

## Note

# Four-electron reduction of dioxygen catalyzed by a decavanadium complex

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**Abstract**

The electroreduction of O<sub>2</sub> in acidic aqueous solutions at an electrode modified with a decavanadium cluster [(V=O)<sub>10</sub>(μ<sub>2</sub>-O)<sub>9</sub>(μ<sub>3</sub>-O)<sub>3</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>6</sub>] (**1**) revealed that it produces H<sub>2</sub>O with four electrons per O<sub>2</sub> molecule near 0.5 V versus SCE. The usefulness of the complex as a reduction catalyst of O<sub>2</sub> with a high selectivity was demonstrated.

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**Keywords:** Electrochemistry; Four-electron reduction; Dioxygen; Decavanadium

**1. Introduction**

The four-electron reduction of O<sub>2</sub> was recently found to be efficiently catalyzed by oxygen bridged complexes, such as μ-oxo divanadium complexes, μ-oxo iron-(III)porphyrins, μ-oxo manganese porphyrins, and other dimeric cobalt porphyrins [1–12]. Recently, we found that a novel decavanadium(V) cluster complex [(V=O)<sub>10</sub>(μ<sub>2</sub>-O)<sub>9</sub>(μ<sub>3</sub>-O)<sub>3</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>6</sub>] (**1**) was very easily prepared from V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub> by the spontaneous elimination of the acac ligand [13,14]. This complex bears ten oxovanadium(V) cores with good solubility in organic solvents due to the peripheral ligands, and is capable of forming a thin layer on a solid surface. The electrochemistry of the complex has been examined in organic electrolyte solutions such as dichloromethane, 1,1,2,2-tetrachloroethane, nitromethane, and acetonitrile containing a supporting electrolyte, which revealed a reversible redox wave near 0.6 V versus Ag/AgCl. It was shown that complex **1** has unique redox chemistry as a 10e<sup>−</sup> reservoir in the single redox process [15]. In order to clarify the multielectron transfer process of the decavanadium complex, we focused on the electroreduc-

tion of O<sub>2</sub> to H<sub>2</sub>O in acid using the modified electrode of complex **1** as the electrocatalyst.

**2. Experimental**

The electrochemical behavior of the modified electrodes: a Nikko Keisoku DPGS-1 dual potentiogalvanostat and a NFG-3 universal programmer were employed along with a Graphtec WX2400 X-Y recorder to obtain the voltammogram. The samples and electrolytes were set up in a conventional two-compartment cell in which a glassy carbon disk electrode served as the working electrode. The counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE).

**3. Results and discussion**

Complex **1** was synthesized and analyzed according to the procedures described in the literature [13]. The electrochemical measurements were carried out using a glassy carbon electrode modified with complex **1** to determine the four-electron reduction selectivity of O<sub>2</sub> under acidic conditions. The 0.1 mM solution of complex **1** in CH<sub>2</sub>Cl<sub>2</sub> was adsorbed on the surface of a glassy carbon electrode by transferring a measured

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volume (10  $\mu\text{L}$ ) onto the surface of electrode and allowing the solvent to evaporate with the rotating at 100 rpm. The modified electrode was then immersed in a 0.5 M  $\text{HClO}_4$  aqueous solution containing 0.1 M  $\text{NH}_4\text{PF}_6$  as the supporting electrolyte.

The electrocatalytic behavior of the oxygen reduction catalyzed by the complex **1** was examined by cyclic voltammetry as shown in Fig. 1. The curve in Fig. 1(a) shows the initial current–potential response obtained at a glassy carbon electrode adsorbed with complex **1** in an argon-saturated aqueous acidic solution (Fig. 1(b) comparison for initial redox to the unmodified electrode). When the electrode was transferred to an oxygen saturated solution, a large catalytic current appeared starting at 0.8 V versus SCE with a peak at 0.5 V (Fig. 1(c)). The limiting current  $i_L$  in the current–potential curves was analyzed using the Levich equation ( $i_L = 0.62nFAD_0^{2/3}\nu^{-1/6}C_0\omega^{1/2}$ ; where  $D_0$  = diffusion coefficient of  $\text{O}_2$  in the solution ( $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) and  $C_0$  = concentration of  $\text{O}_2$  in the solution ( $1.3 \times 10^{-6} \text{ mol cm}^{-3}$ ),  $\nu$  = viscosity of solution ( $0.01 \text{ cm}^2 \text{ s}^{-1}$ )) [16–18]. The current–potential curves obtained with the rotating disk electrode (RDE) were calculated and plotted as Koutecky–Levich plots ( $i_L^{-1}$  vs.  $\omega^{-1/2}$ ) in Fig. 1(d). The number of electrons ( $n$ ) transferred during the  $\text{O}_2$  reduction can be determined from the slopes of the plots. The value of  $n$  was evaluated to be

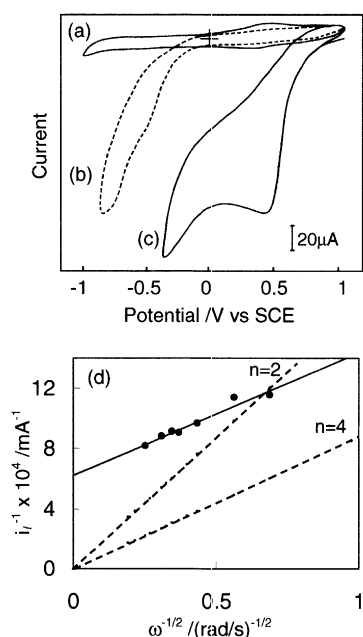


Fig. 1. (a) Cyclic voltammetry on the glassy carbon electrode modified complex **1** recorded in a saturated argon aqueous electrolyte containing 0.5 M  $\text{HClO}_4$  and 0.1 M  $\text{NH}_4\text{PF}_6$ , (b) bare glassy carbon unmodified electrode under  $\text{O}_2$ , and (c) repeat of (a) recorded under  $\text{O}_2$ . Scan rate:  $100 \text{ mV s}^{-1}$ . (d) Koutecky–Levich plots of the plateau current during rotating disk voltammetry for the reduction of  $\text{O}_2$  on the electrode modified complex **1**. The broken lines correspond to the diffusion limited two and four electron reductions of  $\text{O}_2$ , respectively.

4.2 for an electrode coated with complex **1**. These slopes were almost similar to that of the broken line calculated for the theoretical diffusion limited four-electron reduction of  $\text{O}_2$ .

The rotating Pt-ring glassy carbon-disk electrode (RRDE) was used to confirm the four-electron reduction of  $\text{O}_2$ . The disk was glassy carbon (diameter 6 mm), and the ring was Pt with 7.3 and 9.3 mm inner and outer diameters, respectively. The efficiency of the  $\text{O}_2$  reduction to  $\text{H}_2\text{O}$  ( $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ ), i.e.  $\%\text{H}_2\text{O} = (N_0 - N)/(N_0 + N)$ ;  $N$ , collection efficiency ( $i_R/i_D$ ) of RRDE,  $N_0$ , collection efficiency of a complex for a normalization) [10]. Under an acidic condition, the ring potential was maintained at 1.1 V to collect  $\text{H}_2\text{O}_2$  produced by the two-electron reduction of  $\text{O}_2$  at the disk electrode ( $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$ ). In the presence of  $\text{O}_2$  (Fig. 2), the cathodic current  $i_D$  on the disk electrode appeared near 0.8 V. The ring current at potentials higher than 0.6 V was very low. At lower potentials than 0.6 V, the disk current increased and the ring current appeared due to the concomitant two-electron reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$ . At potentials where the plateau current is obtained, the selectivity for the reaction where  $\text{O}_2$  was directly reduced to  $\text{H}_2\text{O}$  by the four-electron reduction was 98%, in comparison with the intrinsic value for the collection efficiency of the electrode determined by the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple ( $N_0 = 0.38$ ).

In summary, it was demonstrated that the vanadium multinuclear complex catalyzes the reduction of  $\text{O}_2$  at a high potential, which is promising to expand the wide application of the catalyst. Although the mechanism of this vanadium-based cluster complex **1** was not yet clarified, the oxophilic [V(III)] of oxovanadium(V) cluster complexes were predicted actively reacts with  $\text{O}_2$  to accomplish a four-electron reduction of  $\text{O}_2$  in acid condition as described in previous literature ( $2[\text{V(III)}]^+ + \text{O}_2 = 2[\text{V(V)O}]^+$ ) [1]. More significant details were under investigation.

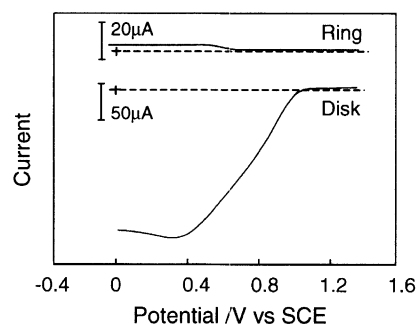


Fig. 2. Rotating-ring disk voltammetry for the reduction of  $\text{O}_2$  on the Pt-ring RRDE in which the disk was modified with the decavanadium complex **1** recorded in aqueous electrolyte solutions saturated with oxygen. The other conditions are as described in Fig. 1. The scan and rotation rates were  $25 \text{ mV s}^{-1}$  and 50 rpm, respectively.

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