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Catalytic Effect of *cis*-Diammineplatinum α-Pyrrolidone Tan Adsorbed on a Platinum Electrode in Electrochemical Oxidation of Water into Molecular Oxygen

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Abstract

Cyclic voltammograms of *cis*-diammineplatinum α-pyrrolidone-blue and -tan, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ ($n = 5$ and 6, respectively) show for either complex only one redox peak at 0.53 V (average potential of the anodic and cathodic peak potentials). Coulometry and UV–Vis spectra of bulk-electrolyzed solution indicated that the redox peak corresponds to the reaction $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+} + 4e \rightleftarrows 2[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+}$. When cyclic voltammetry is carried out in a solution of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ or a platinum electrode adsorbed with $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ is used in the presence of oxidizing agent in the solution, O_2 gas generates from the electrode surface with large catalytic cathodic current at potentials below *ca.* 0.8 V. The O_2 gas was confirmed to generate from water by GC-MS analysis. This abnormal O_2 generation phenomenon is explained with cyclic reactions of chemical surface oxide formation on the electrode by the oxidizing agent and electrochemical reduction of the surface oxide. Oxygen gas generates from the reaction of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ or $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ with OH^- produced in the course of the electrochemical reduction of the electrode surface oxide. The ability of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ and $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ to oxidize OH^- into O_2 has been reported previously.

Introduction

Development of effective catalysts for chemical or electrochemical oxidation of water into oxygen or the backward reaction, that is, oxygen reduction into water (eqn. (1)), has attracted the interest of many chemists in recent years. Development of catalysts for the former reaction has been the most intensively studied subject in the field of artificial photosynthesis where a highly efficient catalyst for photochemical splitting of water into hydrogen and oxygen gases is searched. The latter reaction is technologically important in the field of fuell cells and air batteries.

$$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O \tag{1}$$

Recently, the authors have synthesized and characterized mixed valent tetranuclear platinum complexes, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ ($n = 5$, 6 and 8, C_4H_6NO is deprotonated α-pyrrolidone), and the related dimer complex, $[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ [1–6]. These cations exhibit novel reactions (2) and (3), which signify that the cations oxidize water into molecular oxygen [5, 6]. The authors have been

$$2[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+} + 2OH^- \rightleftarrows 2[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+} + O_2 + 2H^+ \tag{2}$$

$$2[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+} + 2OH^- \rightleftarrows 4[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+} + O_2 + 2H^+ \tag{3}$$

encouraged by the discovery of these reactions and have been studying the possibility that the compounds catalyse the redox reaction between water and molecular oxygen under various conditions. A novel catalytic effect has been found for $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ in that it catalyses, when existing in solution or adsorbed on a electrode together with oxidizing agents, electrochemical oxidation of water into molecular oxygen at a platinum electrode. The oxygen evolves from the electrode surface, surprisingly, with a cathodic current at the potentials below *ca.* 0.8 V (*versus* SCE). The mechanism of this electrochemical reaction has been shown to involve cyclic redox reactions of the platinum complex with surface hydroxide of the electrode material.

Experimental

The platinum complexes, $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$, $[Pt_4NH_3)_8(C_4H_6NO)_4](PF_6)_3(NO_3)_2\text{-}5H_2O$ and $[Pt_2(NH_3)_4(C_4H_6NO)_2](PF_6)_2$, were prepared according to the previously reported methods [2, 7, 8]. All the other chemicals were reagent grade and used without further purification.

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Electrochemical measurements were performed on a Fuso 315A potentiostat with either a platinum disk electrode of 5 mm in diameter or a gold rod electrode, 2.7 mm in diameter and 7.5 mm in length, as a working electrode. The geometrical surface area of the platinum electrode was 1.96×10^{-1} cm^2 and that of the gold was 6.93×10^{-1} cm^2. A platinum wire was used as a counter electrode throughout the measurements. All the measurements were performed with a three electrode system by using SCE as a reference electrode. The platinum electrode was cleaned in hot concentrated sulphuric acid and well washed with deionized and distilled water before each run. The gold electrode was etched in warm aqua regia, cleaned in hot concentrated sulphuric acid and well washed with purified water. The platinum complex adsorbed onto an electrode after repeated measurements was washed out first with concentrated NaOH and then the electrode was cleaned according to the above described cleaning method with acids. The platinum complex was, if necessary, adsorbed onto an electrode by repeating the potential sweep of the elctrode in the potential region 0 to 1.3 V (*versus* SCE) in 0.4 mM $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ solution containing 0.06 M H_2SO_4 for 30 min. Dissolved oxygen concentration was measured with an oxygen electrode, DO-1B from TOA electronics Co. and GC-MS measurements of the evolved oxygen gas were performed on a GCMS-QP1000 from Shimadzu Co. A column of Molecular Sieve 5 A was used and the column and injection port temperatures were 30 and 70 °C, respectively.

Results and Discussion

Cyclic Voltammograms of $[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+}$, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ *and* $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$

Figure 1A shows a cyclic voltammogram of $[Pt_2(NH_3)_4(C_4H_6NO)_2](PF_6)_2$ in 4.5 M H_2SO_4. The single redox wave at $E_p = 0.53$ V ($E_p = (E_{ps} + E_{pc})/2$) corresponds to the reaction $2[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+} - 4e \rightleftarrows [Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ [6]. Although the reaction is a four-electron process as a whole, the actual mechanism seems to involve intermediate oxidation states of the platinum complex and the apparently single redox wave actually consists of several very closely lying one- or two-electron processes involving the formation of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ ($n = 5$ and 6) [6]. This is also supported by Fig. 1B, which is a cyclic voltammogram of $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ and the redox wave basically identical with Fig. 1A suggests that $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ is one of the intermediates in the redox process $2[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+} - 4e \rightleftarrows [Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$.

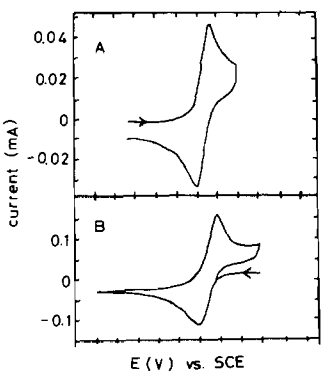


Fig. 1. Cyclic voltammograms of $[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ and $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ ($n = 5$ and 6). (A) $[Pt_2(NH_3)_4(C_4H_6NO)_2](PF_6)_2$ (0.6 mM) in 4.5 M H_2SO_4, sweep rate 0.1 V s^{-1}; (B) $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ (0.8 mM) in 0.06 M H_2SO_4, sweep rate 0.1 V s^{-1}.

The same voltammogram is obtained if the potential sweep is started anodically from 0.0 V. There is no possibility that Fig. 1B is a voltammogram of $[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ produced by reaction (3), since the solution was dark brownish red whose UV–Vis spectrum indicated the existence of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ (λ_{max} 478 nm ($\epsilon = 3.9 \times 10^4$ cm^{-1} M^{-1}) and 415 nm ($\epsilon = 1.5 \times 10^4$ cm^{-1} M^{-1})) [5]. Bulk oxidative electrolysis of the solution in 4.5 M H_2SO_4 at 0.8 V and bulk reductive electrolysis at 0.2 V resulted in the formation of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ and $[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+}$, respectively, also suggesting that Fig. 1A and B are essentially identical. The single wave in Fig. 1A and B shows no pH dependence.

Catalytic Effect of $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ *Adsorbed on a Platinum Electrode in Electrochemical Oxidation of Water into Oxygen*

Figure 2A and B show cyclic voltammograms of a platinum electrode in 9 M H_2SO_4 and 9 M H_2SO_4 with 0.1 M KNO_3, respectively. The broad anodic peak at potentials higher than 1.0 V corresponds to the formation of surface platinum oxide and the broad cathodic peak at 0.65 V corresponds to reduction of the surface platinum oxide [8, 9]. In the presence of $[Pt_4(NH_3)_8(C_4H_6NO_4](NO_3)_6 \cdot 2H_2O$ in 9 M H_2SO_4 containing 0.1 M KNO_3, a large catalytic cathodic current is observed (Fig. 2C) and what is more surprising is that O_2 gas evolves from the electrode surface with the large cathodic current in the potential region less than 0.8 V. At the same time, the bulk solution gradually turns from dark red to yellow, indicating that $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ has been oxidized to $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ by evolved oxygen. This was confirmed by UV–Vis spectra. The catalytic phenomenon was also examined with a Pt electrode adsorbed with $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ in

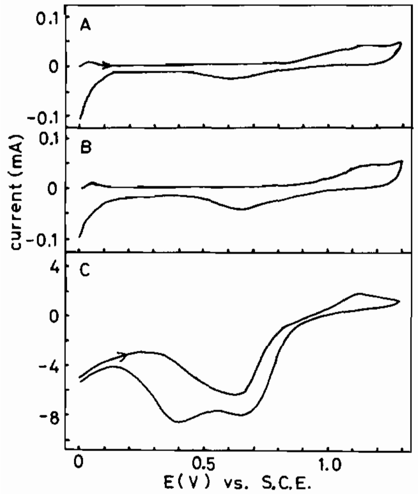
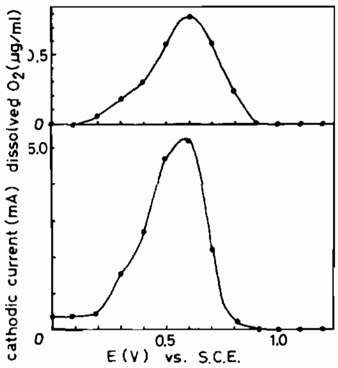


Fig. 2. Effect of oxidizing agents and $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$ in electrocatalytic oxidation of water into molecular oxygen with a platinum electrode. (A) 9 M H_2SO_4, (B) 9 M H_2SO_4 + 0.1 M KNO_3, (C) 9 M H_2SO_4 + 0.1 M KNO_3 + 0.8 mM $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$. Sweep rate was 0.1 V s^{-1}.



F9g. 3. Cathodic catalytic current and dissolved O_2 concentration observed with a platinum electrode adsorbed with $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$. Oxygen concentrations were measured after 3 min electrolysis at each potential in a 9 M H_2SO_4 aqueous solution containing 0.1 M KNO_3.

a solution without the platinum complex in a stationary potential mode. A similar large cathodic current and O_2 evolution were observed at each potential as shown in Fig. 3. Therefore, it seems that the adsorbed platinum complex is the cause of the catalytic effect. The large stationary cathodic current observed in Fig. 3 clearly shows that the reaction is catalytic involving cyclic occurrence of chemical oxidation and electrochemical reduction. Figure 3 shows that molecular oxygen is generated in the cyclic electrochemical reduction, since the O_2 concentration curve is basically in accordance with the stationary current curve, *i.e.* O_2 generation occurs in proportion to the cathodic current. Catalytic cathodic or anodic current has generally been reported to be caused by cyclic reactions of chemical oxidation and electrochemical reduction, or chemical reduction and electrochemical oxidation, respectively [10]. In Fig. 2C a large cathodic current is observed even in the anodic sweep. A similar phenomenon has also been reported generally for other EC (electrochemical–chemical) reactions by Nicholson that on the reverse scan of cyclic voltammogram the current tends to retrace the forward scan current [11].

Since the catalytic reaction is caused by cyclic occurrence of chemical oxidation and electrochemical reduction, in the next step, the identities of these redox reactions were investigated. We soon noticed that the catalytic cathodic current with current peak at 0.68 V is closely related to the reduction of the electrode surface platinum oxide. The reason is as follows: the peak potential of the catalytic current at 0.68 V in Fig. 1C is almost the same as that for the reduction of the surface platinum oxide in Fig. 2A and B. Both catalytic current and O_2 evolution are further increased by maintaining the electrode potential higher than 0.8 V for a few minutes before the cathodic potential sweep is started. On the contrary, the catalytic current and O_2 evolution are markedly decreased when the electrode is maintained at lower potentials, for instance below 0.2 V, before the cathodic potential sweep is started from 0.8 V. Therefore the cathodic current at 0.68 V in Fig. 2C is considered as a catalytically enhanced cathodic current of surface oxide reduction. The second broad peak at 0.4 V in the cathodic sweep in Fig. 2C seems to bear no relation to O_2 generation, since O_2 concentration and cathodic current are very low in this potential region (Fig. 3). The broad cathodic peak at 0.4 V is, however, also catalytic and seems to be a catalytic redox reaction of the platinum complex as explained later in this paper.

The O_2 gas was confirmed to evolve from H_2O by using a $H_2{}^{18}O$ solution and measuring the gas in the head-space of the electrolysis cell with GC-MS. The result in Fig. 4 confirms that O_2 gas is really generated from water oxidation.

Effect of Oxidizing Agents

After repeated experiments, it was found that KNO_3 or any other nitrate salt as well as the platinum complex is indispensable to the catalytic effect. Under the conditions that either the H_2SO_4 concentration is less than 4.5 M or KNO_3 is absent, no catalytic effect is observed. The O_2 evolution is decreased or ceases after prolonged electrolysis but can be restored by adding KNO_3 to the solution. From these facts, it was inferred that the coexistence of strong acid and $NO_3{}^-$ would probably be acting as an oxidizing agent. Therefore, other oxidizing

TABLE I. Effect of Oxidizing Agents in Electrocatalytic Oxidation of Water into Molecular Oxygen Using a Platinum Electrode Adsorbed with $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ Maintained at 0.6 V for 3 min

Oxidizing agent	Temperature (°C)	i (mA)	O_2 generation[a]
0.1 M KNO_3/9 M H_2SO_4	r.t.	1.01	+
0.1 M KNO_3/4.5 M H_2SO_4	r.t.		–
7.5 M HNO_3	r.t.	29.5	+
0.1 M $Na_2S_2O_8$/4.5 M H_2SO_4	r.t.		–
0.1 M $Na_2S_2O_8$/4.5 M H_2SO_4	70	0.91	+
0.1 M $Na_2S_2O_8$/0.06 M H_2SO_4	70		–
0.1 M $KMnO_4$/0.06 M H_2SO_4	r.t.	0.80	+
0.1 M $K_2Cr_2O_7$/1.8 M H_2SO_4	r.t.	0.03	–
0.1 M $NaClO_4$/4.5 M H_2SO_4	70		–
0.1 M Ce^{4+}/0.18 M H_2SO_4	r.t.		–

[a] +, O_2 evolution; –, no O_2 evolution.

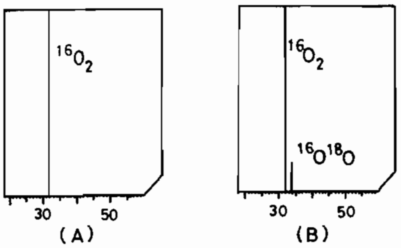


Fig. 4. GC-MS analysis of generated O_2 gas. (A) air, (B) head-space gas in a cell after electrolysis of $H_2{}^{18}O$ (25%) at 0.6 V for 20 min.

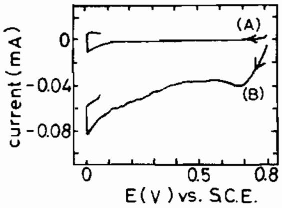


Fig. 5. Catalytic potential sweep curves for a platinum electrode in 9 M H_2SO_4. (A) Immediately after the electrode was cleaned, (B) after the electrode had been soaked in conc. HNO_3 for 10 min.

agents were examined to see whether they were effective for the O_2 generation with a Pt electrode adsorbed with the platinum complex. The results are summarized in Table I. All the oxidizing agents except $NaClO_4$ and Ce^{4+} were effective. Sodium persulfate is ineffective at room temperature because of its low reaction rate, however, it is distinctly effective at 70 °C. It should be noticed that all these effective agents are capable of oxidizing the platinum complex to yellow $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$.

Formation of Surface Platinum Oxide on Platinum Electrode by Oxidizing Agents

From the experiments described thus far, it is obvious that the electrochemical reduction of surface platinum oxide at 0.68 V triggers the O_2 evolution from the electrode surface and O_2 gas is generated in accordance with the electrochemical reduction of the electrode surface oxide. The fact that a large catalytic cathodic current continues stably flowing when the electrode potential is maintained at any value less than 0.8 V suggests that the platinum electrode surface must be oxidized chemically to platinum oxide during the electrolysis. It may seem impossible that platinum oxide is chemically formed under the present experimental conditions. However, we detected experimentally that surface oxide is really chemically formed by conc. HNO_3 on a platinum electrode. Other oxidizing agents in Table I have also been shown to form a similar surface platinum oxide. It has also been reported by Hoare that an electronically conducting surface platinum oxide is formed on treatment of a platinum electrode in conc. HNO_3 [12–14]. In Fig. 5 two cathodic sweep curves are shown for a platinum electrode in 9 M H_2SO_4. Figure 5A is for the potential sweep immediately after the electrode has been completely cleaned. There is no significant cathodic current observed, since the electrode surface is completely clean and no oxide film is present. However, after the electrode has been soaked in conc. HNO_3 for 10 min, the potential sweep shows that surface oxide film is formed on the electrode as observed in Fig. 5B. It should be noticed that the broad cathodic current peak at around 0.68 V in Fig. 5B is in agreement with the cathodic current peak potential observed when O_2 evolution occurs (Fig. 3) and also with the peak potential for the reduction of the surface oxide (Fig. 2). The cathodic current in Fig. 5B gradually decreases when the cathodic sweep is repeated and, after several sweeps, the sweep curve becomes exactly identical with Fig. 5A, indicating the surface oxide has been removed by the repetitive cathodic sweeps.

The structure of the chemical composition of the surface platinum oxide has been a subject of many researches but there seems to be no unequivocal conclusion. There have been many arguments reported on the composition and microstructure of the surface oxide film on a platinum electrode [15, 16] and there still seems to be controversy over the real state of the electrode surface oxide. Therefore, it would be inadequate to extend the discussion here to further details on the nature of the surface oxide formed by conc. HNO_3. It is certain however that treatment of a Pt electrode with conc. HNO_3 forms a surface oxide whose chemical characteristics are very similar to those of the surface oxide produced by electrical anodization, since both oxides exhibit similar current–potential curves in a cathodic sweep (Figs. 2 and 5).

Conway *et al.* reported in their study on the real condition of electrochemically oxidized platinum surface that, in cyclic voltammetry, the cathodic peak potential of surface oxide reduction becomes slightly less positive as the reversal potential from anodic to cathodic sweep is increased to more positive in the potential range above 0.9 V [17]. They minutely examined the platinum surface oxide by cyclic voltammetry and coulometry, and constructed a correlation curve between reversal potential and corresponding cathodic peak potential in cyclic voltammetry. Once this correlation curve is established, one would be able to estimate the real condition of the surface oxide under discussion by measuring the cathodic peak potential and correlating the potential with the correlation curve. One would be able to infer the nature of the surface oxide under discussion. The cathodic peak potential 0.68 V in the present study corresponds, from the correlation curve, to a rather early oxidation state. According to Conway *et al.*, this initial step of the oxidation mechanism would be described as follows

$$Pt + H_2O \longrightarrow Pt_4OH + H^+ + e \qquad (4)$$

$$Pt_4OH + H_2O \longrightarrow Pt_2OH + H^+ + e \qquad (5)$$

$$Pt_2OH + H_2O \longrightarrow PtOH + H^+ + e \qquad (6)$$

In addition to processes (4)–(6), further oxidation occurs at potentials above 0.61 V as follows

$$PtOH \longrightarrow PtO + H^+ + e \qquad (7)$$

In the reduction process, although only one cathodic peak is observed, the peak actually consists of several reduction processes such as reductions of adsorbed OH^- on the Pt lattice, PtOH and PtO.

In spite of these informations on the surface oxide formation and reduction processes intensively studied by Conway *et al.*, the surface oxide, reduced at 0.68 V and probably responsible for the present O_2 generation reaction, cannot be described definitely as one of the surface oxide phases due to the complexity of the phenomenon. Therefore, we hereafter denote the surface oxide responsible for the O_2 generation only as platinum surface oxide. The O_2 evolution must result from the oxidation of OH^-, which is formed from the electrochemical reduction of the surface oxide, by $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$.

All the other oxidizing agents except Ce(IV) (added as $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$) in Table I have similarly been proved to form chemically surface oxide on a platinum electrode. However, with these reagents, the surface oxide is easily removed by the cathodic sweep, the electrode surface being completely cleaned with only one cathodic sweep, which is a distinct contrast to the surface oxide formed by conc. HNO_3. In the latter case, the surface oxide persists on the electrode surface for a substantial period against repeated cathodic sweeps and, after more than 20 t sweeps, the electrode gradually loses its surface oxide and finally becomes cleaned completely. This fact may be related to the surpassing catalytic effect of conc. HNO_3 among other oxidizing agents in Table I. Cerium(IV) is ineffective for the present catalytic reaction. An experiment with Ce(IV) showed that Ce is adsorbed on a platinum electrode when the electrode is soaked in 0.1 M Ce(IV) solution for 10 min. It slightly forms surface oxide but the amount is less than those formed by other oxidizing agents and the oxide can easily be removed by a single cathodic sweep. These facts might at least partly explain the ineffectiveness of Ce(IV) in the present catalytic reaction.

Comparison of the Catalytic Effect for Platinum and Gold Electrodes

Since it is obvious that electrode surface oxide plays an important role in the present O_2 evolution reaction, it would give information and supporting evidence for the mechanism of the O_2 evolution reaction if electrode material other than platinum is employed for the same experiment and the catalytic effects are compared. A gold electrode was selected for the comparison, since its surface oxides have been studied in detail next to those of a platinum electrode. Figure 6 shows the cyclic voltammograms with a gold electrode. To our surprise, a similar O_2 evolution in the range below *ca.* 0.67 V and lower potentials were observed even without the platinum complex (Fig. 6B). The O_2 evolution and the large catalytic current cannot be observed initially in a solution containing only 9 M H_2SO_4 and 0.1 M KNO_3, a cyclic voltammogram exactly the same as Fig. 6A being observed in the initial several sweeps, but after several cycles the current gradually increases and becomes finally as observed in Fig. 6B. Molecular oxygen evolution is also observed in accordance with the large cathodic current in Fig. 6B. Addition of the platinum complex has some additional effect (Fig. 6C) on both the cathodic current intensity and the amount of O_2 evolved. Stationary catalytic current and O_2 concen-

TABLE II. Effect of Oxidizing Agents in Electrocatalytic Oxidation of Water into Molecular Oxygen Using a Gold Electrode Adsorbed with $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ Maintained at 0.6 V for 3 min

Oxidizing Agent	Temperature (°C)	*i* (mA)	O_2 generation[a]
0.1 M KNO_3/9 M H_2SO_4	r.t.	0.49	+
0.1 M KNO_3/4.5 M H_2SO_4	r.t.		–
7.5 M HNO_3	r.t.	117	+
0.1 M $Na_2S_2O_8$/4.5 M H_2SO_4	r.t.		–
0.1 M $Na_2S_2O_8$/4.5 M H_2SO_4	70	0.11	+
0.1 M $Na_2S_2O_8$/0.06 M H_2SO_4	70		–
0.1 M $KMnO_4$/0.06 M H_2SO_4	r.t.	0.29	+
0.1 M $K_2Cr_2O_7$/1.8 M H_2SO_4	r.t.	0.05	+
0.1 M $NaClO_4$/4.5 M H_2SO_4	70		–
0.1 M Ce^{4+}/0.18 M H_2SO_4	r.t.		–

[a] +, O_2 evolution; –, no O_2 evolution.

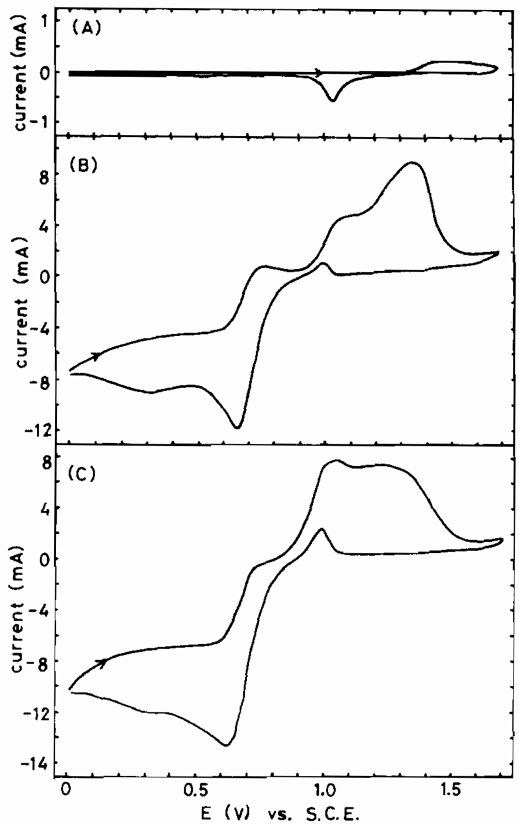


Fig. 6. Effect of an oxidizing agent and $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ in electrocatalytic oxidation of water into molecular oxygen with a gold electrode. (A) 9 M H_2SO_4, (B) 9 M H_2SO_4 + 0.1 M KNO_3, (C) 9 M H_2SO_4 + 0.1 M KNO_3 + 0.8 mM $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$. sweep rate was 0.1 V s^{-1}.

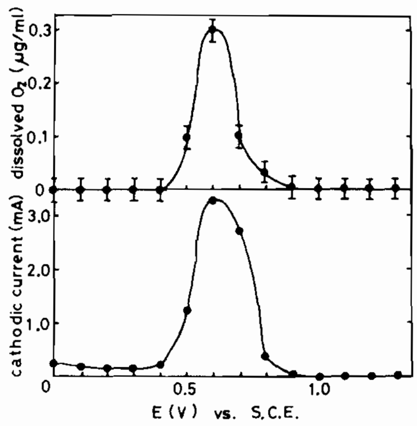


Fig. 7. Cathodic catalytic current and dissolved O_2 concentration observed with a gold electrode adsorbed with $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$. Oxygen concentrations were measured after 3 min electrolysis at each potential in a 9 M H_2SO_4 aqueous solution containing 0.1 M KNO_3.

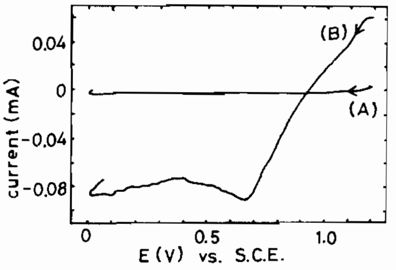


Fig. 8. Cathodic potential sweep curves for a gold electrode in 9 M H_2SO_4. (A) Immediately after the electrode was cleaned, (B) after the electrode had been soaked in conc. HNO_3 for 10 min.

tration for a gold electrode are shown in Fig. 7. Table II shows the effects of oxidizing agents. The result is basically the same for both platinum (Table I) and gold (Table II) electrodes. Chemical formation of gold surface oxide is demonstrated in Fig. 8. The chemically formed gold surface oxide cannot be removed by repeating the cathodic potential sweeps more than 20 times.

It was very surprising at first to find that O_2 evolves also below *ca.* 0.67 V even with a gold electrode, since the potential has seemingly no direct relation to the reduction potential of surface gold oxide. The usually observed reduction potential for surface gold oxide is *ca.* 1.02 V as in Fig. 6A. However, it was found that electrochemical reduction of chemically formed surface gold oxide actually occurs below 0.67 V on a gold electrode. Figure 7 clearly shows that the chemically formed surface gold oxide is electrochemically reduced at 0.67 V. It was confirmed experimentally that surface gold oxide, equivalent to the chemically formed oxide and similarly reduced at 0.67 V, is electrochemically formed by sweeping the electrode potential up to 0.9 V. This fact shows that although, in the usual cyclic voltammogram, surface gold oxide formation and reduction take place at *ca.* 1.40 and 1.02 V, respectively as in Fig. 6A, the actual formation and reduction, although it may be very slight, begin at less possitive potentials. Therefore, it is not unreasonable to think that also, in the case of a gold electrode, electrochemical reduction of the surface oxide at 0.67 V triggers the catalytic O_2 evolution reaction.

There is still one problem remaining in the case of a gold electrode. Why does O_2 gas evolve at such low potentials even without the platinum complex? There is no definite answer and experimental evidence to this question for the moment. What seems most probable is that O_2 evolution would result, in this case, from chemical oxidation of surface gold peroxide to molecular oxygen by the oxidizing agents. Possible existence of surface peroxide on a gold electrode as a transient state during the electrochemical reduction of the surface oxide has been suggested by several workers [18–20].

Possible Mechanism for the Electrochemical O_2 Generation on a Platinum Electrode Catalyzed by $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$

The experimental results of the O_2 generation can be summarized as follows: (a) O_2 generation from electrochemical oxidation of water is observed on a platinum electrode adsorbed with $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ in the potential region below 0.8 V. (b) The platinum complex is required in a catalytic amount, while the oxidizing agent is necessary in an equivalent amount. (c) The oxidizing agent chemically forms surface platinum oxide on the electrode and also oxidizes $[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+}$, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ and $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ to $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$. (d) The chemically formed surface platinum oxide is electrochemically reduced to Pt at *ca.* 0.68 V. (e) OH^- produced during the electrochemical reduction of the surface oxide possibly reacts with $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ and is oxidized to O_2. The real state of the OH^- on the electrode surface is still unknown. It may be adsorbed on the electrode surface or may exist as PtOH in monolayer or less than monolayer. However, it would be clear that OH^- in one of such states is oxidized by $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ to O_2. The overall mechanism is described in Fig. 9. Both or either of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ and $[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ are produced from the reduction of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ by OH^-. The overall reaction can be therefore described as follows.

$$2H_2O + (n + n')e \xrightarrow{\text{oxidizing agent}} O_2 + 4H^+ \qquad (8)$$

Considering the reaction mechanism in Fig. 9, it is not strange that a cathodic current is observed at the start of the voltammetric sweeps in Figs. 2C, 6B, 6C, 10A, 10B and 10C, since the electrode surface and the platinum complex are oxidized by the oxidizing agent in the whole potential range and these oxidized forms are electrochemically reduced at the sweep start. The O_2 evolution ceases when all the oxidizing agent in the solution is consumed but is recovered by adding the oxidizing agent. This fact exactly corresponds to eqn. (8), which shows that the oxidizing agent and electricity are consumed for O_2 generation.

The reaction mechanism in Fig. 9 shows that O_2 generation is possible at any potential below *ca.* 0.8 V (0.8 V corresponds to the potential where reduction of the surface platinum oxide begins in the cathodic sweep). Although Figs. 2 and 3 show that only the cathodic current at 0.68 V is responsible for O_2 generation and the cathodic current at *ca.* 0.4 V seems to have no relation to O_2 evolution, it was found that O_2 evolution can be observed under certain conditions, as predicted by the mechanism in Fig. 9, in the whole potential range below 0.8 V. This is shown in Fig. 10. Figure 10A shows one of the cycles under the experimental conditions identical with those in Fig. 2C. Due to large cathodic current and vigorous O_2 evolution in the whole potential range below 0.8 V no current–potential structure like that in Fig. 2C is observed. The profile

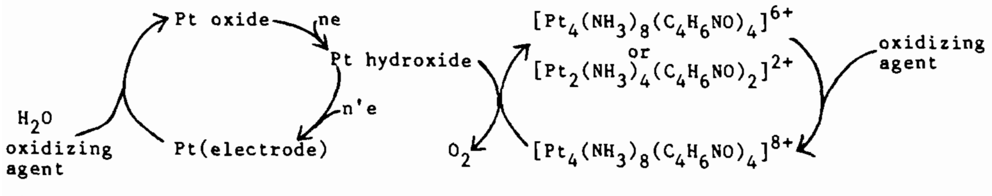


Fig. 9. Reaction mechanism for electrocatalytic generation of oxygen gas.

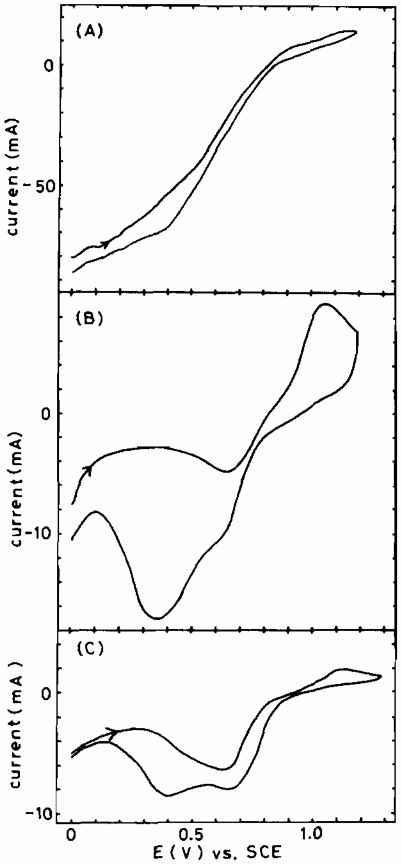


Fig. 10. Current–potential curves for catalytic electrochemical O_2 evolution. A platinum electrode adsorbed with $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$; sweep rate 0.1 V s^{-1}, 9 M H_2SO_4 with 0.1 M KNO_3. (A), (B) and (C) correspond in this order to the profile change during prolonged electrolysis. See the text for the details.

in Fig. 10A is observed in the several starting cycles, when the electrode surface is relatively clean and KNO_3 concentration is high, therefore the chemical reaction rate being exceedingly high compared with the electrochemical reaction rate. But after the electrolysis has continued for a while, the KNO_3 concentration is decreased and the electrode surface becomes somewhat unfavorable for the chemical formation of the oxide film and the chemical oxidation rate is diminished. In this case the current–potential profile becomes those in Fig. 10B or C, depending on the relative rate of chemical oxide formation to electrochemical reduction. The cathodic wave at *ca.* 0.4 V in Fig. 2C would be mostly due to the catalytic reactions of chemical oxidation of the platinum complex and electrochemical reduction of the complex, therefore having no relation with O_2 evolution. The profiles in Fig. 10 do not depend on the oxidizing agent used. The variation of the current–potential profiles as shown in Fig. 10 during prolonged electrolysis is in accordance with what Nicholson and Shain explained in their theory on the current–potential profiles for catalytic chemical and electrochemical reactions [21]. According to their theory, apparent catalytic current peak becomes less distinct as the relative reaction rate of the chemical oxidation to electrochemical reduction is increased. Their calculation predicts that in the extreme case where the chemical reaction rate is exceedingly high compared with the electrochemical reaction rate, the cyclic voltammogram loses its peak-shaped appearance and the cathodic current monotonously increases as the potential is swept cathodically until it reaches a limiting current. This is basically the same as we saw in our experiment concerning the current intensity and the current peak profile as shown in Fig. 10. The catalytic current at potentials below *ca.* 0.4 V in Fig. 10A and B contains therefore electrochemical reductions of both surface platinum oxide and the platinum complex.

Electrochemical O_2 evolution from water at potentials less than 1.0 V has been believed to be impossible from the thermodynamic point of view. However, the present study demonstrates that it is possible if a suitable electrocatalyst is employed. Since in the present experiment O_2 evolves from the working electrode surface with a cathodic current, O_2 generation takes place during the electrolysis both from the working and counter electrodes. This phenomenon can also be easily understood with the present reaction mechanism.

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