

Electrocatalysis for dioxygen reduction by a μ -oxo decavanadium complex in alkaline medium and its application to a cathode catalyst in air batteries

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Abstract

The redox behavior of a decavanadium complex $[(V=O)_{10}(\mu_2-O)_9(\mu_3-O)_3(C_5H_7O_2)_6]$ (**1**) was studied using cyclic voltammetry under acidic and basic conditions. The reduction potential of V(V) was found at less positive potentials for higher pH electrolyte solutions. The oxygen reduction at complex **1** immobilized on a modified electrode was examined using cyclic voltammetry and rotating ring-disk electrode techniques in the 1 M KOH solutions. On the basis of measurements using a rotating disk electrode (RDE), the complex **1** was found to be highly active for the direct four-electron reduction of dioxygen at -0.2 V versus saturated calomel electrode (SCE). The complex **1** as a reduction catalyst of O_2 with a high selectivity was demonstrated using rotating ring-disk voltammograms in alkaline solutions. The application of complex **1** as an oxygen reduction catalyst at the cathode of zinc–air cell was also examined. The zinc–air cell with the modified electrode showed a stable discharge potential at approximately 1 V with discharge capacity of 80 mAh g^{-1} which was about five times larger than that obtained with the commonly used manganese dioxide catalyst.

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1. Introduction

The electrochemical reduction of oxygen by metal complexes has been widely studied with biological [1–7], polymer synthetic [8–10] as well as fuel cell [4,11] and metal–air batteries applications [12–17] via $2e^-$ (acidic: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$; basic: $O_2 + 2H_2O + 2e^- \rightarrow HO_2^- + OH^-$) or $4e^-$ (acidic: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$; basic: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) electron transfer at chemically modified electrodes. Most of the electroreduction reactions of oxygen were studied under acidic conditions. Only a few catalysts were effective in both acidic and basic media, such as the planar MN_4 cyclic chelates (cofacial Co-porphyrins and Cu-phenanthroline) which were found to be the four-electron reduction catalysts at various pH values [6,15]. However, the catalyst that can react with oxygen under basic conditions (pH > 12) is very rare to our knowledge. Here we describe the novel μ -oxo decavanadium complex as a catalyst that has a high efficiency for the electroreduction of oxygen under basic conditions.

In previous reports, the μ -oxo type decanuclear vanadium complex $[(V=O)_{10}(\mu_2-O)_9(\mu_3-O)_3(C_5H_7O_2)_6]$ (**1**) was realized as a good multi-electron transfer catalyst in homogenous electrolytes and an active four-electron reduction catalyst with a very high yield in the conversion of O_2 to H_2O , in which the H_2O_2 by-product is limited to not more than 2%, at approximately 0.5 V versus saturated calomel electrode (SCE) under acidic solutions [16,17]. In the present study, the redox behavior of various pH solutions and the electrocatalytic reduction of oxygen in oxygen-saturated alkaline aqueous solutions were studied by cyclic voltammetry and rotating-ring disk voltammetry (RRDV). The electrochemical results are discussed in view of the factors for determining the reduction pathway.

Furthermore, we describe the application of the complex **1** as an oxygen reduction catalyst in the cathode of zinc–air batteries for trial purposes. The R&D study of metal–air batteries has been done for more than 30 years, and the performance needed for metal–air batteries is the high theoretical energy density, but the output power density is still very low. Seemingly, it is due to the low activity of air electrodes that are included in the metal–air batteries. To solve this problem of cathode materials for air electrodes, the high catalytic

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activity and chemical stability of an oxygen reduction catalyst have been required. Many authors and their cited references have investigated various electrode catalysts, including noble metal, oxide, nitrides, and organo metallic compounds [13,14,18]. On the other hand, the high valent μ -oxo type vanadium complex in non-planar structure is capable of reducing O_2 and is expected to be a new material for the cathode which is reactive in both acidic and alkaline media.

2. Experimental

Materials and procedures: All reagents and solvents from commercial sources were used without further purification. The decavanadium cluster **1** was synthesized and analyzed according to the procedures as already described in the literature [16,20]. The electrode modified with complex **1** was built in the same manner as previously described [17]. The Sorensen buffer electrolytes (pH 4.48, 10.11) and the neutral solution containing NH_4PF_6 as a supporting electrolyte, which were prepared using deionized water, was used as a solvent in the electrochemical experiments. For oxygen reduction measurement, 1 M potassium hydroxide (Kanto Chem. Co.) electrolyte solutions with deionized water was used at room temperature under pure oxygen. Carbon (0.5–1.7 mm, 10–30 mesh), graphite powder (75–106 μ m, 150–200 mesh), zinc powder (with 99.9% grade) and paraffin binder were purchased from the Kishida Co. and Kanto Chem. Co. The carbon paste electrode (ϕ 1 cm) with a MnO_2 catalyst and the porous separator were a gift from the Matsushita Elec. Co. and Celgard Co.

Analytical instruments were performed as follows: The electrochemical behavior of the modified electrodes was determined using a Nikko Keisoku DPGS-1 potentiogalvanostat, NFG-3 function generator and a Graphtec WX2400 X-Y recorder. The sample and electrolytes were setup in a conventional two-compartment cell where a glassy carbon disk electrode (0.28 cm^2) served as the working electrode. The counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode. The Pt-glassy carbon ring electrode was used in the rotating-ring disk voltammetry measurements, where the disk was glassy carbon (ϕ 6 mm), and the ring was Pt with 7.3 and 9.3 mm inner and outer diameters, respectively. Under alkaline conditions, the ring potential was kept at 0.4 V to collect the HO_2^- produced by the two-electron reduction of O_2 at the disk electrode.

Measurements of battery performances were done as follows: The catalyst **1** (30 wt.%) and a carbon powder (60 wt.%; which contained carbon black and graphite in ratio of 1:1) and binder (10 wt.%) were blended to make an oxygen electrode and pressed into 1-cm diameter pellets at 400 $kg\ cm^{-2}$ and room temperature. The final air electrode weighed 0.2 g, which was then combined with a 1 g zinc anode and 2 ml of 1 M KOH electrolyte with a separator (ϕ 2.6 cm, Celgard 5550). A Hokuto Denko discharge analyti-

cal instrument was used to measure the electrical discharge characteristics of the test cells at a 1 mA discharge current and room temperature. The compartment cell (ϕ 2.6 cm) was manually constructed with oxygen flowing at the oxygen electrode side.

3. Results and discussions

3.1. Redox behavior of decavanadium complex in alkaline solutions

The cyclic voltammogram obtained with a glassy carbon electrode coated with dichloromethane solution containing complex **1** at a scan rate of $50\ mV\ s^{-1}$ in argon-saturated aqueous solution of various pHs are shown in Fig. 1. Fig. 1(a) was obtained in pH 4.5 buffer solution which showed the reduction potential of complex **1** at 0.1 V versus SCE with no oxidation potential. Fig. 1(b) was obtained in a neutral solution that showed a large reduction current appearing near 0.05 V versus SCE with a slight oxidation peak near 0.3 and 0.8 V. The peak at 0.3 V was determined as the oxidation potential of V_{10} in the homogenous solution [17]. The additional oxidation peaks at 0.8 V of complex **1** corresponded to the oxidation of $VO(acac)$ (H_2acac : acetylacetone) which was also observed when the electrode was modified with dinuclear $V_2O_4(acac)_2$ complex under the same solutions (data not shown) [21]. Indeed, the complex **1** was a spontaneous cluster assembly in dichloromethane using dinuclear complex $V_2O_4(acac)_2$ as a precursor [16,20]. In Fig. 1(c) that was obtained in pH 10.1, the reduction of complex **1** was observed in a broad peak near -0.1 V versus SCE, with an oxidation peak at 0.8 V. As shown on Fig. 1, the reduction potential of the complex **1**, E_p , is negatively shifted at high pH values, which is almost 0.5 V less positive for alkaline media than that in the acidic media (0.3 V) [16]. Although the complex **1** was to be slightly decomposed to

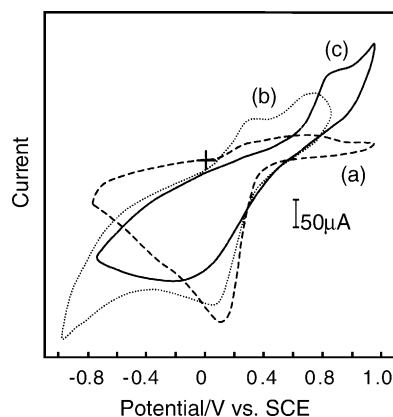


Fig. 1. Cyclic voltammetry of the glassy carbon electrode modified complex **1** recorded in an argon-saturated Sorensen buffer electrolyte adjust to pH (a) 4.5 and (c) 10.1. (b) Neutral aqueous solution containing 0.1 M NH_4PF_6 as supporting electrolyte. Scan rate: $50\ mV\ s^{-1}$.

the mononuclear complex at high pH values, this may only occur at the surface of the modified electrode in the basic solutions; however, the structure was considered to be more stable in acidic solutions.

3.2. The dioxygen reduction process

In our previous report, the modified electrode of decavanuclear vanadium complex **1** was realized as a good catalyst in the acidic solution, and showed a reduction potential at 0.5 V versus SCE under oxygen conditions [17]. Here we described the cyclic voltammogram for the oxygen reduction of a glassy carbon electrode coated with the complex **1** at a scan rate of 50 mV s^{-1} in a 1 M KOH aqueous solution as shown in Fig. 2. The KOH electrolyte was used without any other supporting electrolyte. After the CH_2Cl_2 solvent (volume of $10 \mu\text{l}$) on the electrode surface, used to coat the complex **1**, was evaporated, the modified electrode was immersed in an argon-saturated electrolyte. Fig. 2(a) showed the redox potential with a broad reduction peak near -0.1 V and the oxidation peak at 0.8 V versus SCE. When the electrode was repeated in the oxygen-saturated 1 M KOH electrolyte solution, almost the same catalytic current was shown

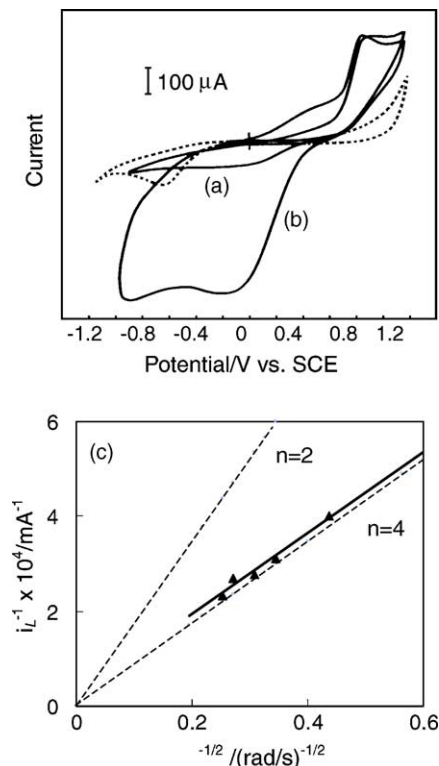


Fig. 2. (a) Cyclic voltammetry of the glassy carbon electrode modified complex **1** recorded in an argon-saturated aqueous electrolyte containing 1 M KOH solution. The broken line cyclic voltammogram is a bare glassy carbon unmodified electrode under O_2 , (b) repeat of (a) recorded under O_2 . Scan rate: 50 mV s^{-1} . (c) Koutecky–Levich plots of the plateau current during rotating disk voltammetry for the reduction of O_2 . The broken lines correspond to the diffusion limited two- and four-electron reductions of O_2 , respectively.

starting at 0.4 V versus SCE with a broad peak near -0.2 V and a slight oxidation peak at 0.8 V (Fig. 2(b)).

The limiting current i_L in the current–potential curves of Fig. 2(b) were analyzed using the Levich equation ($i_L = 0.62nFAD_0^{2/3}\nu^{-1/6}C_0\omega^{1/2}$; where D_0 is the diffusion coefficient of O_2 in the solution ($1.76 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and C_0 is the concentration of O_2 in the solution at 25°C ($1.103 \times 10^{-6} \text{ mol cm}^{-3}$), ν is the kinetic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$)) [22,23]. The current–potential curves obtained with the rotating disk electrode (RDE) were calculated and plotted as Koutecky–Levich plots (i_L^{-1} versus $\omega^{-1/2}$) in Fig. 2(c). The number of electrons (n) transferred during the O_2 reduction can be determined from the slope of the plots. The value of n was evaluated to be 4.1 for an electrolyte of 1 M KOH using the electrode coated with the complex **1**. These slopes were almost similar to that of the broken line calculated for the theoretical diffusion limited four-electron reduction of O_2 . The electron number for the oxygen reduction in acidic solution was also near 4.2 [16], which means that the oxygen reduction through the four-electron transfer is independent of pH, while the E_p of the oxygen reduction depended on the pH. It is noticeable that the kinetic current i_k , determined by the intercept of the Koutecky–Levich plot at the y-axis ($\omega = \infty$), is so small that an accomplishment of an almost diffusion limited reduction of O_2 could be anticipated.

In Fig. 3, the typical disk and ring currents obtained in the RRDE analysis are shown, which revealed the O_2 -reduction efficiency of the complex **1** under alkaline conditions (1 M KOH as electrolyte). The rotating Pt-ring glassy carbon-disk electrode (RRDE) was used to confirm the four-electron reduction of O_2 . The efficiency of the O_2 reduction to OH^- , i.e. $\% \text{OH}^-$, was calculated in the same manner as that for $\% \text{H}_2\text{O}$ [17]. In the presence of O_2 (Fig. 3, solid line), the cathodic current i_D on the disk electrode appeared starting

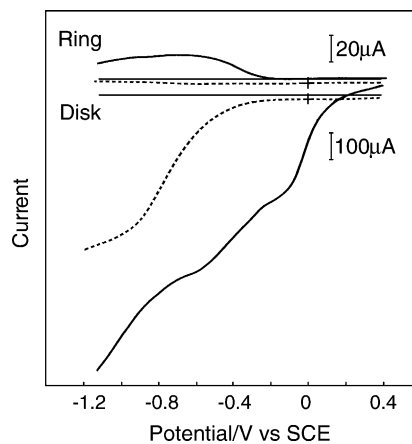


Fig. 3. Rotating-ring disk voltammetry for the reduction of O_2 on the Pt-ring glassy carbon-disk electrode in which the disk was modified with the decavanadium complex **1** recorded in aqueous electrolyte solutions of 1 M KOH saturated with oxygen. The broken lines correspond to the unmodified electrode. The scan and rotation rates were 50 mV s^{-1} and 50 rpm, respectively.

from 0.2 V and continued to flow as negative as -0.6 V versus SCE. At lower potential than -0.2 V, the disk current gradually increased and the ring current appeared due to the concomitant two-electron reduction of O_2 to HO_2^- . At potentials where the plateau current is obtained, the selectivity for the reaction where O_2 was directly reduced to OH^- by the four-electron reduction was 72%, in comparison to the intrinsic value for the collection efficiency of the electrode determined by the $Fe(CN)_6^{3-/4-}$ couple in potassium ferricyanide solution ($N_0 = 0.37$). The present result revealed that the decavanadium complex is capable and highly effective in catalyzing the reduction of O_2 in alkaline solutions.

3.3. The application to cathodes in air batteries

The decavanadium complex **1** that provided a multi-electron transfer reduction process of O_2 was used to make a cathode catalyst in a zinc–air battery. The oxygen reduction current was found to be continuously obtained using the multi-electron transfer process of the decavanadium complex, and here we described a battery of high capacity for trial purposes. The MnO_2 catalyst was chosen as the reference to the decavanadium catalyst for their well-documented activity for oxygen reduction. The discharge current when the decavanadium complex was used was compared to the conventional MnO_2 cathode electrode, using a Zn anode (anode reaction: $Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$) in a 1 M KOH electrolyte. As shown in Fig. 4(b), when the average voltage of the cell was maintained at 1 V during the discharge, the electrical discharge capacity became 80 mAh g^{-1} and a 112 h discharge time was established under pure oxygen conditions. It was approximately five times greater than the 15 mAh g^{-1} , and 70 h discharge time at a cell voltage of 1.3 V for a MnO_2 catalyst which was done in the same manner (Fig. 4(a)). The gravimetric energy density for the decavanadium complex electrode was calculated to be 93 mWh g^{-1} (current drain \times service hour \times average discharge voltage/weight of cell). Thus, we were successful in preparing new types of zinc–air batteries using the de-

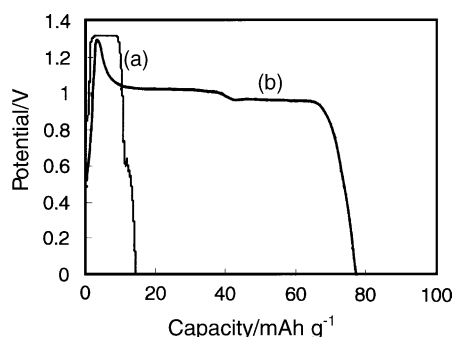


Fig. 4. Discharge performance obtained in zinc–air cell using oxygen electrode loaded with (a) MnO_2 and (b) decavanadium complex **1** as catalyst. Discharge current was 1 mA under oxygen condition. Separator and electrolyte were Cellgard 5550 (ϕ 2.6 cm) and 2 ml of 1 M KOH solution.

cavanadium complex. Although the average voltage of the complex **1** cell was 0.3 V less positive than that of MnO_2 , the complex **1** continuously provided the current due to the multi-electron transfer with a high discharge time. The reason for this phenomenon may be that the core of the central geometry of the decavanadium complex was very important for determining the dioxygen reduction process in all pH solutions. Similar reason was also described in the case of the MN_4 chelates, Co-dimeric complexes, such that the planar structures favored the maximum interaction between oxygen and the central transition metal ion [15]. The size effect of the catalyst was previously studied by many authors to produce a high dispersion catalyst [24–26]. Herein, the decavanadium complex **1** has a diameter of 1.5 nm which is the most suitable size of catalyst that easily adsorbs at the surface of the carbon electrode compared to the Pt particle (1.5–4 nm) which is known as an active oxygen reduction catalyst [17,20].

4. Conclusions

The electrochemical properties of the decavanadium complex in acidic and alkaline media have been investigated. The data obtained from the electrochemical studies in various aqueous solutions reveal that the decavanadium cluster is capable of acting as an excellent oxygen reduction catalyst over a wide pH range. While the oxides of V, Cr, Mn, and Co seem to be the most promising solid-state cathode catalyst for high performance secondary batteries and also others with the heat treatment process [19], we successfully used the rare complex of vanadium (V) without any heat treatment. The present work concerns the fundamental study of oxygen reduction in the presence of this cluster complex in acidic and alkaline media.

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