

## Mechanism of Dioxovanadium(V) Ion Reduction on Oxygen-enriched Carbon Surface

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### Introduction

Vanadium redox flow batteries (VRFBs), which have recently attracted much attention as one of the promising large-scale energy storage technologies, suffer from the slow kinetics of the discharge reaction at the positive carbon electrodes. The enhancement of the kinetics by the enrichment of oxygen-containing functional groups on the carbon surface has been reported (Fig. 1); however, the detailed reduction mechanism of the active material, dioxovanadium(V) ion ( $\text{VO}_2^+$ ), has not yet been clarified. In this study, the  $\text{VO}_2^+$  reduction was fundamentally investigated using glassy carbon rotating disk electrodes (GC RDEs) as a model of the VRFB carbon electrodes.

### Experimental

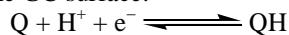
A GC RDE, which consisted of a GC rod (Sigradur<sup>®</sup> G, made from phenolic resin by solid phase pyrolysis at 1100 °C followed by a high-temperature treatment up to 2200 °C) sealed in a polyether ether ketone holder, was polished with a 0.05  $\mu\text{m}$  alumina suspension on a polishing cloth and then ultrasonically cleaned in high-purity water for use as the working electrode. The geometric surface area of the electrode was 0.071  $\text{cm}^2$  (3-mm diameter).

The electrochemical oxidation of the GC surface was carried out using a three-electrode cell with carbon cloth as the counter electrode and Ag/AgCl/NaCl(3 M) as the reference electrode (0.212 V vs. standard hydrogen electrode) by holding the GC electrode potential at 1.8 V for various lengths of time in the Ar-saturated 1 M  $\text{H}_2\text{SO}_4$  at 25 °C. After the oxidation, the electrode potential was scanned between -0.2 and 1.0 V at the scan rate of 50  $\text{mV s}^{-1}$  until a stable voltammogram was obtained.

The current-potential relationships were obtained in Ar-saturated  $\text{VO}_2^+$ (5 mM)- $\text{VO}^{2+}$ (5 mM)- $\text{H}_2\text{SO}_4$ (1 M) at 25 °C and various rotation speeds. The scan rate of the potential was fixed at 10  $\text{mV s}^{-1}$ . The background current was similarly measured in the Ar-saturated 1 M  $\text{H}_2\text{SO}_4$  without rotation.

### Results and discussion

The cyclic voltammograms for the GC electrodes before and after the electrochemical surface oxidation are shown in Fig. 2. The sign of the oxidation current was taken as positive. The current in both the anodic and cathodic scans increased with an increase in the surface-oxidation time; in particular, the anodic and cathodic peaks at around 0.4 V were enhanced. These peaks were caused by the redox reaction of the quinone-like functional groups on the GC surface:



This result indicated the generation of oxygen-containing functional groups on the GC surface and their increase with an increase in the surface-oxidation time. In addition to the redox reaction, the charging current for the electrochemical double layer increased with an increase in the oxidation time due to the surface roughening.

The kinetic current at the GC surface without the influence of mass transfer in the solution,  $I_k$ , was

determined by the Koutecky-Levich equation using the current-potential relationships measured at the various electrode rotation speeds.

Figure 3 shows the relationships between the electrode potential and  $\log(-I_k/A)$  (Tafel plots). The  $\text{VO}_2^+$  reduction was enhanced by the electrochemical GC surface oxidation and the current was increased with an increase in the oxidation time.

A nearly linear relationship was observed at the GC electrode before the electrochemical surface oxidation treatment in the low overpotential region and the slope (Tafel slope) was  $-0.161 \text{ V decade}^{-1}$ . These behaviors were in agreement with those previously reported.<sup>1</sup>

Linear relationships were also observed for the GC surface after the electrochemical surface oxidation treatment in the low overpotential region; however, the Tafel slope was  $-0.087 \text{ V decade}^{-1}$ , nearly independent of the surface oxidation time, which is clearly different from the Tafel slope before the surface oxidation. A new reaction mechanism involving the redox reactions of the quinone-like surface functional groups will be proposed in the presentation to explain this value.

### References

1. M. Gattrell, J. Park, B. MacDougall, J. Apte, S. McCarthy, and C. W. Wu, *J. Electrochem. Soc.*, **151**, A123 (2004).

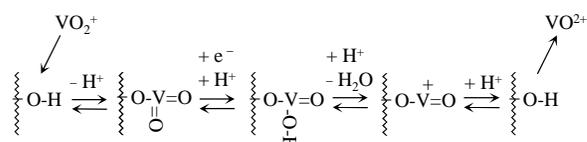


Fig. 1. Proposed model for dioxovanadium(V) ion reduction at VRFB positive electrode. Wavy lines represent surface of carbon electrodes.

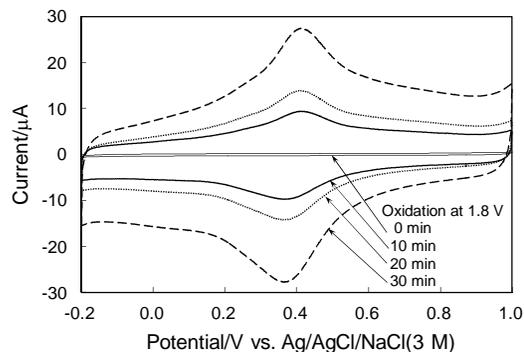


Fig. 2. Cyclic voltammograms for GC electrodes in Ar-saturated 1 M  $\text{H}_2\text{SO}_4$  before (0min, thin line) and after electrochemical surface oxidation for 10 min (solid line), 20 min (dotted line), and 30 min (dashed line). Geometric electrode surface area: 0.071  $\text{cm}^2$ . Scan rate: 50  $\text{mV s}^{-1}$ .

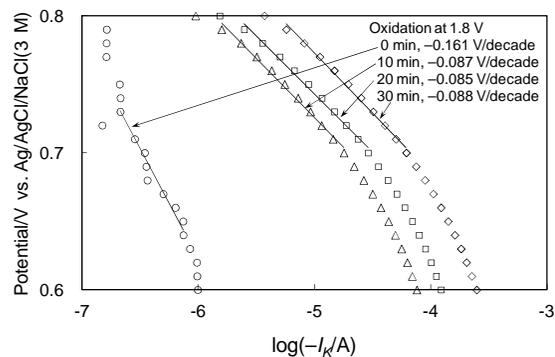


Fig. 3. Tafel plots in low overpotential region for  $\text{VO}_2^+$  reduction in  $\text{VO}_2^+$ (5 mM)- $\text{VO}^{2+}$ (5 mM)- $\text{H}_2\text{SO}_4$ (1 M) at GC before (0 min, circle) and after surface oxidation for 10 min (triangle), 20 min (square), and 30 min (diamond).