

Investigation on V(IV)/V(V) species in a vanadium redox flow battery

Gaku Oriji*, Yasushi Katayama, Takashi Miura

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan

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Abstract

Stokes radii of V(IV) and V(V) species in concentrated sulfuric acid solutions were determined from their diffusion limited current densities on a rotating platinum disk electrode and the solution viscosity. In addition, V(IV) and V(V) species were estimated based on their solubility, UV-Vis spectra, and cyclic voltammetric data. The possible ion-pair formation of V(IV) cation with SO_4^{2-} and/or HSO_4^- and the spontaneous polymerization of V(V) at a low H_2SO_4 concentration were discussed.

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1. Introduction

The vanadium redox flow cell proposed by Skyllas-Kazacos and co-workers [1–3] in 1985 have been investigated extensively [4,5]. Recently, several demonstration plants of ~1000 kW have been operated in Japan. Two redox couples of V(II)/V(III) and V(IV)/V(V) are employed as the negative and positive electrode reactions, respectively. The negative half-cell electrolyte containing V(II)/V(III) couple and the positive half-cell electrolyte containing V(IV)/V(V) couple are stored in each reservoir vessel and flowed through the electrode compartment by pumps. The capacity of this cell is determined principally by the number of electrochemical equivalence of V(II)/V(III) or V(IV)/V(V) couple. In contrast to usual secondary batteries employing solid active materials, charge/discharge reactions in this redox flow cell are based entirely on the redox reactions between soluble ionic species. Accordingly, a long cycle life can be expected for this rechargeable cell.

Although the overall cell performance depends on various factors, the fundamental knowledge of negative and positive electrode reactions are still important to optimize the cell operation and to realize high energy efficiency. So far, Gattrell et al. [6] reported recently that the reduction of V(V) to V(IV) proceeds by CEC mechanisms at low overpotentials and by ECC mechanisms at high overpotentials, although the concentration of V(V) investigated was low

(about 0.1–250 mM) compared with that in a redox flow cell. Several papers [7–11] discussed the dissolved states of V(IV) and V(V) in concentrated sulfuric acid (H_2SO_4) solutions based on spectroscopic and/or dynamic electrochemical data, whereas the conclusions seemed somewhat different from a report to another. However, it might be accepted that both V(IV) and V(V) form some complex species with sulfate (SO_4^{2-}) or hydrogen sulfate (HSO_4^-) anion [4,7–11]. In the present study, the Stokes radii of V(IV) and V(V) were determined by voltammetric measurements under hydrodynamic control at a platinum rotating disk electrode as functions of H_2SO_4 concentration up to practical ~9 M. Furthermore, the dissolved states of V(IV) and V(V) were discussed based on their sizes, solubility, and spectroscopic data.

2. Experimental

2.1. Preparation of V(IV)- and V(V)-sulfuric acid solutions

V(IV) solutions were prepared by dissolving $\text{VOSO}_4 \cdot n\text{H}_2\text{O}$ (Soekawa Chemicals, $n = 5.56$ according to thermogravimetric analysis) in 1–9 M H_2SO_4 . V(V) solutions, on the other hand, were obtained by anodic oxidation of V(IV)- H_2SO_4 solutions in a two-compartment cell separated by a cation-exchange membrane (Nafion 117, DuPont), where lead electrodes were used for both anode and cathode.

* Corresponding author.

These solutions were permitted to stand at 25 °C for several weeks in order to let excess amount of V precipitate. The V(IV) concentration was determined by potentiometric redox titration using a standardized potassium permanganate solution. The V(V) concentration was determined by the same method after reducing V(V) to V(IV) by bubbling SO₂ gas and removing excess SO₂ by heating under N₂ atmosphere. Preliminary experiments starting from a V(V) solution of reagent V₂O₅ ensured that the above redox titration gives an error less than 1%. The solution density was determined based on its mass and volume as usual. The solution viscosity was measured by an oscillation-type viscometer (Viscomate VM-1G, Yamaichi Electronics). The UV-Vis absorption spectra were obtained with a double-beam spectrometer (Shimazu, UV-2200) referenced to V-free H₂SO₄ solutions. The solubility of V(IV) and V(V) species were determined after equilibration at 25 °C for 40 and 60 days, respectively. The obtained precipitates were investigated by X-ray diffraction measurements (Rigaku, RAD-C).

2.2. Electrochemical measurements

Linear sweep voltammetry was carried out using a Pt rotating disk electrode (3 mm Ø) under controlled hydrodynamic conditions (HR-201 and -202, Hokuto Denko). The rotating angular velocity ω was set from 100 to 700 rpm and the electrode potential was swept at 5 mV s⁻¹. Pt wire was used as a counter electrode. Ag/AgCl electrode was employed as a reference electrode. Electrochemical data were collected by a computerized potentio/galvanostat (HZ-3000, Hokuto Denko). The diffusion coefficient D was calculated from the limiting current density, i_L , obtained from the hydrodynamic voltammetry [12].

$$i_L = 0.62nF\omega^{1/2}\nu^{1/6}D^{2/3}C^* \quad (1)$$

where n , F , ν and C^* are the number of transferred electrons per electroactive species, Faraday constant, kinematic viscosity of the solution, and bulk concentration of the electroactive species, respectively. The Stokes radius of the electroactive species can be estimated from D assuming the spherical shape.

$$R = \frac{kT}{6\pi D\eta} \quad (2)$$

where k , T , and η are the Boltzmann constant, absolute temperature, and viscosity of the solution, respectively.

It might be required to examine several underlying assumptions in our treatments. The Stokes' law contained in Stokes–Einstein Eq. (2) is essentially an approximated Navier–Stokes equation for small Reynolds numbers compared to unity. The Reynolds number Re for a moving hard sphere having a radius of R is defined by [12]

$$Re = \frac{vR\rho}{\eta} \quad (3)$$

where v and ρ are the relative velocity of a sphere and density of the fluid medium, respectively. In the present electrochemical system, the electrolyte solutions have the density of 1.2–1.5 g cm⁻³ and the kinematic viscosity of 3–20 g m⁻¹ s⁻¹ (cP). On the other hand, the moving velocity of vanadium species to the electrode lies in a range of 0.00367–0.0147 m s⁻¹ after assuming their mass balance at the one-dimensional diffusion limits for $C^* = 1$ –2 M and $i_L = 5$ –20 mA cm⁻²

$$vFC^* = i_L \quad (4)$$

When R is 50 nm, for example, Re is as small as 1.37×10^{-8} , which satisfies the above condition of $Re \ll 1$.

3. Results and discussion

3.1. Cyclic voltammograms of V(IV)- and V(V)-sulfuric acid solutions

Fig. 1(a)–(c) shows the cyclic voltammograms of a stationary platinum electrode in 1–9 M H₂SO₄ solution containing V(IV) and V(V). In both cases, the oxidation peak of V(IV) shifts to negative potential and the reduction peak of V(V) to positive with an increase in the H₂SO₄ concentration. The similar dependence of the peak potentials has been reported on a graphite reinforced carbon (GRC) electrode and attributed to the complex formation of V(V) and V(IV) with SO₄²⁻ [4]. Several kinds of SO₄²⁻- or HSO₄⁻-coordinated V(V) and V(IV) species, namely VO₂SO₄⁻, VO₂(SO₄)₂³⁻ having the oxidation number of +5 or VO(SO₄)₂²⁻, VOHSO₄⁺, etc. having the oxidation

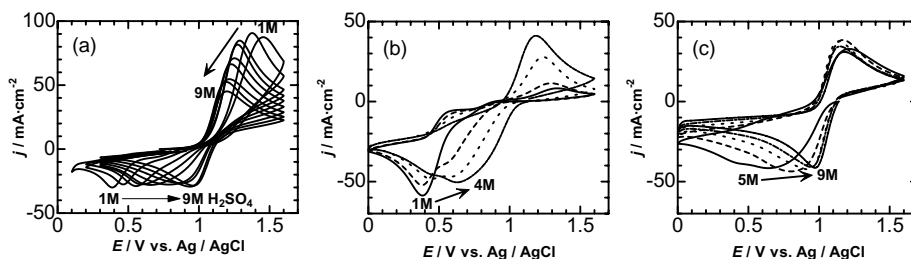


Fig. 1. (a) Cyclic voltammograms of a stationary Pt electrode in 1–9 M H₂SO₄ solution containing 2 M V(IV) at 25 °C. Scan rate = 40 mV s⁻¹. (b) Cyclic voltammograms of a stationary Pt electrode in 1–4 M H₂SO₄ solution containing 0.8, 1.0, 1.4, 1.7 M V(V), respectively, at 25 °C. Scan rate = 40 mV s⁻¹. (c) Cyclic voltammograms of a stationary Pt electrode in 5–9 M H₂SO₄ solution containing 2 M V(V), respectively, at 25 °C. Scan rate = 40 mV s⁻¹.

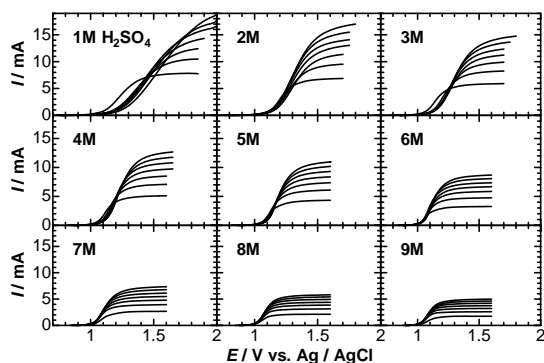


Fig. 2. Linear sweep voltammograms of a Pt rotating disk electrode in 1–9 M H_2SO_4 solution containing 2 M V(IV) at 25°C . Scan rate = 5 mV s^{-1} and $\omega = 100\text{--}700 \text{ rpm}$.

number of +4, have so far been proposed in the concentrated H_2SO_4 solutions [7,9]. In addition, $\text{V}_2\text{O}_3^{4+}$ is proposed as a predominant V(V) species at an extremely high H_2SO_4 concentration (10–16 M) [8]. If V(IV) and V(V) are present as such complexes, then their radii should be much larger than well-known species of VO^{2+} (aq, oxidation number of +4) or VO_2^+ (aq, oxidation number of +5) designated on the conventional Pourbaix diagram.

3.2. Dissolved state of V(IV)

Hydrodynamic voltammetric data for V(IV) oxidation on a Pt rotating disk electrode are shown in Fig. 2. The limiting current density was proportional to the square root of angular velocity as shown in Fig. 3, ensuring that these data are consistent with Levich equation. The limiting current density at a certain angular velocity decreased with increasing H_2SO_4 concentration because of the increased solution viscosity as seen in Fig. 4. The Stokes radius of the electroactive V(IV) species, finally, is given in Fig. 5 as a function of the H_2SO_4 concentration.

In acidic media, an aquo cation of VO^{2+} (aq) is widely accepted V(IV) species and the radius of octahedrally coordinated $\text{VO}(\text{H}_2\text{O})_5^{2+}$ is roughly estimated as 2.8 \AA based on crystallographic data (V-O interatomic distance for VO^{2+} plus radius of O^{2-} [13]). The determined Stokes radius of

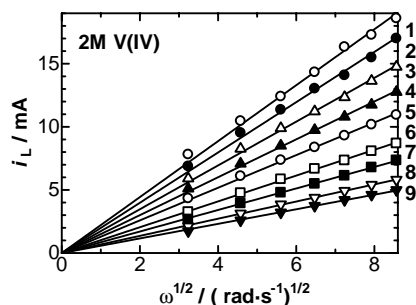


Fig. 3. Dependence of the limiting current on the square root of the angular velocity in the voltammetric measurements using the Pt rotating disk electrode for the oxidation of V(IV) .

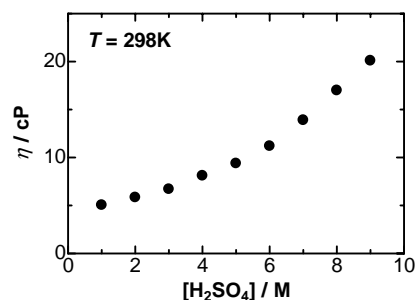


Fig. 4. Dependence of the viscosity of the $\text{V(IV)}\text{-H}_2\text{SO}_4$ solution on the H_2SO_4 concentration at 25°C .

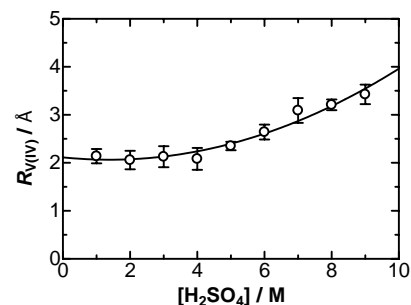


Fig. 5. Stokes radius of V(IV) as a function of the H_2SO_4 concentration.

V(IV) coincides substantially with this value at lower H_2SO_4 concentration region of $<4 \text{ M}$. On the other hand, another larger V(IV) species seems to exist at higher H_2SO_4 concentration region of $>5 \text{ M}$. However, UV-Vis spectra of V(IV) solutions are independent of H_2SO_4 concentration as can be seen in Fig. 6. These facts indicate that the electronic states of V(IV) species are little affected by H_2SO_4 concentration up to 9 M .

As seen in Fig. 7, the solubility of VOSO_4 was confirmed to decrease with increasing H_2SO_4 concentration in accordance with the literature data [9]. The reason why the Stokes radius of V(IV) species increases at the higher H_2SO_4 concentration region of $>5 \text{ M}$ might be explained by these complex formation with SO_4^{2-} and/or HSO_4^- . Although the splitting of $\text{V } 3d\text{-orbitals}$ in VO^{2+} remains almost unchanged even at $>5 \text{ M}$, VO^{2+} tends to form ion pair with anions in its circumstances and becomes less mobile. As the outer-most

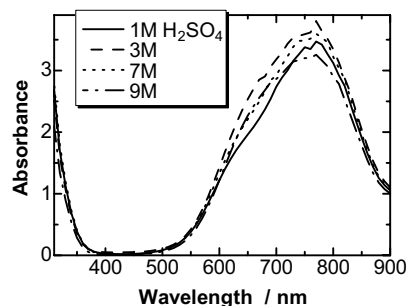


Fig. 6. UV-Vis absorption spectra of the $\text{V(IV)}\text{-H}_2\text{SO}_4$ solution at various H_2SO_4 concentrations.

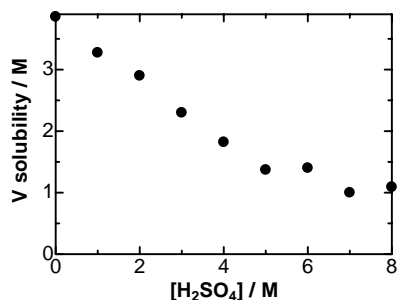


Fig. 7. Dependence of the solubility of the V(IV)-H₂SO₄ solution on the H₂SO₄ concentration at 25 °C.

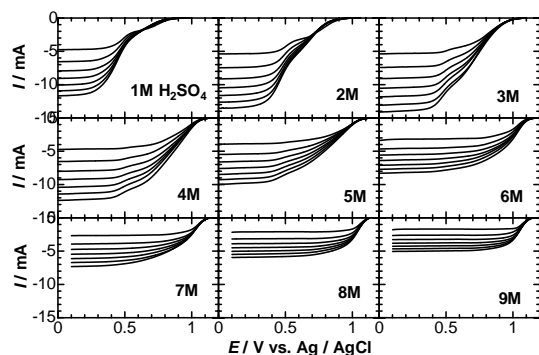


Fig. 8. Linear sweep voltammograms of a Pt rotating disk electrode in 1–9 M H₂SO₄ solution containing 1–2 M V(V) at 25 °C. Scan rate = 5 mV s⁻¹ and ω = 100–700 rpm.

electronic states of V(IV) species are substantially independent of the H₂SO₄ concentration, the oxidation potential of V(IV) remains almost constant. On the other hand, as seen in the cyclic voltammograms in Fig. 1, the oxidation wave of V(IV) is principally quasi-reversible on the polarographic criteria. The CV curves tend to become reversible with increasing H₂SO₄ concentration, i.e. the viscosity.

3.3. Dissolved species of V(V)

Analogous data for V(V) solutions and the reduction of V(V) are presented Figs. 8–11. The reduction of V(V) gave a single wave at higher H₂SO₄ concentration than 7 M,

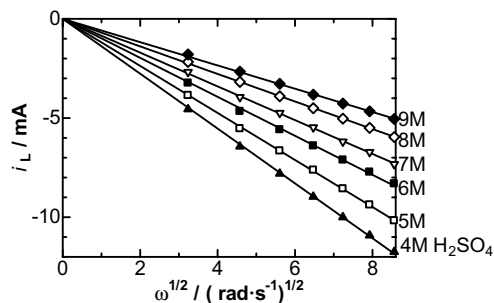


Fig. 9. Dependence of the limiting current on the square root of the angular velocity in the voltammetric measurements using the Pt rotating disk electrode for the reduction of V(V).

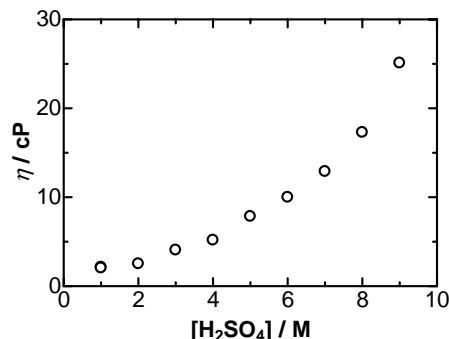


Fig. 10. Dependence of the viscosity of the V(V)-H₂SO₄ solution on the H₂SO₄ concentration at 25 °C.

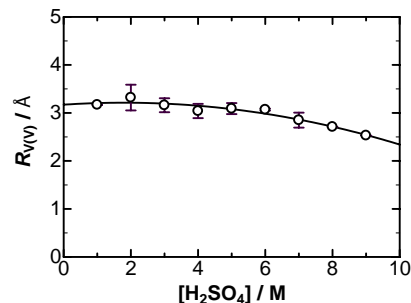


Fig. 11. Stokes radius of V(V) as a function of the H₂SO₄ concentration.

whereas it gave obvious two-step wave in 1–7 M H₂SO₄ solutions. The stepwise reduction of polymerized V(V) species is concerned in 1–7 M H₂SO₄ solutions as mentioned below. When H₂SO₄ was concentrated up to 9 M, the Stokes radius of V(V) decreased to about 2.5 Å. Ion-pair formation between V(V) cation and SO₄²⁻ or HSO₄⁻ anion can never explain such a decrease in Stokes radii at a high H₂SO₄ concentration. At a low pH region, V(V) species seems to exist as VO₂⁺ (aq) [14] and the estimated radius for VO₂(H₂O)₄⁺ is close to the determined Stokes radius of ~2.5 Å at 9 M H₂SO₄.

The main absorption band of V(V) due to the d–d transition was found to shift depending on the H₂SO₄ concentration as in Fig. 12. This fact revealed that the nearest neighbor of V(V) atom is affected by the H₂SO₄ concentration in contrast to V(IV).

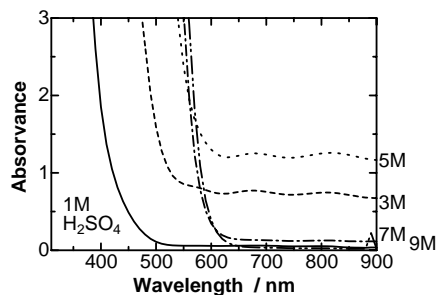


Fig. 12. UV-Vis absorption spectra of the V(V)-H₂SO₄ solution at various H₂SO₄ concentrations.

The two-step reduction wave of V(V) confirmed at low H_2SO_4 concentration range might suggest in general either that two different kinds of V(V) species are present, or that the cathodic reduction of a unique V(V) species proceeds stepwise. According to the literature [15,16], however, the cathodic reduction of polyoxometalates of transition metals tends to give a single wave at low pH and multi-step wave at high pH. Especially in the case of molybdenum [16], the effects of solution pH on the single-step/multi-step transition had been clearly demonstrated. In the present case of V(V), the reduction wave showed steps only at $<7\text{ M H}_2\text{SO}_4$. These facts support that V(V) might be in a polymeric form at a low H_2SO_4 concentration.

Our experimental data showed clearly that a smaller V(V) species formed at a higher H_2SO_4 concentration and were against the opinion that dimer V(V) cation of $\text{V}_2\text{O}_3^{4+}$ exists in extremely concentrated H_2SO_4 medium.

4. Conclusions

In concentrated H_2SO_4 solutions, V(IV) forms complex species neither with SO_4^{2-} nor with HSO_4^- . When the solution becomes viscous at higher H_2SO_4 concentration, the oxidation peak potential of V(IV) shifts to positive side on cyclic voltammograms. In addition, V(V) does not form any complex. Both the relatively large Stokes radii and the characteristic multi-step reduction waves of V(V) observed at a

low H_2SO_4 concentration region, instead, suggest that V(V) exists in a certain polymeric form.

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