

Investigations on V(IV)/V(V) and V(II)/V(III) redox reactions by various electrochemical methods

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Received 9 January 2004; received in revised form 25 February 2004; accepted 1 March 2004

Available online 18 November 2004

Abstract

The positive pole V(IV)/V(V) and negative pole V(II)/V(III) reactions in a vanadium redox flow cell have been investigated on a glassy carbon electrode by various techniques. Several parameters for these electrode reactions were obtained at high concentrations of both sulfuric acid and V species in addition to the mobility (diffusion coefficient and Stokes radius) of V(V), V(IV), V(III) and V(II) species. © 2004 Elsevier B.V. All rights reserved.

Keywords: Vanadium redox flow cell; V(IV)/V(V); V(II)/V(III); Glassy carbon; Parameters

1. Introduction

The vanadium redox flow cell is now expected as a large scaled secondary battery system. Several 20–50 kW pilot plants have already been tested mainly in Japan for electric load leveling or unfailable power source (UPS) [1]. Because extremely concentrated sulfuric acid solutions are employed in both positive and negative electrode compartments, however, the fundamental aspects on V(IV)/V(V) and V(II)/V(III) redox reactions and on the dissolved electroactive species are not yet completely clarified. So far, both V(IV)/V(V) and V(II)/V(III) redox reactions in moderate aqueous media had been described in several reports [2–4].

In the present study, these redox reactions between dissolved vanadium species in 5–12 M H₂SO₄ have been investigated by means of various electrochemical methods such as cyclic voltammetry, chronopotentiometry and chronoamperometry. The mechanisms of V(IV)/V(V) and V(II)/V(III) electrode reactions have been further discussed based on Nicholson's treatments [6].

2. Experimental

2.1. Preparation of electrolyte solutions

VOSO₄·*n*H₂O (Soekawa Chemicals, *n* = 5.56 according to thermogravimetric analysis) was dissolved in 5 M H₂SO₄

to give a V(IV) solution containing 1.6 g-atom(V) dm⁻³ + 4.2 M H₂SO₄. By oxidizing this solution on a lead anode in a two-compartment cell with a cation exchange membrane (Nafion 117, DuPont), a V(V) solution was prepared. A constant current density of 20 mA cm⁻² was given with the aid of a lead plate counter electrode. V(II) and V(III) solutions, furthermore, were prepared by analogous electroreduction of a V(IV) solution. The complete oxidation or reduction of V(IV) was ensured by changes in both the working electrode potentials and UV-Vis absorption spectra.

2.2. Determination of vanadium concentration

The concentration of V species was determined by coulometric titration using graphite felt (Toyobo) and carbon plate electrodes. The amount of V(V) species was determined from the reduction charge to V(IV) until the potential dropped abruptly. Similarly, V(IV) was determined by the oxidation charge to V(V). A preliminary experiment for a known V(V) solution showed an error of less than 5%. The amount of V(II) or V(III) was determined by analogous coulometric method.

2.3. Electrochemical measurements

All the electrochemical measurements were carried out in a beaker cell with a computerized potentio/galvano-stat (Hokuto Denko, HZ-3000). The glassy carbon working electrode was immersed in the test solution for 9 h before measurements. A platinum and Ag/AgCl electrodes were

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employed as a counter and the reference electrodes, respectively. In case of a V(II) solution a graphite counter electrode was employed, because hydrogen evolved spontaneously on the Pt surface. The potential sweep rate in cyclic voltammetry was varied widely from 1 to 10 V s^{-1} in order to elucidate the diffusion coefficient of electroactive species and other kinetic parameters. All the potentials were referred to the Ag/AgCl electrode in this paper.

In addition, chronopotentiometric and potential step measurements were carried out. The exchange current densities and transfer coefficients were determined from [the current density at zero infinity time] versus [step potential] plots in the absence of concentration polarization.

3. Results and discussion

3.1. Cyclic voltammograms in V(IV) or V(V) solution

Cyclic voltammograms in a V(IV) solution at various scan rates (ν) were compared in Fig. 1, where the sweep limits were set narrower for slow sweeps. The separation between oxidation and reduction peak potentials (ΔE_p) was wider than 100 mV even at the slowest sweep of 0.2 mV s^{-1} , suggesting that V(IV)/V(V) redox reaction is not electrochemically reversible, because the peak separation is wider than 60 mV even at an extremely low potential sweep rate. The same reaction, instead, is quasi reversible as deduced by the proportionality between the anodic peak current density (i_{pa}) and $\nu^{1/2}$ seen in Fig. 2. Since the half-wave potential ($E_{p/2}$) shifts almost linearly with $\log \nu$ as in Fig. 3, furthermore, the so-called EC mechanisms may be applied according to the established criteria [6]. According to the electroanalytical treatments of the CV waves [6], the mechanisms of an electrode reaction can be deduced to some extent from the shift of half-peak potentials ($\Delta E_{p/2}$) with the potential sweep rate (ν). When $\Delta E_{p/2}/\Delta \log \nu$ decreases with increasing ν for a given cathodic reaction, for example, quite reversible chemical step might be suspected to follow the irreversible electron transfer step. Thus, a certain chemical reaction step is suspected to follow the electron transfer step of this reaction. The positive pole reaction in a vanadium redox flow

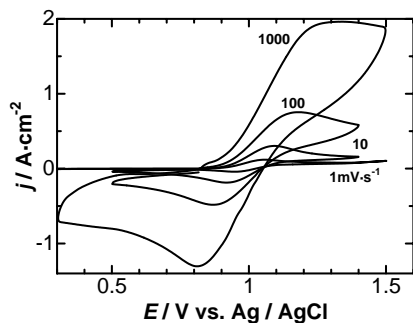


Fig. 1. Cyclic voltammograms for V(IV)/V(V) reaction on a carbon plate electrode in $1.69 \text{ g-atom(V) dm}^{-3} \text{ V(IV)} + 4.2 \text{ M H}_2\text{SO}_4$ solution.

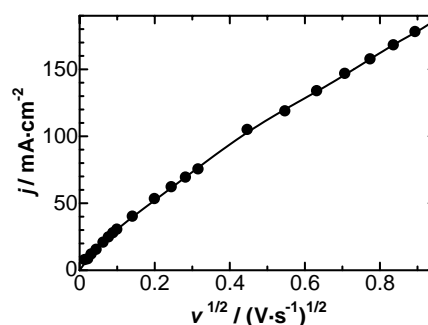


Fig. 2. Peak current density as a function of the square root of a sweep rate for V(IV) oxidation.

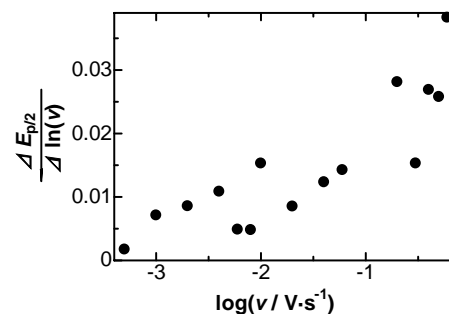


Fig. 3. Half wave potential density as a function of the logarithmic sweep rate for V(IV) oxidation.

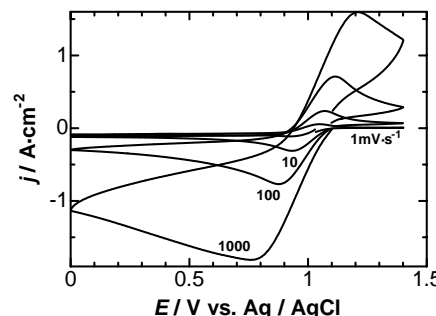


Fig. 4. Cyclic voltammograms for V(V)/V(IV) reaction on a carbon plate electrode in $1.69 \text{ g-atom(V) dm}^{-3} \text{ V(V)} + \text{H}_2\text{SO}_4$ solution.

cell is described as $\text{VO}_2^+/\text{VO}^{2+}$ in general, and the actually observed open-circuit potential is close to its reversible potential. Redox reactions between VO_2^+ and VO^{2+} should contain the breaking/formation of the V–O chemical bond which seems to be the most probable chemical step.

In another case of a V(V) solution, not only cyclic voltammetric data seen in Fig. 4 but also $i_{pc}-\nu^{1/2}$ and $E_{p/2}-\log \nu$ relationships are substantially similar to those obtained in a V(IV) solution. These facts might suggest that V(IV)/V(V) redox processes in both directions are not simple and the electron transfer is followed by a certain chemical step.

3.2. Cyclic voltammograms in V(II) or V(III) solution

The V(II)/V(III) couple is apparently irreversible compared with V(IV)/V(V) as can be recognized in Fig. 5.

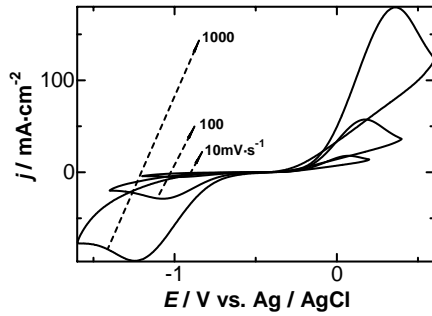


Fig. 5. Cyclic voltammograms for V(II)/V(III) on a glassy carbon electrode in 1.75 g-atom(V) dm⁻³ V(II) + H₂SO₄ solution.

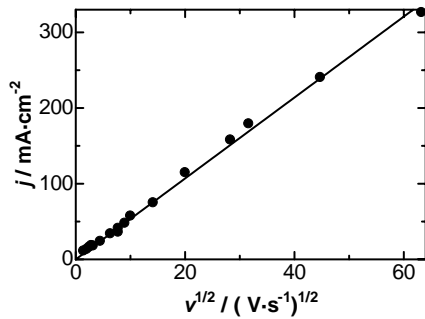


Fig. 6. Peak current density as a function of the square root of a sweep rate for V(II) oxidation.

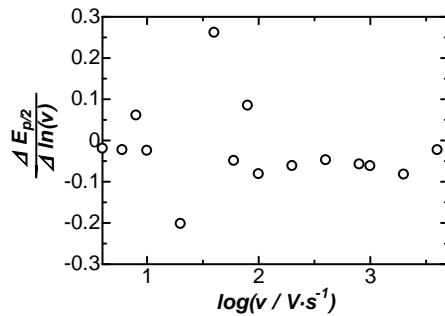


Fig. 7. Half-wave potential as a function of the logarithmic sweep rate for V(II) oxidation.

Furthermore, i_{pc} is proportional to $v^{1/2}$ as in Fig. 6 and ΔE_p becomes wider with increasing v . According to the known criteria [6], the plotted $E_{p/2}-v$ data in Fig. 7 suggest that some chemical step precedes the electron transfer. The V(II)/V(III) couple behaves quite irreversibly also in a V(III) solution as seen in Fig. 8. The $E_{p/2}-v$ dependence as in Fig. 9 suggest that some chemical step follows the electron transfer to V(III).

3.3. Potentostatic polarization for the V(IV)/V(V) couple

The small polarization data for the V(IV) + V(V) solution are presented in Fig. 10, after extrapolating the polarization current to a time of zero on the linearized $i-t^{1/2}$ plots in order to eliminate the concentration polarization. The preliminarily analyzed concentrations of V(IV) and V(V) were

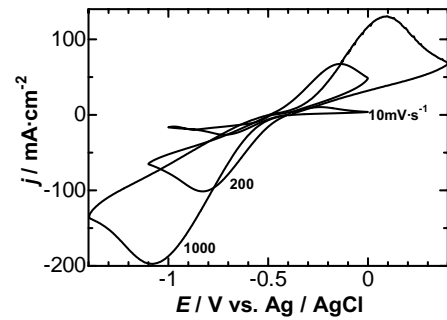


Fig. 8. Cyclic voltammograms for V(II)/V(III) on a glassy carbon electrode in 1.61 g-atom(V) dm⁻³ V(III) + H₂SO₄ solution.

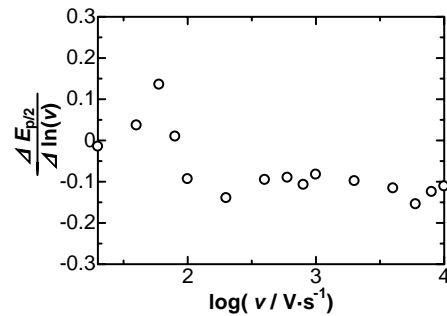


Fig. 9. Half-wave potential as a function of the logarithmic sweep rate for V(III) reduction.

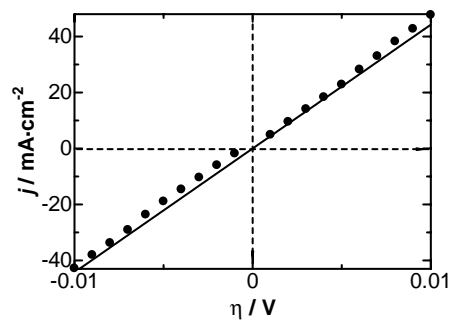


Fig. 10. Small polarization of V(V)/V(IV) solution on a glassy carbon electrode.

0.68 and 0.85 g-atom(V) dm⁻³, respectively. Although reliable Tafel lines are hardly observed, the exchange current density (j^0) is found to be 1.1×10^2 A m⁻² from the slope of small polarization data.

3.4. V(II)/V(III)

In contrast to a V(IV) + V(V) mixture, Tafel lines can be clearly observed for a V(II) + V(III) solution as in Fig. 11, giving the parameters of j^0 (A m⁻²) = 0.50, $\alpha_+ = 0.43$, $\alpha_- = 0.50$, k^0 (m s⁻¹) = 1.0×10^{-8} . The j^0 value determined from the small polarization resistance is in good agreement with the above data. These facts suggest the electron transfer is much slower for V(II)/V(III) than for V(IV)/V(V). The estimated k^0 value at pH < -1 is small compared with literature [2] data of

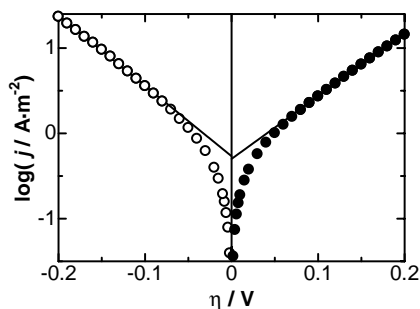


Fig. 11. Relationship between current density and overpotential in $0.875 \text{ g-atom(V) dm}^{-3} \text{ V(II)}/0.805 \text{ g-atom(V) dm}^{-3} \text{ V(III)} + \text{H}_2\text{SO}_4$ solution.

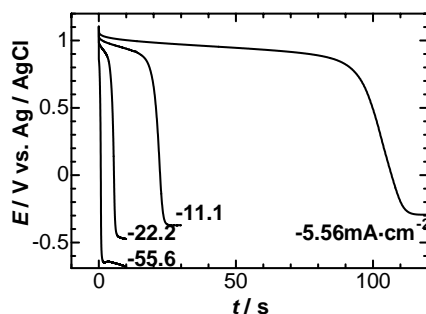


Fig. 12. Chronopotentiograms for V(V)/V(IV) reaction at various current densities in $1.81 \text{ g-atom(V) dm}^{-3} \text{ V(V)} + 5 \text{ M H}_2\text{SO}_4$ solution on a glassy carbon electrode.

$2 \times 10^{-7} \text{ m s}^{-1}$ at pH 0 because of different experimental conditions.

3.5. The diffusion coefficient and Stokes radius of V species

The galvanostatic reduction of V(V) on a GC electrode gives a potential plateau at around 1.0 V as in Fig. 12. The square root of a transition time is found to be inversely proportional to the applied current density, and the diffusion coefficient of V(V) can be determined as $1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ by using Sand's equation. Finally the Stokes radius of V(V) is estimated as 0.28 nm based on the actually observed solution viscosity of 7.7 cP. Because this radius agrees with the previous data [7], V(V) species probably has the form of VO_2^+ .

By applying analogous treatments for V(IV) oxidation, V(III) reduction and V(II) oxidation, [diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), Stokes radius (nm)] could be determined as [$1.0 \times$

10^{-6} , 0.21], [0.57×10^{-6} , 0.32], [1.1×10^{-6} , 0.32] for V(IV), V(III) and V(II) species, respectively. When we consider the size of V^{4+} and oxygen, V(IV) species likely has the form of VO_2^+ . V(III) and V(II) species, on the other hand, seem to form $\text{V(H}_2\text{O)}_6^{3+}$ and $\text{V(H}_2\text{O)}_6^{2+}$, respectively.

4. Conclusions

Positive and negative pole reactions in a vanadium redox flow cell have been investigated at high concentrations of both sulfuric acid and V species. The V(II)/V(III) reaction is controlled by electron transfer, whereas a certain chemical step seems to play the dominant roles during another V(IV)/V(V) reaction. The diffusion coefficient and Stokes radius of related V(V), V(IV), V(III) and V(II) species have been determined based on electrochemical and viscosity measurements.

Acknowledgements

The authors thank Mr. S. Nagou and Mr. S. Ohta of Toyobo Ltd. for providing carbon felt used as an electrode in order to determine the vanadium concentration.

This work was supported by Grant-in-Aid for the 21st Century COE program "KEIO Life Conjugate Chemistry" from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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Further reading

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