

Effects of Sulfuric Acid Concentration on Positive Half Cell Reaction in a Vanadium Redox-Flow Cell

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1. Introduction

The vanadium redox flow cell has been extensively studied as a large-scaled secondary battery and already in practical use in Japan at present.

In its positive half cell, tetra- and penta-valent vanadium(V(IV) and V(V)) couple in a sulfuric acid solution is employed. Their species are not yet clarified completely, although several papers [1-3] suggested that V(IV) or V(V) might be in a polymeric form such as dimer or be a complex with sulfate or bisulfate anion.

In this study, redox behaviors of V(IV) and V(V) were investigated by a rotating Pt-disk electrode at various sulfuric acid concentrations.

2. Experimental

2 g-atom/dm³ V(IV) solutions were prepared by dissolving VOSO₄ · nH₂O (VOSO₄=62%) in 1-9M H₂SO₄. V(V) solutions obtained by electrochemical oxidation of V(IV) were kept at 25 °C for 2-4 months. Both V(IV) and V(V) were determined by potentiometric titration with a standard permanganate solution.

By using a Pt rotating disk (3mmφ) electrode, Stokes radii (*a*) of V(IV) and V(V) were determined from Stokes equation;

$$a = \frac{kT}{6\pi\eta D} \quad (1),$$

where, *k*, *T*, *η* and *D* are Boltzmann constant, temperature, solution viscosity and diffusion coefficient, respectively.

3. Results and Discussion

Cyclic voltammograms in V(IV) + 1-9M H₂SO₄ solutions compared in Fig. 1 are in good agreement with the literature [4] data, where, V(V) reduction peak shifts to positive with increasing the sulfuric acid concentration. At the same time, the oxidation peak shifts to negative and the oxidation peak current decreases with sulfuric acid concentration, which can be explained by the

increase of solution viscosity.

Stokes radii of V(IV) and V(V) species determined by the rotating disk technique are shown in Fig.2 as functions of sulfuric acid concentration. V(IV) can be considered as VO²⁺ aquo-complex at 1-4 M H₂SO₄ as commonly accepted, whereas it may form some larger species at 5-9 M H₂SO₄. V(V), on the other hand, usually believed as VO₂⁺ aquo-complex tends to become smaller at a high sulfuric acid concentration, and settled to 2.5 Å. Aqua-complex of VO₂⁺ is commonly considered as V(V) in low pH region. So, it is suggested that concentrated H₂SO₄ media, VO₂⁺_{aq} become predominant species. Furthermore, it is unlikely that V(V) makes complex with sulfate or bisulfate ion because the size of complexes with these ion is considered to be larger than 4 Å, and the amount of them increase with increasing sulfuric acid concentration.

4. References

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- [2] C. Madic *et. al.*, *Inorg. Chem.*, **23** (1984) 469.
- [3] A.A. Ivakin, *Zh. Prikl. Khim.*, **39** (1966) 1203.
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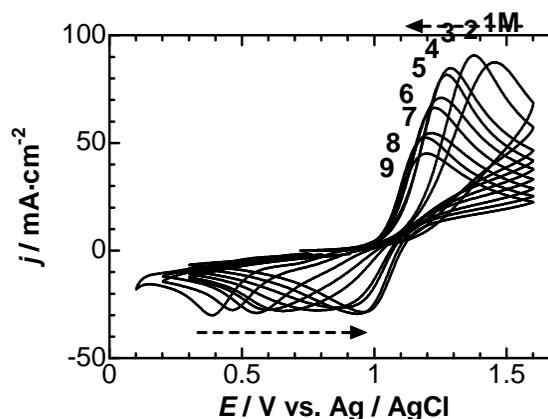


FIG. 1 Cyclic voltammograms for 2 g-atom/dm³ V(IV) + 1-9M H₂SO₄ soln. on a Pt electrode.

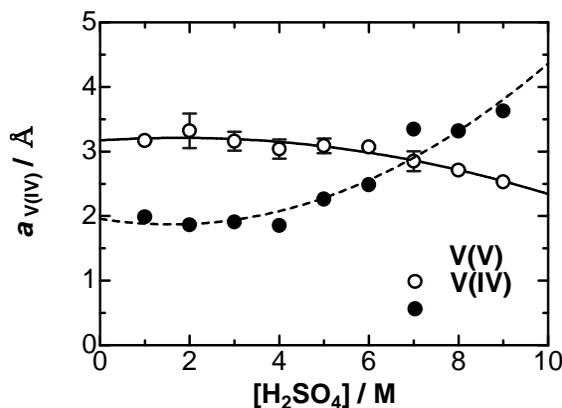


FIG. 2 Stokes radii of V(IV) and V(V) as a function of concentration of sulfuric acid.