Preparation of manganese dioxide using Ag^+ ions as an electrocatalyst

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Abstract

The production of manganese dioxide by the conventional electrolytic process is based on the direct oxidation of Mn^{2+} ions on an anode in sulfuric acid solution. The process is complicated. A new method for the preparation of manganese dioxide has been reported recently by the authors. This method uses Ag^+ ions to electrocatalyze the anodic oxidation of Mn^{2+} ions. To show the difficulty in the direct anodic oxidation of Mn^{2+} ion and the electrocatalytic mechanism of Ag^+ ions, the anodic oxidation behaviour of Mn^{2+} and Ag^+ ions and the electrocatalytic behaviour of Ag^+ ions on the anodic oxidation of Mn^{2+} ion are studied using a rotating ring disc electrode, a.c. impedance and voltammetry techniques. Mn^{3+} ion or MnO_2 will be formed when Mn^{2+} ion is oxidized on an anode, as determined by the sulfuric acid concentration. Mn^{2+} ion is oxidized on the surface with OH groups and some compounds with Mn^{2+} or Mn^{3+} are formed before Mn^{3+} ions or MnO_2 are produced. This causes difficulties in the preparation of Mn^{3+} ions or MnO_2. Ag^+ ions can be oxidized easily on an anode to form Ag^{2+} ions. In turn, Mn^{2+} ions can be oxidized easily by the Ag^{2+} ions. Thus, the anodic oxidation of Mn^{2+} ions can be electrocatalyzed by using Ag^+ ions. This is a homogeneous electrocatalysis and allows MnO_2 to be prepared in a convenient process. © 1997 Elsevier Science S.A.

Keywords: Manganese dioxide; Batteries; Silver ions; Electrocatalysis

1. Introduction

Electrolytic manganese dioxide (EMD) is one of the best positive materials for high-performance Zn/MnO_2 batteries. Its preparation has been changed little since the process was first proposed by Van Arsdale and Maier [1]. Conditions for the preparation of EMD are [2]:
$MnSO_4$: 0.5–1.2 M;
H_2SO_4: 0.5–1.0 M;
temperature: 88–98 °C, and
anodic current density: 0.007–0.012 A cm^{-2}.

There are two disadvantages in the production technology for EMD, namely: (i) the production efficiency is low due to the low anodic current density, and (ii) the production process is complicated due to the high temperature and the fact that the product is deposited on the anode surface. To overcome these disadvantages, Welsh [3,4] developed an alternative process to produce EMD. The conditions are:
$MnSO_4$: 0.3–0.4 M;
H_2SO_4: 2–2.5 M;

temperature: 20 °C, and
anodic current density: 0.4 A cm^{-2}.

The product MnO_2 is prevented from adhering to the anode by gaseous oxygen and is formed in electrolyte. Inevitably, the current efficiency in the Welsh process must be lower than that in the conventional process due to the evolution of oxygen evolution via water decomposition.

Ag^+ ions are a good electrocatalyst for the oxidation of Mn^{2+} ions [5,6]. Using Ag^+ ions as an electrocatalyst, a new process to produce MnO_2, called ECMD (electrocatalytic manganese dioxide), has been reported by the authors [7]. Using this process, activated MnO_2 can be prepared at high current efficiency and high current densities in a simple way. The conditions are:
$AgNO_3$: 0.008–0.02 M;
$MnSO_4$: 0.1–0.3 M;
H_2SO_4: 1–2 M;
temperature: room temperature, and
anodic current density: 0.1–0.7 A cm^{-2}.

The work reported here examines the direct anodic oxidation behaviour of Mn^{2+} and Ag^+ ions and the electrocatalytic behaviour of Ag^+ ions on the oxidation of Mn^{2+} ions on platinum electrodes in sulfuric acid solutions by using a

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rotating ring disc electrode (RRDE), a.c. impedance (ACI), voltammetry and potential-step techniques. The aim is to recognize the difficulty in the direct anodic oxidation of Mn^{2+} ions and the electrocatalytic mechanism of Ag^+ ions, with a prospect to replace the complicated conventional EMD process with the new and more efficient process.

2. Experimental

RRDE experiments are accomplished on a rotating electrode instrument (Model ASR2E, Pine Instrument) and a double x–y recorder (Type 3036, Hohushin Electronics). The diameter of the disc electrode was 0.3825 cm, the inner and outer diameters of the ring electrode were 0.3985 and 0.4215 cm, respectively. The disc and the ring were made from platinum. A.c. impedance, voltammetry and potential-step experiments were performed with a potentiostat (Model 273 EG&G). The working electrode was a platinum electrode with an area of 0.23 cm². All the experiments were carried out in a cell with three chambers. The electrolyte volume in the working electrode chamber was 200 ml. The counter electrode was a platinum electrode with a large area. The reference electrode was a Hg/Hg_2SO_4, saturated K_2SO_4 electrode and all potentials are reported with respect to this electrode.

The product from the oxidation of Mn^{2+} ions depends on the concentration of sulfuric acid. MnO_2 is formed from the disproportionation of Mn^{3+} ions in less concentrated sulfuric acid [8]. Solutions used for the formation of MnO_2 in this study are those with 1.8 M H_2SO_4. To demonstrate the formation process of MnO_2 and the difficulty in direct anodic oxidation of Mn^{2+} ions, solutions with 9.2 M H_2SO_4 are also used where Mn^{3+} ions is the product from the oxidation of Mn^{2+} ions. Chemicals were all analytically pure. Solutions were prepared with water de-ionized and redistilled twice. All the experiments were performed at room temperature.

3. Results and discussion

3.1. Direct anodic oxidation of Mn^{2+} ions

Voltammograms obtained from the platinum RRDE in 9.2 and 1.8 M H_2SO_4 solutions with and without Mn^{2+} ions are shown in Figs. 1 and 2. On the ring electrode, the reduction current of Mn^{3+} ions is detected in the solution with 9.2 M H_2SO_4 but is hardly recorded in the solution with 1.8 M H_2SO_4. On the disc electrode, a black MnO_2 deposit is formed in the solution 1.8 M H_2SO_4 but is not produced in the solution with 9.2 M H_2SO_4. Thus, the product from the oxidation of Mn^{2+} ions depends on the sulfuric acid concentration: Mn^{3+} ions are formed in more concentrated sulfuric acid and MnO_2 in less concentrated sulfuric acid.

The Mn^{2+} ions exhibit the same anodic oxidation behaviour in both 9.2 and 1.8 M H_2SO_4 solutions: the oxidation of
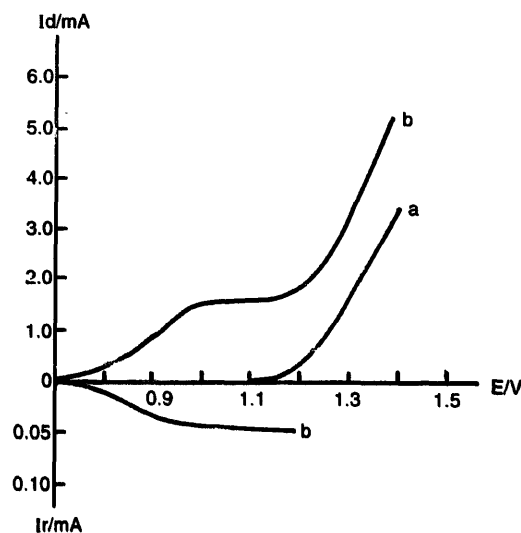
Fig. 1. Voltammograms for the platinum RRDE in: (a) 9.2 M H_2SO_4, and (b) 9.2 M H_2SO_4 + 0.05 M $MnSO_4$, 600 rpm; disk electrode: 10 mV s⁻¹; ring electrode: 0.6 V.
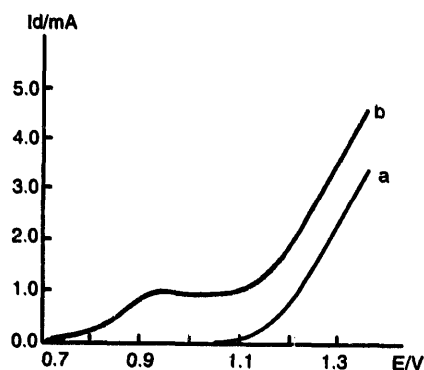
Fig. 2. Voltammograms for the platinum RRDE in: (a) 1.8 M H_2SO_4, and (b) 1.8 M H_2SO_4 + 0.05 M $MnSO_4$, 600 rpm; disk electrode: 10 mV s⁻¹; ring electrode: 0.6 V.

Mn^{2+} ions takes place at a potential that is much lower than that for oxygen evolution from water decomposition (curve (b) in Figs. 1 and 2), while the oxidation current of Mn^{2+} ions increases slowly and a plateau current occurs as the anodic potential of the disc increases. The plateau current is not the limiting diffusion current of Mn^{2+} ions because it is not directly proportional to the square of the electrode rotating speed. In fact, there exists a large electrochemical reaction resistance under the potential where the plateau current occurs as Fig. 3 shows. Nyquist plots are composed of semicircles at high frequencies and Warburg straight lines at low frequencies at potentials from 0.8 to 1.3 V in the solution with only Mn^{2+} ions. The electrochemical reaction resistances obtained from Nyquist plots in several solutions are listed in Table 1. The direct anodic oxidation process of the Mn^{2+} ions is mainly controlled by electrochemical reaction because of the large electrochemical reaction resistances. With increasing anodic potential, the electrochemical reaction resistances decrease at first, then increase, and decrease again. The a.c. behaviour at 1.4 V is much the same in solutions with and without Mn^{2+} ions, namely, oxygen evolution from

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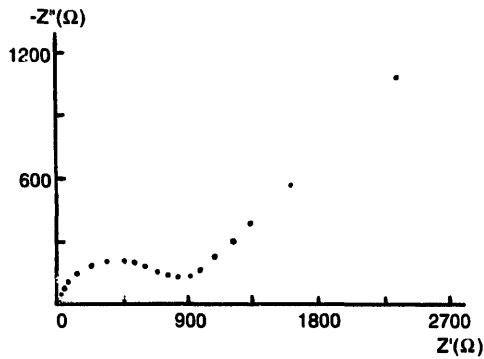
Fig. 3. Nyquist plot on the platinum electrode in 0.05 M MnSO₄ + 9.2 M H₂SO₄ solution at 1.25 V, frequency from 10^5 to 0.1 Hz.

Table 1
Electrochemical resistance obtained from Nyquist plots

Anodic potential (V)	Reaction resistance (Ω cm^2) [a]			
	a	b	c	d
0.8		85.1		105.0
0.9		50.3		49.7
1.0		93.7		101.2
1.1	1171.i	185.7	1214.4	207.0
1.2	227.8	251.7 (616.2)		6.1 (4.3)
1.3	84.6	111.1		4.9
1.4	19.5	26.1	2.5	2.1

[a] a: 9.2 M H₂SO₄; b: 9.2 M H₂SO₄ + 0.05 M MnSO₄; c: 9.2 M H₂SO₄ + 0.01 M AgNO₃; d: 9.2 M H₂SO₄ + 0.01 M AgNO₃ + 0.05 M MnSO₄. In parentheses: b: 1.8 M H₂SO₄ + 0.05 M MnSO₄; d: 1.8 M H₂SO₄ + 0.01 M AgNO₃ + 0.05 M MnSO₄.

water decomposition. It is difficult to accerelate the anodic oxidation of Mn²⁺ ions by improving the anodic potential. A new factor may appears that impedes the electrochemical reaction of Mn²⁺ ions and oxygen evolution will occur if the anodic potential is further increased.

From the above results, it is concluded that Mn³⁺ ions or MnO₂ can be prepared from direct anodic oxidation of Mn²⁺ ions at a very high current efficiency as long as the anodic potential is lower than that for oxygen evolution from water decomposition. It is very difficult, however, for Mn²⁺ ions to be oxidized directly on an anode.

The current of Mn³⁺ ions on the ring electrode is proportional to the oxidation current of Mn²⁺ ions on the disc electrode, but the capture index (I_r/I_d) is much smaller than the theoretical value ($N = 0.1789$). The capture indices obtained at different electrode rotating speeds are listed in Table 2. The capture index of Mn³⁺ ions at 200 rpm is 0.039, only 21.8% of the theoretical value. The capture index of Mn³⁺ ions increases as the speed of electrode rotation decreases. This means that the product of Mn²⁺ ions oxidation leaves the disc electrode in the form of a Mn³⁺ compound that cannot be reduced and decomposes to Mn³⁺ ions that can be reduced on the ring electrode at a potential of 0.6 V. The Mn³⁺ compound may be one of those that impede the oxidation of Mn²⁺ ions.
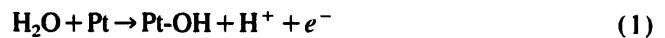
Table 2
Effect of electrode rotating speed (W) on capture index (I_r/I_d); ring potential = 0.6 V

W (rpm)	I_r/I_d	
	a	b
200	0.039	0.012
600	0.031	0.050
1000	0.024	0.125
2000	0.014	0.160
4000	0.006	0.168

a: 0.05 M MnSO₄ + 9.2 M H₂SO₄, at disc potential of 1.1 V.
b: 0.01 M AgNO₃ + 9.2 M H₂SO₄, at disc potential of 1.25 V.

It is widely accepted by many researchers [9–12] that some intermediates with Mn³⁺ or Mn⁴⁺ are formed during the oxidation of Mn²⁺ ions to Mn³⁺ ions or MnO₂. The formation of these intermediates may be explained as follows.

In the sulfuric acid solution without Mn²⁺ ions, electrode reactions on a platinum anode include the adsorption of OH radicals and the evolution of oxygen:

$$H_2O + Pt \rightarrow Pt\text{-}OH + H^+ + e^- \tag{1}$$

$$Pt\text{-}OH \rightarrow Pt\text{-}O + H^+ + e^- \tag{2}$$

$$2Pt\text{-}O \rightarrow O_2 + 2Pt \tag{3}$$

Reaction (1) takes place above 0.3 V, and reactions (2) and (3) at above 1.1 V as shown by curve (a) in Fig. 4. From 0.7 V, Mn²⁺ ions begin to be oxidized as shown by curve (b) in Fig. 4.

The oxygen evolution reaction of water decomposition is controlled completely by an electrochemical step. Nyquist plots are nearly semicircles at different anodic potentials in sulfuric acid solution without Ag⁺ or Mn²⁺ ions, see Fig. 5. The higher the anodic potential, the smaller is the reaction resistance of oxygen evolution (see Table 1).

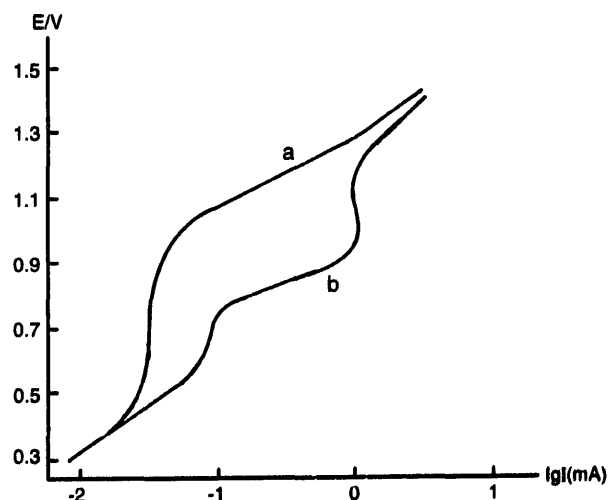Because the oxidation of Mn²⁺ ions is very slow, it takes place at the platinum with adsorbed OH radicals:

E/V

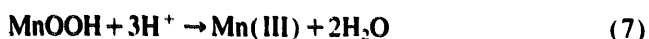Fig. 4. E–log(I) plot on the platinum electrode in: (a) 9.2 M H₂SO₄, and (b) 9.2 M H₂SO₄ + 0.05 M MnSO₄; 10 mV s⁻¹.
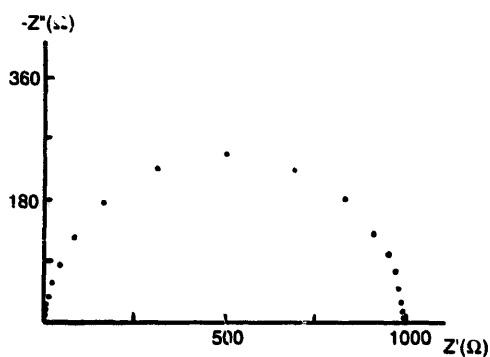
Fig. 5 Nyquist plot on the platinum electrode in 9.2 M H_2SO_4 at 1.25 V; frequency from 10^5 to 0.1 Hz.

$$H_2O + Pt \rightarrow Pt\text{-}OH + H^+ + e^- \tag{1}$$

$$2Pt\text{-}OH + Mn(II) \rightarrow (Pt\text{-}O)_2Mn(II) + 2H^+ \tag{4}$$

$$(Pt\text{-}O)_2Mn(II) + H_2O$$

$$\rightarrow (Pt\text{-}O)_2Mn(III)OH + H^+ + e^- \tag{5}$$

$$(Pt\text{-}O)_2Mn(III)OH + H_2O \rightarrow 2Pt\text{-}OH + MnOOH \tag{6}$$

$$MnOOH + 3H^+ \rightarrow Mn(III) + 2H_2O \tag{7}$$
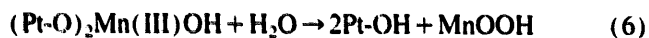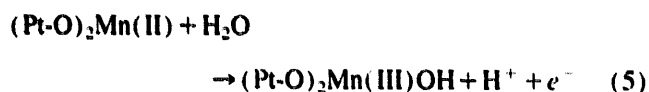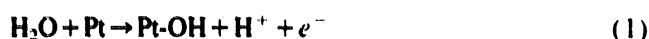
The formation of Mn^{3+} ions is composed of the adsorption and the oxidation of Mn^{2+} ions, the adsorption of Mn^{3+} ions, and the formation and decomposition of Mn^{3+} oxide that cannot be reduced on the ring electrode. The presence of adsorbed Mn^{2+} and Mn^{3+} makes it more difficult for Mn^{2+} ions to be further oxidized.

In the case of MnO_2 formation, disproportionation of the adsorbed Mn^{3+} takes place to give adsorbed Mn^{2+} and Mn^{4+}. The existence of adsorbed Mn^{2+}, Mn^{3+} or Mn^{4+} oxide renders it more difficult for Mn^{2+} ion to be further oxidized. Thus, the formation of MnO_2 is more difficult than that of Mn^{3+} ion.

Chronoammograms obtained from potential-step experiments in 1.8 M H_2SO_4 solution are shown in Fig. 6. There are two current plateaus on the chronoammograms. The first represents the oxidation of Mn^{2+} ions on the platinum with adsorbed OH radicals, which can be improved by increasing the anodic potential. The second represents the oxidation of Mn^{2+} ions on the accumulated MnO_2, which is virtually independent of the anodic potential. From curve (c) in Fig. 6, it can be seen that the oxidation of Mn^{2+} ions on the accumulated MnO_2 is more difficult than that on platinum. Increase in the anodic potential does not improve the oxidation of Mn^{2+} ions but causes the oxygen evolution from water decomposition. The electrochemical reaction resistance in column (b) of Table 1 shows the difficulty in the formation of MnO_2.

3.2. Anodic oxidation of Ag^+ ions

The anodic oxidation behaviour of Ag^+ ions in 1.8 and 9.2 M H_2SO_4 solutions are very similar. Voltammograms obtained from RRDE experiments in 9.2 M H_2SO_4 solutions
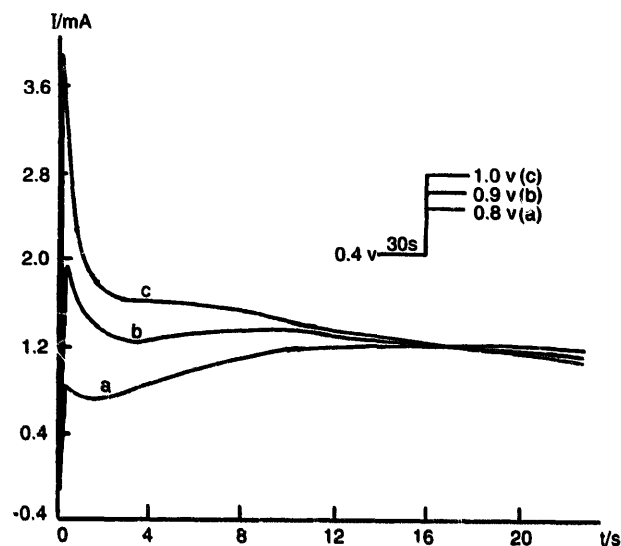

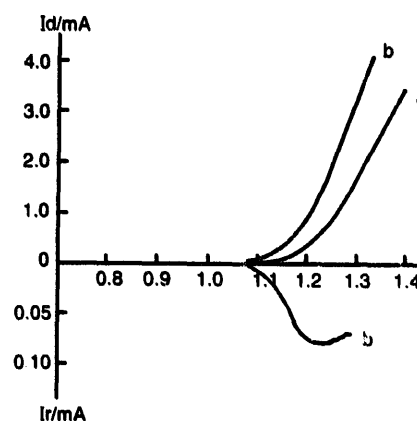Fig. 6. Chronoammograms on the platinum electrode in 1.8 M H_2SO_4 solution.

Fig. 7. Voltammogram on the platinum RRDE in: (a) 9.2 M H_2SO_4, and (b) 9.2 M $H_2SO_4 + 0.01$ M $AgNO_3$, 600 rpm; disk electrode: 10 mV s^{-1}; ring electrode: 0.6 V.

with and without Ag^+ ions are shown in Fig. 7. The anodic potential for the oxidation of Ag^+ ions is very close to that for oxygen evolution. If these two reactions are independent, the current efficiency of Ag^+ ion oxidation would be low due to the oxygen evolution.

Ag^{2+} ions, the product of Ag^+ ion oxidation, is recorded on the ring electrode as the disc electrode is anodized. The ring electrode current increases at first and reaches a maximum value; it then decreases and oscillates. The capture index of Ag^{2+} ions at the maximum increases and approaches the theoretical value ($N = 0.1789$) as the electrode rotating speed increases (see Table 2). This means that reactions taking place on the disc electrode are not independent and the oxidation of Ag^+ ions to form Ag^{2+} ions (reaction (8)) is a main reaction

$$Ag^+ \rightarrow Ag^{2+} + e^- \tag{8}$$
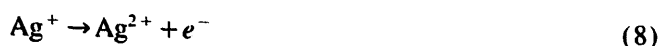
The Nyquist plots at the potentials for the oxidation of Ag^+ ions in the solution with Ag^+ ions are Warburg straight lines, as Fig. 8 shows. The reaction (8) is so fast that it is controlled by the diffussion of Ag^+ ion.
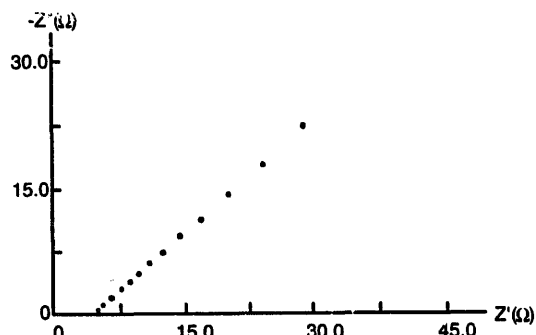
Fig. 8. Nyquist plot on the platinum electrode at 1.25 V in 9.2 M $H_2SO_4 + 0.01$ M $AgNO_3$; frequency from 10^5 to 0.1 Hz.

other species on an anode with a silver oxide film because of the existence of the heterogeneous catalytic reaction (10). Thus, the current efficiency of Mn^{3+} ions or MnO_2 is low in a solution with Ag^+ and Mn^{2+} ions when the anodic potential is high [7].

3.3. Electrocatalysis of Ag^+ ions on Mn^{2+} ions

Figs. 10 and 11 are voltammograms for the platinum RRDE in 9.2 and 1.8 M H_2SO_4 solutions with 0.01 M $AgNO_3$ and 0.05 M $MnSO_4$.

When the anodic potential is lower than that for oxidation of Ag^+ ions, the oxidation of Mn^{2+} ions on the disc electrode
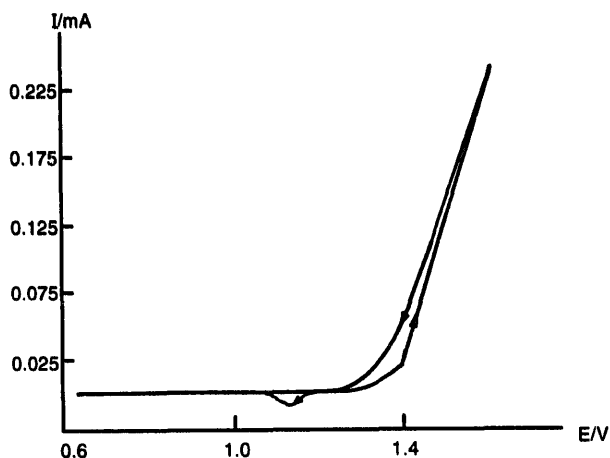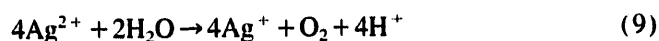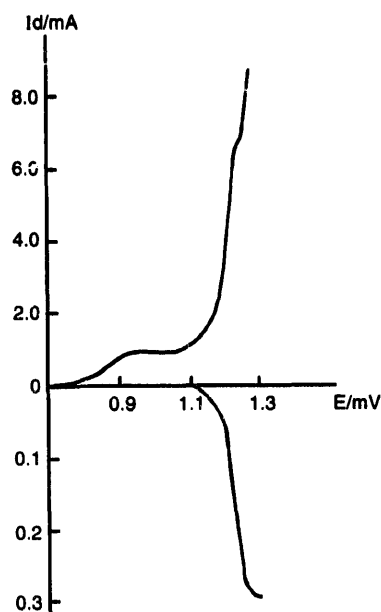

Fig. 9. Voltammogram on the platinum electrode in 0.01 M $AgNO_3 + 1.8$ M H_2SO_4; 10 mV s^{-1}.

The fact that the capture indices are lower than the theoretical values at low electrode rotating speeds can be explained by the reaction of Ag^+ ions with water

$$4Ag^{2+} + 2H_2O \rightarrow 4Ag^+ + O_2 + 4H^+ \tag{9}$$

This reaction is so slow that Ag^{2+} ions can be recorded on the ring electrode.

The decrease and oscillation of the ring electrode current are caused by the formation of a silver oxide film on the disc and the oxygen evolution from water decomposition on the oxide film. The formation of a silver oxide film was recognized early [13,14]. This oxide film has a strong heterogeneous catalytic effect on the oxygen evolution from water decomposition in sulfuric acid solution

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{10}$$

The oxide film is formed more easily in less concentrated sulfuric acid solution. Fig. 9 shows this catalysis; there is a sharp increase in current at about 1.4 V in the forward-going potential scan, where silver oxide film is formed. The reduction current of the oxide film appears at about 1.1 V in the negative-going potential scan. The Nyquist plot for reaction (10) is a semicircle, but the electrochemical reaction resistance is very small (see Table 1). It is hard to oxidize any

Fig. 10. Voltammogram on the platinum RRDE in 0.05 M $MnSO_4 + 0.01$ M $AgNO_3 + 1.8$ M H_2SO_4; disk electrode: 10 mV s^{-1}; ring electrode: 0.6 V.
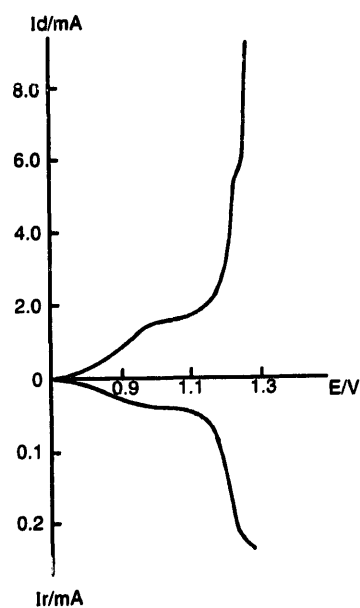

Fig. 11. Voltammogram on the platinum RRDE in 0.05 M $MnSO_4 + 0.01$ M $AgNO_3 + 9.2$ M H_2SO_4; disk electrode: 10 mV s^{-1}; ring electrode: 0.6 V.
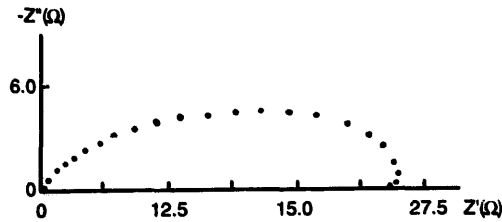
Fig. 12. Nyquist plot on platinum electrode in 0.01 M AgNO₃+0.05 M
MnSO₄ + 1.8 M H₂SO₄ at 1.25 V; frequency from 10⁵ to 0.1 Hz.

is nearly the same as that in the solution without Ag^+ ions. Nevertheless, there is a sharp increase in disc current when the anodic potential reaches a value at which the oxidation of Ag^+ ions takes place. At the anodic potential of 1.25 V, the Nyquist plot for a platinum electrode in 9.2 M H_2SO_4 solution with Mn^{2+} and Ag^+ ions is a typical depressed semicircle (as Fig. 12 shows). The electrochemical reaction resistance is lower than one hundredth of that in a solution with only Mn^{2+} ions (see Table 1).
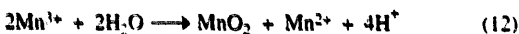
Whether in 9.2 M or in 1.8 M H_2SO_4 solution, Ag^+ ions exert a strong electrocatalytic effect on the oxidation of Mn^{2+} ions. This is a homogeneous electrocatalysis and proceeds via the electrochemical reaction (8) on the anode surface and the chemical reaction of Ag^{2+} ions with Mn^{2+} ions in the solution.

In 9.2 M H_2SO_4 solution, the electrocatalytic reactions are:

$$Ag^+ \longrightarrow Ag^{2+} + e^- \qquad (8)$$

$$Mn^{2+} + Ag^{2+} \longrightarrow Ag^+ + Mn^{3+} \qquad (11)$$
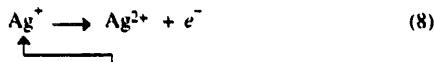
the product is Mn^{3+} ions. The solution turns from clear to purple.

In 1.8 M H_2SO_4 solution, the electrocatalytic reactions are:

$$Ag^+ \longrightarrow Ag^{2+} + e^- \qquad (8)$$

$$Mn^{2+} + Ag^{2+} \longrightarrow Ag^+ + Mn^{3+} \qquad (11)$$

$$2Mn^{3+} + 2H_2O \longrightarrow MnO_2 + Mn^{2+} + 4H^+ \qquad (12)$$

the product is MnO_2. Deposited MnO_2 forms in solution instead of adhering to the anode surface in the solution without Ag^+ ions. Mn^{3+} ions are formed as intermediate species that can be detected on the ring electrode (see Fig. 10).

The electrocatalytic reactions are very fast because the reactions are controlled by the diffusion of Mn^{2+} ions. Increases in electrode rotation speed or Mn^{2+} ion concentration will improve the electrocatalytic current.

Taking the disc current in sulfuric acid solution with only Ag^+ ions as the electrocatalytic current of reactions:

$$Ag^+ \longrightarrow Ag^{2+} + e^- \qquad (8)$$

$$4Ag^{2+} + 2H_2O \xrightarrow{k_{H_2O}} 4Ag^+ + O_2 + 4H^+ \qquad (9)$$
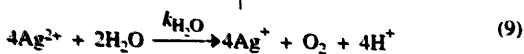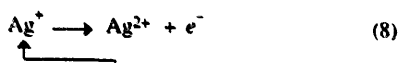
and that in solution with Ag^+ and Mn^{2+} ions as the one of reactions:

$$Ag^+ \longrightarrow Ag^{2+} + e^- \qquad (8)$$

$$2Ag^{2+} + 2Mn^{2+} + 2H_2O \xrightarrow{k_{Mn}} Ag^+ + MnO_2 + 4H^+ \qquad (13)$$
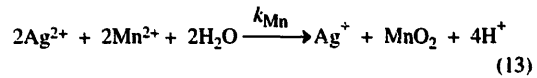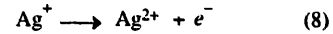
It is found that k_{Mn}/k_{H_2O} is 10.8 at 1.25 V, based on the following relationship of disc current (i) with electrocatalyst concentration (C) [15]

$$i = nFD^{0.5}k^{0.5}C \qquad (14)$$

That is to say, the reaction speed for the formation of MnO_2 is an order of magnitude larger than that for oxygen evolution. Thus, a very high current efficiency for ECMD can be obtained by using Ag^+ ions as an electrocatalyst [7].

4. Conclusions

Deposited MnO_2 accumulates on the anode surface during the direct oxidation of Mn^{2+} ions. This causes many difficulties for the preparation of conventional EMD, i.e., low current density, high temperature, and complicated technology. Mn^{2+} ions can be oxidized easily by Ag^+ ion electrocatalysis on an anode and the product MnO_2 is formed in solution. The electrocatalysis takes place at the potential for the oxidation of Ag^+ ions to Ag^{2+} ions. Thus, it is a homogeneous electrocatalysis. Although the anodic potential for Ag^+ ion oxidation is very close to that for oxygen evolution from water decomposition, the reaction taking place on the anode at the potential for oxygen evolution in a solution without Ag^+ ions is very similar to the oxidation of Ag^+ ions in a solution with Ag^+ ions. Accordingly, MnO_2 can be prepared by a simple method that uses Ag^+ ions as an electrocatalyst at a high current density and a high current efficiency.

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