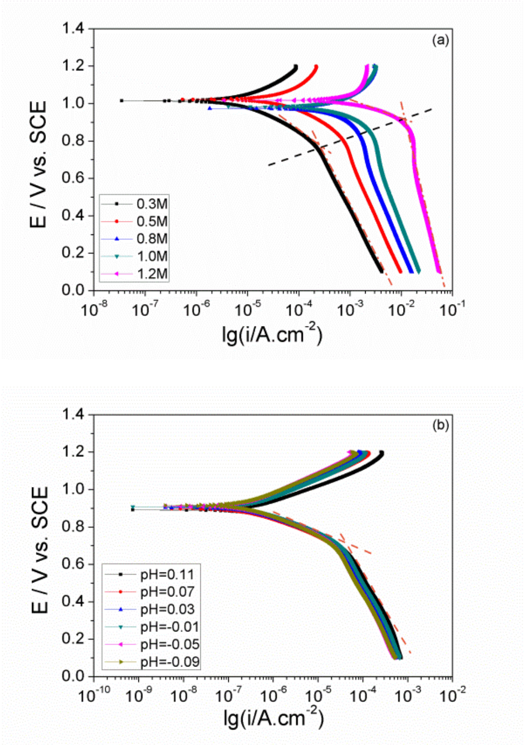


Fig. 1. The polarization curves on the pyrolytic graphite electrode at 1mV s-1 with the rotating rate of 2000 rpm in V (V) + 3.0 M H2SO4 solutions at varying concentrations of V (V) ions (a) and 0.3 M V (V) + H2SO4 solutions at varying pH (b).

Figs. 1a and 1b present the polarization plots of the GB electrode at 2000 rpm in V (V) acidic solutions containing various concentrations of V (V) ions and diverse pH, respectively. Different with the anodic polarization curves of VO^{2+} in the previous work, [3] Fig. 1a shows clearly that an abrupt increase in the cathodic Tafel slope occurs at a transition potential (E_K), with Tafel slopes higher than 400 mV·dec^{-1} at high Tafel slope region. It is considered that the abrupt change in the Tafel slope of the polarization plots of V (V) ions at high cathodic overpotentials suggests the change of reduction mechanism, just as what Gattrel et al. did.[7] Moreover, the Tafel slope changes little with the concentration of V (V) ions at low cathodic overpotentials, but tends to increase with the increase in the concentration of V (V) ions. Meanwhile, the transition potential E_K shifts positively with increasing the concentration of V (V) ions. Unlike V (V) ions, pH of the solutions has little effect on the Tafel slope and E_K.

To confirm the change of the mechanism with increasing the cathodic polarization potential, Fig. 2a gives the EIS plots at various electrode potentials on the GB electrode in 1.2 M V (V) + 3.0 M H_2SO_4 solution. As observed in Fig. 2a, the Nyquist plots are composed of a depressed semi-circle at the high frequency and a linear portion except several irregular points at the low frequency, suggesting that the reduction process of V (V) ions is a mixed kinetic-diffusion controlling process. An equivalent circuit (included in Fig. 2b) is applied to simulate the electrode reaction and calculate the value of charge transfer resistance (R_{ct}).[9] The elements in the equivalent circuit contain ohmic

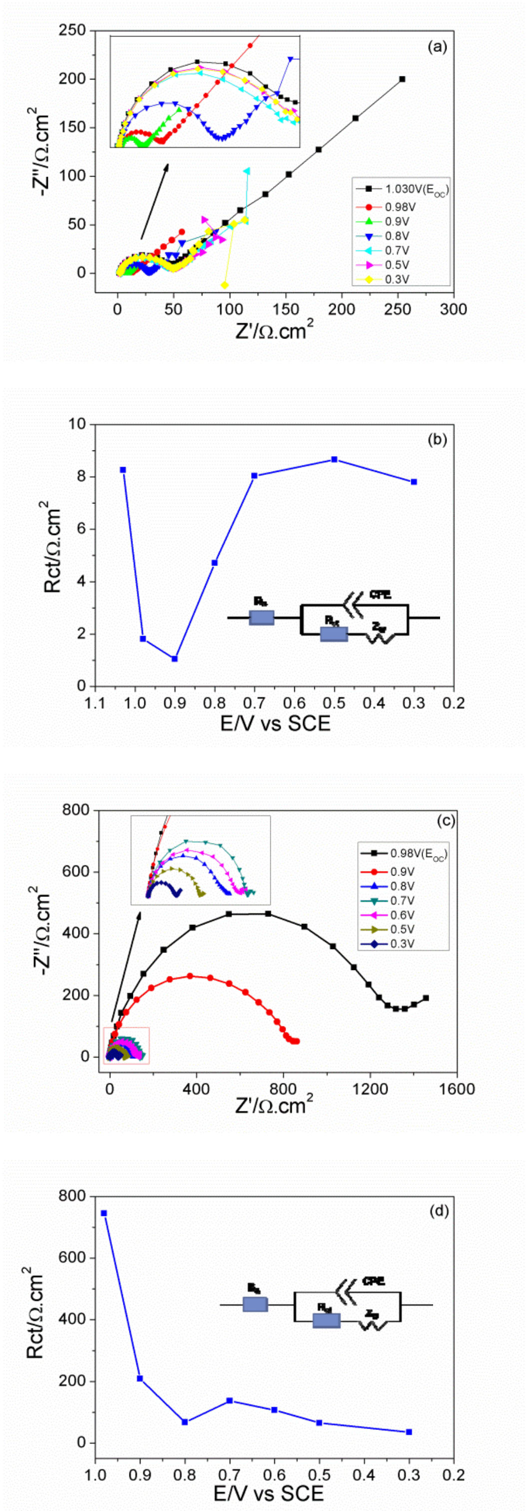


Fig. 2. Impedance spectra at various potentials and the shift of the charge transfer resistance (Rct) with the potential on the GB electrodes in V (V) + 3.0 M H2SO4 solutions at varying concentrations of V (V) ions: 1.2 M (a, b); 0.3 M (c, d).

resistance of the electrolyte and the working electrode (R_s), R_{ct} at the interface between the electrode and the electrolyte, a constant phase element (CPE, double layer) applied to substitute pure capacitance, and Warburg impedance (Z_w). Table 1 lists the fitting results of R_s, R_{ct} and CPE for the EIS plots at various electrode potentials. The shift of R_{ct} with the applied electrode potential is reported in Fig. 2b. It is shown that R_{ct} decreases with the increasing overpotential at low cathodic overpotentials, reflecting the characterization of the electrochemical polarization process as the rate controlling step. However, an abnormal increase in the plot of R_{ct} vs. E is observed between 0.8 and 0.9V, in according with the sudden increase of the Tafel slope between 0.8 and 0.9 V for the same electrolyte in Fig. 1a, suggesting that the mechanism of the V (V) reduction reaction on the GB electrode has an abrupt transformation at a transition potential (E_K) between 0.8 and 0.9 V in this electrolyte. In the solutions containing other concentrations of V (V), similar abnormal change of R_{ct} with the polarization potential was also observed. Fig. 2c and Table 2 give the Nyquist plots in 0.3 M V (V) + 3.0 M H_2SO_4 solution and their fitting results, respectively. Fig. 2d gives the change of R_{ct} with the applied electrode potential. An abrupt increase in the plot of R_{ct} vs. E can be seen between 0.7 and 0.8 V, while the sudden change of the Tafel slope for the same electrolyte occurs between 0.7 and 0.8 V in Fig. 1a. Therefore, it is concluded that the mechanism of the V (V) reduction reaction has an abrupt transformation at a transition potential E_K, but with different values of E_K for various concentrations of V (V) ions.

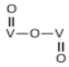
Table 1 The values of R_s, R_{ct} and CPE at various electrode potentials obtained from fitting the EIS plots with the equivalent circuit in1.2 M V (V) + 3.0 M H_2SO_4 solution.

E/V	R_s/Ω.cm^2	CPE		R_{ct}/Ω.cm^2
		Y_0	n	
1.03	0.38	1.17E-04	0.890	8.26
0.98	0.53	2.99E-04	0.804	1.81
0.90	0.50	2.63E-04	0.809	1.04
0.80	0.43	1.21E-04	0.875	4.71
0.70	0.40	1.27E-04	0.877	8.04
0.50	0.41	1.45E-04	0.863	8.66
0.30	0.41	1.30E-04	0.877	7.80

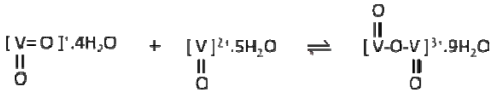
Table 2 The values of R_s, R_{ct} and CPE at various electrode potentials obtained from fitting the EIS plots with the equivalent circuit in 0.3 M V (V) + 3.0 M H_2SO_4 solution.

E/V	R_s/Ω.cm^2	CPE		R_{ct}/Ω.cm^2
		Y_0	n	
0.98	0.18	1.03E-04	0.890	744.4
0.90	0.18	8.70E-05	0.804	208.8
0.80	0.18	9.19E-05	0.809	67.61
0.70	0.18	8.99E-05	0.875	136.5
0.60	0.17	8.61E-05	0.877	107.1
0.50	0.22	1.01E-04	0.863	65.35
0.30	0.16	1.24E-04	0.877	35.17

The above results indicate that the abrupt increase of the Tafel slope on the GB electrode is probably related to the change of the reduction mechanism of V (V) ions. Gattrel et al. reported that the reduction mechanism of V (V) ions shifts at a transition potential from a chemical (C)-electrochemical (E)-chemical (C) at low overpotentials to an ECC mechanism at high overpotentials, and the unusually high Tafel slope may be caused by the emergence of a poorly soluble adsorbed intermediate such as VO_2^0.[7-8] Since the initial V (V) reactants and final V (IV) resultants involved in the CEC mechanistic pathway are the same as those in the ECC mechanistic pathway, the transformation in the reduction mechanism of V (V) at E_K has little relation with the concentrations of the initial V (V) reactants. Thus, it is also reasonable to consider that E_K changes little with the concentration of V (V) ions based on the above model.[8] The authors also suggested that the mechanism change appears at around 0.6 V for most of the polarization curves, with some deviations at higher concentrations owing to the formation of possible vanadium complexes such as $V_2O_3^{3+}$.[8] However, the examination of polarization curves showed clearly that the transition potential E_K shifts positively with increasing the concentration of V (V) ions over a range from 0.03125 to 280 mM,[8] as observed in the present study (Fig. 1a). Clearly, it is difficult to use the present model to explain the shift of E_K with the concentration of V (V) ions. This problem may be related to the doubtful consideration that the initial V (V) reactants involved in the reduction process at low overpotentials are identical with those at high overpotentials.

It is generally reported that dinuclear oxovanadium (IV, V) species containing a $[V_2O_3]^{3+}$ core can be instantaneously formed when VO_2^+ (aq) is mixed with VO^{2+} (aq) due to their favorable thermodynamic stability, and can also disappear quickly as the mixed solution is diluted because of their kinetic lability.[10-15] Moreover, a clear decrease in the stability of the formed complex occurs for acidities up to 8.0 M in H_2SO_4 medium.[11] The $[V_2O_3]$ moiety is accepted to be of the structure given as  $O{=}V{-}O{-}V{=}O$,

having a nearly linear V-O-V bridge with the terminal oxo groups in mutually transpositions.[11, 13-15] In acidic solutions with a H_2SO_4 concentration less than 4.0 M, VO^{2+} and VO_2^+ are considered to exist as the octahedrally coordinated cation $VO^{2+}\cdot 5H_2O$ and the mononuclear aquadioxo cation $VO_2^+\cdot 4H_2O$, respectively.[16-18] Thus, the complex reaction between VO_2^+ and VO^{2+} species can be presented as follows:



$$[O{=}V{=}O]^{+}\cdot 4H_2O + [V{=}O]^{2+}\cdot 5H_2O \rightleftharpoons [O{=}V{-}O{-}V{=}O]^{3+}\cdot 9H_2O \quad (1)$$

Although there are many alternative possible pathways to the formation of mixed valence dimers, we thought one route is the possibility that a monomeric VO^{2+} ion generated by the reduction of VO_2^+ ions rapidly combines with a monomeric VO_2^+ ion (not yet reduced) to form a mixed valence $V_2O_3^{3+}$ complex in vanadium acidic solutions. Then, the large $V_2O_3^{3+}$ cations might be accumulated on the electrode surface with lots of negative electrons through electrostatic adsorption. In this case, the accumulated $V_2O_3^{3+}$ ions might directly take part in reduction reactions, whose contribution depends on the cathodic overpotentials and the concentration of V (V) ions.

In view of the possibility that the complex $V_2O_3^{3+}$ ions may be involved in the reduction reaction, especially at high overpotentials, a new model shown in Fig. 3 is proposed to describe the cathodic polarization behavior of the GB electrode in the present vanadium system, involving the VO_2^+-centered reduction at low overpotentials and the $V_2O_3^{3+}$-centered reduction at high overpotentials. Based on the new model, the abrupt change of the cathodic Tafel slope on the GB electrode may be attributed to the change of reduction mechanism, from a VO_2^+-centered to a $V_2O_3^{3+}$-centered reduction. The accumulation of $V_2O_3^{3+}$ ions on the electrode surface inhibits the direct reduction of VO_2^+, and thus probably reduces the rate of reduction reaction. Increasing the concentration of VO_2^+ helps the formation and accumulation of $V_2O_3^{3+}$ ions, and thereby makes E_K shift positively.

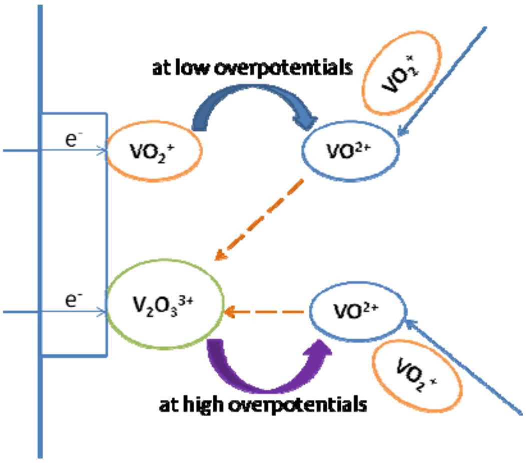


Fig. 3. A new model of the reduction reaction of V (V) ions on the GB electrode surface.

In summary, an abrupt change in the cathodic Tafel slope and R_{ct} of V (V) ions is observed at E_K on the GB electrode, with Tafel slopes higher than 400mV·dec^{-1} at high cathodic overpotentials. Moreover, the concentration of V (V) ions has a significant effect on E_K and Tafel slope at high cathodic overpotentials. However, pH has little effect on them. The abrupt change of the cathodic Tafel slope and R_{ct} may be attributed to the change of reduction mechanism, and the formation of possible vanadium complex $V_2O_3^{3+}$ may result in the change of the reduction mechanism of V (V) ions, from a VO_2^+-centered reduction at low overpotentials to a $V_2O_3^{3+}$-centered reduction at high overpotentials. Although the conjecture we proposed for the reduction reaction of V (V) ions can be applied to explain the experimental results to a certain extent, it is still lack of ample evidence. More extensive investigations are still required to understand the new mechanism, including the reduction reaction of V (V) ions on different carbon electrodes, the reaction intermediates involved, etc.

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