Homogeneous and Heterogeneous Catalytic Reactions in a Cobalt Oxide/Graphite Air Electrode. Part IV. Mechanistic Studies on a Ring-Disk Carbon Electrode in Alkaline Solution

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Abstract: The redox properties of HCoO₃ on a glassy carbon electrode in the absence and presence of hydrogen peroxide have been investigated by using cyclic voltammetry and UV-Vis spectroscopy in alkaline solution. Corresponding rotating ring-disk experiments showed that the disk current increased by about 60% in the presence of HCoO₃, confirming the important role played by HCoO₃ in the homogeneous decomposition of hydrogen peroxide. 

Key words: H₂O₂, cobaltoxide, oxygen reduction.

INTRODUCTION

Oxygen reduction on metal oxide/graphite electrodes is a very important subject in electrochemical studies. In previous papers of this series,¹⁻³ it was reported that the decomposition of hydrogen peroxide by dissolved cobalt ions (i.e. HCoO₂⁻) plays an important role in homogenous and heterogeneous catalytic reaction mechanisms in Co₃O₄/graphite air electrode systems and related oxygen reduction processes. It is very difficult to perform characterization and accurate kinetic analysis of the redox process of HCoO₂ and related oxygen reductions in such porous Teflon-bonded carbon electrode systems. This paper deals with some mechanistic studies using a rotating ring (Pt) disk (glassy carbon) electrode. The redox properties of HCoO₃ on a glassy carbon electrode in alkaline solution in the presence and absence of hydrogen peroxide or oxygen were studied by cyclic voltammetry using a rotating ring-disk electrode. The existing state of HCoO₂ and possible intermediates between HO₂⁻ and HCoO₂ were also characterized by using UV-Vis spectroscopic techniques.

EXPERIMENTAL

Some practical and theoretical considerations

The reduction of oxygen should ideally follow a four-electron process:

O₂ + 2H₂O + 4e⁻ = 4OH⁻ (1)
However, the reaction is highly irreversible at low temperatures and the oxygen reduction process in alkaline solution on graphite or carbon electrodes follows a two-electron step:

\[ \text{O}_2 + \text{H}_2\text{O} + 2e^- = \text{HO}_2^- + \text{OH}^- \]  

(2)

The electroreduction of \( \text{H}_2\text{O}_2 \) is unlikely to occur at normal operating potentials and further reaction would involve the decomposition of \( \text{HO}_2^- \), if \( \text{HO}_2^- \) ions are present.

\[ 2\text{HO}_2^- = 2\text{OH}^- + \text{O}_2 \]  

(3)

The released oxygen is then further reduced, leading to higher efficiency and open circuit voltage. Traditionally, semiconducting oxides are used as the peroxide decomposition catalysts. However, recent work by Jiang et al.\(^1\)\(^-\)\(^3\) has shown that the decomposition of peroxide is most effective when there is \( \text{HCoO}_2^- \) present, since it acts as a homogeneous catalyst for the decomposition of \( \text{HO}_2^- \).

In order to study the role of \( \text{HCoO}_2^- \) in greater detail, the present study involves the addition of a small amount of \( \text{H}_2\text{O}_2 \) to the electrolyte in the presence and absence of oxygen and measuring the oxygen reduction reaction on a glassy carbon or a glass carbon, Pt ring-disk rotating disk electrode. The use of a rotating disk electrode ensures that the rate of diffusion of reactant species to the electrode can be accurately controlled. When the rotating ring-disk electrode is used, the ring potential can be set at a different potential to the disk electrode and this enables the concentration of peroxide after oxygen reduction to be measured. Such experiments will allow clarification of the mechanism of oxygen reduction in the presence of \( \text{HCoO}_2^- \) in far greater detail than on the porous electrodes which were used in previous studies.

Methods

The electrochemical experiments were done by using a Ministat (H. B. Thompson & Associate, UK) and rotating Pt ring-glassy carbon (GC) disk electrode (RRDE) system (Oxford Electrode Ltd, UK). The dimensions of the GC-disk and Pt ring electrodes are: \( r_1 \) (disk radius) = 0.358 cm, \( r_2 \) (ring inside radius) = 0.368 cm\(^2\). The collection efficiency \( (N)^4 \) is calculated to be 0.219. In addition, a GC-disk electrode was used as the working electrode in cyclic voltammetry. The radius of the electrode is 0.3 cm, the surface area is 0.28 cm\(^2\). It was made by pressing a small glassy carbon rod (Beijing Artificial Crystal Institute, China) into a Teflon cylinder. A piece of Pt gauze was used as counter electrode. A saturated calomel electrode (SCE) was used as reference electrode. All chemical reagents used in this work were of analytical reagent-grade (CoO\(^+\) BDH, UK; \( \text{H}_2\text{O}_2 \): Merck, 30% (w/w); KOH: Fisons, UK). The solutions were prepared by using Mill-Q water (Millipore Ltd, USA). Two g CoO (BDH) was added to 200 cm\(^3\) 5 M KOH solution. The solution was then filtered and the blue, clear solution was used as the electrolyte containing \( \text{HCoO}_2^- \). The solution is not stable in air, thus if not used immediately, it was kept under a nitrogen atmosphere. Earlier studies have shown that the concentration of \( \text{Co}^{2+} \) is 1.75 ppm, i.e. \( 3 \times 10^{-5} \) M\(^1\) in such a solution. Before performing rotating ring-disk electrode or cyclic voltammetric experiments, nitrogen or oxygen was bubbled into the electrolyte for at least 10 min. The electrode was carefully polished and cleaned ultrasonically in the presence of Milli-Q water for 5 min.

UV-Vis spectroscopic experiments were performed by using a PU8700 series UV/VIS spectrometer (Philips Company, Inc., UK). Bandwidth, 2 nm; scan rate, 2000 nm min\(^{-1}\); cell width, 1 cm; cell type, silica). Hydrogen peroxide was added to the solution until the concentration reached 0.464 M. The experiments were carried out in a thermostatted cell at 30°C.

RESULTS AND DISCUSSION

Cyclic voltammetry of the \( \text{HCoO}_2^- \) in 5 M KOH

Figure 1 shows a typical cyclic voltammogram (100 mV s\(^{-1}\), -0.55 V to +0.15 V) of a glassy carbon disk electrode in the presence of \( 3 \times 10^{-5} \) M \( \text{HCoO}_2^- \). In the presence of \( \text{HCoO}_2^- \), there is an oxidation peak at -0.1 V and a reduction peak at -0.15 V. The oxidation peak is wider and larger than the reduction peak. This suggests that the redox process involved in the oxidation and reduction of \( \text{HCoO}_2^- \) in 5 M KOH is not very reversible. This redox couple reaction corresponds to the following process:\(^5\)

\[ \text{HCoO}_2^- \rightarrow e^- \Leftrightarrow \text{COOH} \]  

(4)

Since the above process involved the formation of a solid phase (CoOOH), the rate of subsequent reaction is unlikely to be as fast as the rate of deposition. This is confirmed by the observation that there is a pinkish deposit on the surface of the carbon electrode after a period of potential cycling. Therefore, it is not surprising that the oxidation peak is larger than the reduction peak.

The dependence of the oxidation current peak on rate \([\langle V \rangle]\) and \([\langle V \rangle \]^1/2\) was measured and calculated. There is a linear relationship between peak current and square root of potential scan rate (Fig. 2), indicating that the oxidation process is diffusion controlled. This conclusion is also confirmed by the observation that by
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Fig. 1. Cyclic voltammograms of a glassy carbon electrode in the presence (a) and absence (b) of $3 \times 10^{-3}$ M HCoO$_2$ in 5 M KOH under nitrogen at room temperature. Scan rate = 100 mV s$^{-1}$.

Increasing the bubbling rate of nitrogen, the current peaks also increased significantly.

In a previous paper,$^1$ it was shown that HCoO$_2$ has a significant activity for the decomposition of hydrogen peroxide in 5 M KOH. Figure 3 is a comparison of cyclic voltammograms of the HCoO$_2$ in 5 M KOH before and after the addition of H$_2$O$_2$ ($C_{H_2O_2} = 1.98 \times 10^{-3}$ M). If the concentration of hydrogen peroxide added is too high, no redox peaks are observed since all the HCoO$_2^-$ will have reacted with the H$_2$O$_2$. By using a lower concentration of hydrogen peroxide, both the oxidation and reduction peak decrease but are still present (Fig. 3). The reactions involve:  

$$
6\text{HCoO}_2^- + 4\text{HO}_2^- = 2\text{CO}_3\text{O}_4^- + 10\text{OH}^- + \text{O}_2 \quad (5)
$$

$$
4\text{HCoO}_2^- + 4\text{HO}_2^- = 2\text{CO}_2\text{O}_3^+ + 8\text{OH}^- + \text{O}_2 \quad (6)
$$

**Rotating ring-disk experimental results**

Figure 4 shows the disk and ring potential–current curves in N$_2$, 5 M KOH + $3 \times 10^{-3}$ M HCoO$_2^-$. There are two peaks in the disk voltammogram. There is a sharp peak at $-0.15$ V, and a wider one at $-0.20$ V. These two peaks are attributed to the following reactions:

$$
\text{CoOOH} + \text{e}^- = \text{HCoO}_2^- \quad (7)
$$

$$
\text{CoOOH} + \text{H}_2\text{O} + \text{e}^- = \text{Co(OH)}_2^- + \text{OH}^- \quad (8)
$$

Since CoOOH is not very stable in alkaline solution, it may transform to other cobalt oxide species: Co(OH)$_2$, Co$_3$O$_4$, Co$_2$O$_3$. The actual processes occurring on the disk electrode are more complicated than those depicted in eqns (4) and (5). After application of potential at the ring electrode (+0.1 or +0.3 V), the ring current increases with disk electrode potential. Thereafter, it reaches a limiting value when the disk potential is more negative than $\sim -0.2$ V. The reason for the changes of the ring current with disk potential is not clear. Possibly, the increase of ring current is caused by the formation of a new phase on the ring-electrode surface. This kind of formation, which at some stage involves a three-dimensional nucleation and growth
Fig. 3. Cyclic voltammograms of a glassy carbon electrode with (b) and without (a) addition of \( \text{H}_2\text{O}_2 \) (1.98 \( \times \) 10\(^{-3}\) m) in 3 \( \times \) 10\(^{-5}\) m \( \text{HCoO}_2^- \) + 5 m KOH.

The process may result in current increase. In fact, when the ring electrode potential was kept more positive than -0.1 V, the main reaction on the ring electrode should have been on the formation of CoOOH from \( \text{HCoO}_2^- \).

The corresponding rotating ring-disk electrode \( V-i \) curves in the absence and the presence of \( \text{HCoO}_2^- \) in 5 m KOH containing dissolved oxygen are shown in Fig. 5. The limiting disk current increased by 60% in the presence of \( \text{HCoO}_2^- \). However, the ring current also increased significantly, which is surprising. \( \text{HO}_2^- \) is decomposed readily by \( \text{HCoO}_2^- \) and the amount of \( \text{HO}_2^- \) diffusing to the ring electrode should decrease, leading to a lower ring current. But in the present system, \( \text{HCoO}_2^- \) is oxidized at the ring potential [eqn (1)] and it is impossible to use the ring current to analyse oxygen reduction kinetics in detail.

UV-Vis spectroscopic characterization of existing state of soluble metal-complex in alkaline solution

In order to characterize the existing state of metal ions in the solution and study the reaction pathway of the system, UV-Vis spectroscopic studies were performed and the nature of intermediates determined.

Figure 6(a) shows the UV-Vis spectra of \( \text{HCoO}_2^- \) in alkaline solution. The peak of 532.8 nm is attributed to the contribution of a tetrahedral \(^{24}\text{Co} \) complex. However, the nature of the peak at 583.2 nm is not clear. It may result from the absorption-shift of the tetrahedral \(^{24}\text{Co}\)-complex (violet-shift) in the alkaline solution. Moreover, the result implies that the existing form of \( \text{HCoO}_2^- \) in the solution is hydrated, forming [(\( \text{HCoO}_2^- \)(\( \text{H}_2\text{O} \))\(_6\)]. Based on this spectra, it is con-
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Fig. 5. Comparison of RRDE curves in the absence (———) and presence (-----) of $3 \times 10^{-5}$ M HCoO$_2^-$ in 5 M KOH HCoO$_2^-$ in 5 M KOH ($V_0 = 5$ mV s$^{-1}$), dissolved oxygen, $f = 50$ Hz, $\phi \Gamma = +0.3$ V.

Fig. 6. Comparison of UV-Vis spectra of HCoO$_2^-$ (a: --------) and possible intermediates of metal-HO$_2^-$ complex (b: ———) in 5 M KOH.

cluded that main existing form of HCoO$_2^-$ in the solution is octahedral because the extinction coefficient of the tetrahedral form is 50 times larger than that of the octahedral. If the tetrahedral form concentration in equal to the octahedral form concentration is this system, the intensity of the peak at 532.8 nm will be stronger, but the results did not shown this. Therefore, the results suggest that the octahedral form is predominant in alkaline solution. The results also suggest that both octahedral and tetrahedral forms co-exist in the solution.

On the addition of some H$_2$O$_2$ solution ($C_{H_2O_2} = 0.464$ M into 5 M KOH containing $3 \times 10^{-5}$ M HCoO$_2^-$, the peaks at 532.8 nm, 583.2 nm, and 620.2 nm overlap peaks which appeared between 230 and 330 nm [central peak is positioned at 292 nm, see Fig. 6(b)]. In the experiments, the peaks between 230 and 330 nm decreased as the reaction time increased, but the peak at
The redox properties of HCoO$_2^-$ and the effect of addition of hydrogen peroxide have been studied by using cyclic voltammetry and UV-Vis spectrophotometric techniques. It seems that interaction between HCoO$_2^-$ and hydrogen peroxide plays an important role in the decomposition of hydrogen peroxide in an alkaline air electrode system. The use of a solid glassy carbon electrode allowed us to perform more quantitative analysis to study the effect of HCoO$_2^-$ on the oxygen reduction process.

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**REFERENCES**


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400 nm increased in the same time range (see Fig. 7, the interval of each curve is about 2 min). Blank experimental results (no metal ions, only 2.5 cm$^3$ 5 M KOH + 0.4 cm$^3$ H$_2$O$_2$, silica cell) showed that the overlap peaks between 230 and 330 nm come from the contribution of hydrogen peroxide and its dissociation products, i.e.: $O_2^-$, HO$_2^-$, etc. In aqueous solution, the UV absorption peak of $O_2^-$ is at 245 nm ($\varepsilon$ = 2350), HO$_2^-$ at 225 nm ($\varepsilon$ = 1400). In the present system, the changes in the range 230–330 nm are large, indicating that the amount of $O_2^-$ and HO$_2^-$ present is quite high. Baxendale and Wells found that the peak at 400 nm in Co$_3$O$_4$ solution changed distinctively on changes in the acidity of solution. Therefore, the peak at 400 nm may be related to a Co$_3$$+^+$ – HO$_2^-$ complex, or its dissociation product. The spectroscopic results clearly indicate the presence of HCoO$_2^-$, which participates in the decomposition of hydrogen peroxide in alkaline solution although the free-radical route is also one of the reaction pathways.

**CONCLUSIONS**

Relationship between reaction of oxygen reduction and cobalt oxide or hydroxide catalyst/carbon air electrode system

Based on above experimental results and discussions, it is clear that in the Co$_3$O$_4$/graphite air electrode system, at the potential of oxygen reduction, some part of supported cobalt oxide (i.e. CoOOH and Co$_3$O$_4$) will be dissolved and form HCoO$_2^-$. The HCoO$_2^-$ ion will react with HO$_2^-$ and produce CoOOH and other forms of cobalt oxide, releasing oxygen, thereby increasing the cathodic current for oxygen reduction.