

## 망간(II)을 함유한 황산용액에서 Pb-Ag 양극의 산화반응

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### Anodic Reactions at a Pb-Ag Anode in Sulfuric Acid Solutions Containing Manganese(II)

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#### 요 약

황산용액에 함유된 망간(II)의 농도가 Pb-Ag양극의 산화거동에 미치는 영향을 1.8에서 2.0 V의 범위에서 정전위법으로 조사하였다. 산화전위가 높고 망간의 초기 농도가 낮은 조건에서는 망간(III)의 농도가 높았으며, 산화반응 후 용액을 분광학적으로 분석하여 이를 확인하였다. 1.8과 1.9 V에서는  $MnO_2$ 가 망간(II)의 산화에 의해 생성되나, 2.0 V에서는 망간(III)의 불균등화반응에 의해 형성되었다. 1.8 V에서 용액에 망간(II)이 존재하면 정전위조건에서 산화시킬 때 납이  $PbO_2$ 로 산화되지 않았다. 그러나 1.9와 2.0 V에서는 망간(II)농도가 증가함에 따라  $PbO_2$ 가 망간(II)에 의해 화학적으로 환원되어  $PbO_2$ 의 양이 감소하였다.

**주제어** : 산화, Pb-Ag양극, 망간(II), 납산화물

#### Abstract

The effect of Mn(II) concentration on the anodic reactions occurring on a Pb-Ag electrode in sulfuric acid solutions has been studied by potentiostatic oxidation in the potential range of 1.8 to 2.0 V. High oxidation potentials and low initial concentrations of Mn(II) resulted in higher concentrations of soluble Mn(III) ions which were obtained from spectrophotometric analysis of the solution after oxidation.  $MnO_2$  was deposited on the electrode by electrochemical oxidation of Mn(II) at 1.8 and 1.9 V, while it was formed by disproportionation of Mn(III) at 2.0 V. No  $PbO_2$  was formed in the presence of Mn(II) during potentiostatic oxidation treatment for two hours at 1.8 V. Chemical reduction of  $PbO_2$  with Mn(II) led to a decrease in the amount of  $PbO_2$  as Mn(II) concentration increased at 1.9 and 2.0 V.

**Key words** : Oxidation, Pb-Ag anode, Manganese(II), Lead dioxide

· Received : May 17, 2017 · Revised : May 30, 2017 · Accepted : June 9, 2017

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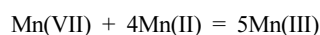
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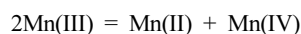
## 1. Introduction

Lead-silver alloys with 0.5~1.0 wt% Ag are widely used as anode materials in the electrowinning of zinc<sup>1</sup>. The electrolyte for zinc electrowinning typically contains about 2~15 g/L of Mn(II) ions<sup>2</sup>. The presence of Mn(II) in the electrolyte decreases the corrosion rate of the anodes by the formation of a protective layer of manganese oxides that also assist in purification of the electrolyte by adsorption of other metal ions. By contrast, the presence of less than 0.1 g/L of Mn(II) ions during the electrowinning of copper has been claimed to be detrimental because the lead content of the cathodes increases in the presence of manganese in the electrolyte. In addition, the formation of Mn(III) and Mn(VII) at the anodes of lead-calcium-tin alloys can lead to the degradation of the reagents used in the solvent extraction of copper in so-called SX/EW operations<sup>3</sup>.

The chemistry of the higher oxidation states of manganese in aqueous solution depends on the concentration of sulfate and acid. Therefore, not only MnO<sub>2</sub> but also Mn(III) and Mn(VII) ions, can exist as stable oxidation products of Mn(II). Several studies of the anodic reactions on lead alloy electrodes in solutions containing manganese ions have reported that high concentrations of Mn(II), slower scan rates, and low potential favour the formation of Mn(III) ions, while Mn(VII) is the main product at low concentrations of Mn(II) and high potentials<sup>4,5</sup>. A summary of the chemistry of manganese in sulfate systems relevant to the electrowinning of zinc has been published<sup>6</sup>. Mn(VII) is not stable in the presence of excess Mn(II) ions due to the reaction,



while Mn(III) ions disproportionate by the equilibrium



Mn(IV) ions are meta-stable in concentrated acidic solutions and will hydrolyze to MnO<sub>2</sub>. The deposited MnO<sub>2</sub> leads to a build-up of scale on the anodes which should be periodically removed from the anode<sup>4</sup>.

Although several studies have been performed on the

mechanism of Mn(II) oxidation in sulfuric acid solutions on various electrodes, much work needs to be done to establish the extents of manganese and lead oxidation as a function of operating conditions at Pb-Ag and Pb-Ca-Sn anodes under conditions typical of the electrowinning of zinc and copper. The objectives of this study was to quantify the fractions of the current used for oxygen evolution, lead oxidation and manganese oxidation during anodic polarization and to establish the deportment of the various oxidation states of manganese under conditions similar to those used during the electrowinning of zinc.

## 2. Experimental

The electrolytes were prepared using Milli-Q distilled water and analytical grade reagent manganous sulfate and sulfuric acid. The main electrolyte used in this study contained 150 g/L sulfuric acid and the effect of Mn(II) concentration was investigated by adding either 1 or 10 g/L Mn(II) to this electrolyte. The main electrolyte will be referred to as BM while BMn(1) and BMn(10) represent the electrolytes in which the concentrations of Mn(II) are 1 and 10 g/L, respectively.

Electrochemical measurements were performed using a thermostatted three-electrode system in a modified Metrohm glass cell covered with a detachable lid. The working electrode was a rotating disc (5 mm diameter) made from Pb-0.64 wt% Ag commercial alloy. The reference electrode was a KCl saturated calomel electrode that was joined to the main cell by a Luggin capillary passing through a screw fitting in the base of the cell. The Luggin capillary was placed below the surface of the working electrode. The counter electrode was a platinum wire electrode housed in a glass tube that was separated from the bulk solution by a glass frit.

The rotating disc electrode was rotated using a drive consisting of an optically controlled unit coupled to a dc motor. Voltammetric experiments were carried out using an EG&G Princeton Applied Research (PAR) Model 173 Potentiostat together with an EG&G PAR Model 175 Universal programmer. Analogue data from the potentiostat were collected using a National Instrument

data acquisition board controlled by Labview software. The temperature of the electrolyte was maintained at 40.1°C. The concentration of Mn(II) was estimated by spectrophotometric measurements at 475 nm using a UV-Visible spectrophotometer (Agilent 8453).

Prior to every experiment, the exposed surface of working electrode was wet-ground with Milli-Q water on 800 and 1200 silicon carbide paper. The electrode was transferred to the cell immediately after washing with Milli-Q water. Prior to the start of experiments, the working electrode was maintained at open-circuit potential in the electrolyte for 3 minutes. The solution volume used for all experiments was 100 cm<sup>3</sup>. All potentials are quoted with respect to the standard hydrogen electrode (SHE). Unless stated otherwise, all potential sweeps were carried out at 10 mV/s with the disc electrode rotated at 500 rpm.

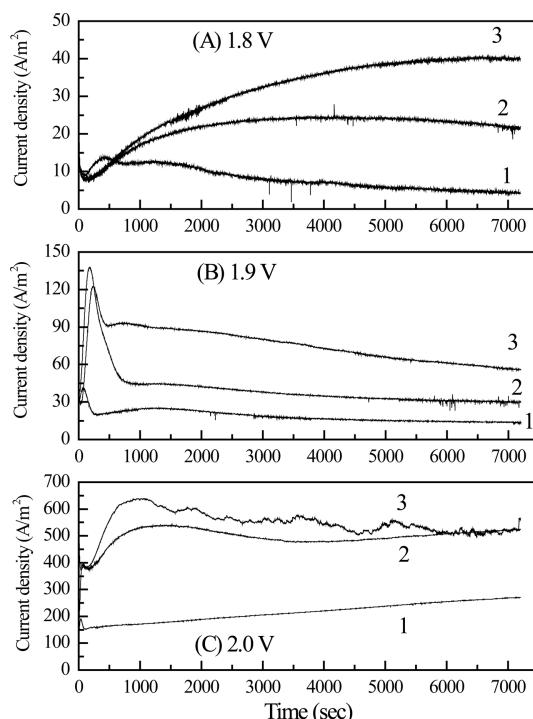
### 3. Results and Discussion

#### 3.1. Potentiostatic experiments

Table 1 lists the electrode potential of various half cell reactions at 25°C which can occur during the oxidation of Pb-Ag electrode in sulfuric acid solution containing Mn(II)<sup>7,8</sup>. Fig. 1 shows the effect of Mn(II) concentration on the current-time behaviour of Pb-Ag electrode during potentiostatic oxidation for 2 h in 150 g/L sulfuric acid solution in the potential range of 1.8 to 2.0 V. A current peak appears during the early stages

**Table 1.** Standard electrode potentials of various half cell reactions at 25°C

Reactions	E°	Reference
$\text{Ag}^+ + \text{e} = \text{Ag}$	0.799	Pourbaix
$\text{Mn}^{3+} + \text{e} = \text{Mn}^{2+}$	1.484	HSC
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e} = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.228	Pourbaix
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e} = \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.507	Pourbaix
$\text{PbSO}_4 + \text{H}^+ + 2\text{e} = \text{Pb} + \text{HSO}_4^-$	-0.299	Cifuentes et al.
$\text{PbO} + 2\text{H}^+ + 2\text{e} = \text{Pb} + \text{H}_2\text{O}$	0.248	Pourbaix
$\text{PbO}_2 + 2\text{H}^+ + 2\text{HSO}_4^- + 2\text{e} = \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.595	HSC
$\text{O}_2 + 4\text{H}^+ + 4\text{e} = 2\text{H}_2\text{O}$	1.230	Pourbaix



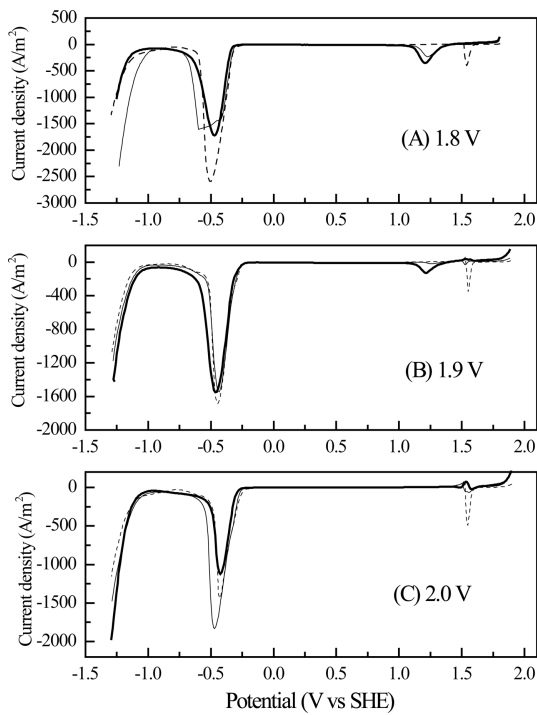
**Fig. 1.** Effect of Mn(II) concentration on current-time transients of Pb-Ag electrode during oxidation in 150 g/L sulfuric acid solutions. (1: without Mn(II), 2: 1 g/L Mn(II), 3: 10 g/L Mn(II))

of oxidation with the exception of the experiment at 1.8 V in the BMn(1) and BMn(10) electrolytes. According to previous studies<sup>9</sup>, this is due to the nucleation and growth of  $\beta\text{-PbO}_2$  on the  $\text{PbSO}_4$  surface layer. As could be expected, the time necessary for the oxidation of  $\text{PbSO}_4$  to  $\beta\text{-PbO}_2$  decreased with increasing potential. During oxidation in the base (BM) electrolyte, the current density slowly decreased to low values after the peak at 1.8 and 1.9 V, while it gradually increased at 2.0 V. Oxygen evolution was visible only at 2.0 V and it is likely that the current at the lower potentials was due to oxidation of the lead.

In the presence of manganese ions, the currents were greater and, except at 2.0 V, were greater at the higher manganese concentration. During oxidation at 1.9 V, the current density slowly decreased with time after the maxima in both BMn(1) and BMn(10) electrolytes. At a potential of 2.0 V, the current density sharply increased

**Table 2.** Cumulative anodic charge (coulomb) during oxidation for 2 h

	1.8 V	1.9 V	2.0 V
H <sub>2</sub> SO <sub>4</sub> 150 g/L	1.14	2.64	30.35
H <sub>2</sub> SO <sub>4</sub> 150 g/L + Mn 1 g/L	3.64 (3.2)	5.80 (2.2)	70.22 (2.3)
H <sub>2</sub> SO <sub>4</sub> 150 g/L + Mn 10 g/L	4.86 (4.3)	10.65 (4.0)	77.28 (2.5)



**Fig. 2.** Cathodic voltammograms of Pb-Ag electrode after oxidation in 150 g/L sulfuric acid solutions for 2H. Sweeps initiated in a negative direction at a scan rate of 10 mV/sec. (---- : without Mn(II), — : 1 g/L Mn(II), — : 10 g/L Mn(II))

after the maximum and then remained nearly constant in the BMn(1) electrolyte. The fluctuations in current density at 2.0 V was associated with the disturbances

created by the evolution of oxygen gas in the BMn(10) electrolyte.

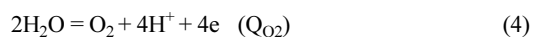
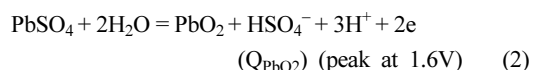
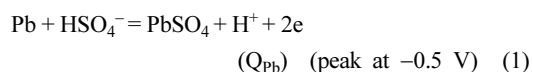
The cumulative anodic charge ( $Q_a$ ) passed during oxidation for 2 h was obtained from the current-time curve and is summarized for the various conditions in Table 2. The number in parentheses is the ratio of  $Q_a$  in the presence of Mn(II) to that without Mn(II). As expected, the cumulative charge increased with increasing potential. It also increased with increasing Mn(II) concentration confirming that Mn(II) ions are being oxidised at these potentials although the ratio decreases as the current associated with oxygen evolution increases.

Fig. 2 shows the reductive sweeps after potentiostatic oxidation for 2 h as shown in Fig. 1. The peaks at 1.6 V and -0.5 V are characteristic of the reduction of species formed during the anodic oxidation of lead and are due to the reduction of PbO<sub>2</sub> to PbSO<sub>4</sub> and PbSO<sub>4</sub> to Pb respectively. The remaining peak at about 1.2 V was only obtained in the presence of Mn(II) ions and can therefore be assigned to the reduction of MnO<sub>2</sub> (or MnOOH) formed on the electrode during the oxidation period. This suggestion is supported by the value of the electrode potential for this reaction listed in Table 1. Table 3 summarizes the total cathodic charge,  $Q_c$  (above -1.0 V) for each condition. The ratio of  $Q_c/Q_a$  is given in parentheses.

The most likely reactions occurring at the anode during oxidation are

**Table 3.** Total cathodic charge (coulomb) during reduction sweeps after oxidation for 2 h

	1.8 V	1.9 V	2.0 V
H <sub>2</sub> SO <sub>4</sub> 150 g/L	0.89 (0.78)	0.51 (0.19)	0.42 (0.014)
H <sub>2</sub> SO <sub>4</sub> 150 g/L + Mn 1 g/L	0.74 (0.20)	0.48 (0.083)	0.60 (0.009)
H <sub>2</sub> SO <sub>4</sub> 150 g/L + Mn 10 g/L	0.67 (0.14)	0.62 (0.058)	0.33 (0.004)



It is not clear from previous work whether oxidation of Mn(II) ions under the conditions of these experiments will yield Mn(III) and/or Mn(VII) and reaction (3) has been written assuming the former.

Disproportionation of Mn(III) will yield MnO<sub>2</sub> as a solid product and visual inspection of the electrodes after oxidation showed that a fine black deposit was formed on the surface of the disc and the surrounding resin. This was particularly apparent in the presence of 1 g/L manganese at 2.0 V. At the higher manganese concentration, a black deposit was found on the walls of the cell but not on the electrode surface after oxidation at 2.0 V.

The total anodic charge can be expressed as

$$Q_a = Q_{\text{Pb}} + Q_{\text{PbO}_2} + Q_{\text{Mn}} + Q_{\text{O}_2}$$

while the total cathodic charge is

$$Q_c = -(Q_{\text{Pb}} + Q_{\text{PbO}_2}) - Q_{\text{MnO}_2} \text{ (cathodic charge negative)}$$

in which  $Q_{\text{MnO}_2}$  is the charge associated with the reduction of MnO<sub>2</sub> on the surface of the electrode.

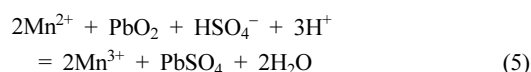
On the other hand,

$$Q_{\text{Mn}} = -Q_{\text{MnO}_2} - Q_{\text{Mn}}'$$

in which  $Q_{\text{Mn}}'$  is equivalent to the charge for the reduction of Mn<sup>3+</sup> ions that are transported from the anode. This quantity is, in turn made up of Mn<sup>3+</sup> ions that remain in the electrolyte and MnO<sub>2</sub> precipitated by disproportionation of Mn<sup>3+</sup> ions away from the electrode.  $Q_{\text{Mn}}'$  can be estimated from a chemical analysis of the oxidized forms of manganese in the solution and precipitated as MnO<sub>2</sub>. This can be achieved by reduction with excess of an acidic solution of ferrous ions of known concentration and the excess ferrous obtained by titration with dichromate. If necessary, the Mn<sup>3+</sup> ions in solution can

be estimated by measuring the absorbance at 475 nm.

As the potential and Mn(II) concentration increase, the ratio  $Q_c/Q_a$  decreases. It is interesting to note that the amount of PbO<sub>2</sub> on the surface decreases in the presence of manganese in solution as found by<sup>11)</sup> and also that the amount of MnO<sub>2</sub> on the surface decreased with increasing potential during oxidation. The decrease in the charge associated with the PbO<sub>2</sub> reduction peak with increasing Mn(II) concentration could be ascribed to the chemical reduction of PbO<sub>2</sub> by Mn(II) ions<sup>4)</sup>.



During oxidation in the BMn(1) electrolyte at 2.0 V, the whole surface of the rotating disc together with the epoxy was covered by MnO<sub>2</sub>. In the case of the BMn(10) electrolyte at the same potential, MnO<sub>2</sub> was formed away from the electrode surface. However, Fig. 3-(C) clearly shows that there is no peak for MnO<sub>2</sub> reduction at 2.0

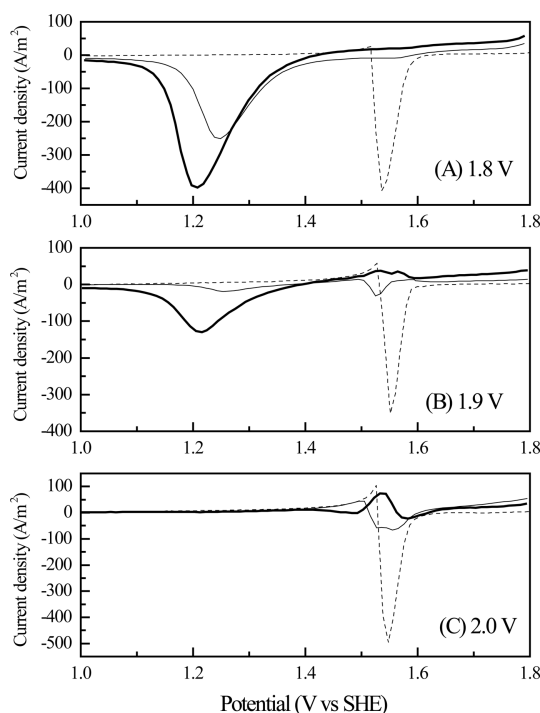
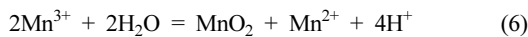


Fig. 3. Magnified cathodic voltammograms of Pb-Ag electrode shown in Fig. 2. (---- : without Mn(II), — : 1 g/L Mn(II), — : 10 g/L Mn(II))

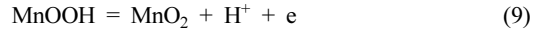
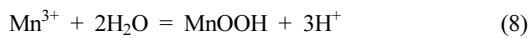
**Table 4.** Mn(III) concentrations (mM) measured at 475 nm after oxidation for 2 h

	1.8 V	1.9 V	2.0 V
Mn(II) 1 g/L	0.24 (0.64)	0.22 (0.37)	0.49 (0.067)
Mn(II) 10 g/L	0.24 (0.47)	0.27 (0.24)	0.38 (0.048)

V in both BMn(1) and BMn(10) electrolytes. In order to understand these two apparently inconsistent results, the Mn(III) concentration was measured by UV at 475 nm wavelength<sup>12)</sup> after oxidation for 2H and is represented in Table 4. The value in bracket represents the percentage of the measured Mn(III) concentration to the Mn(III) concentration calculated by assuming 100% current efficiency. Table 4 shows that Mn(III) concentration increases with increasing potential and BMn(1) electrolyte results in higher Mn(III) concentration than BMn(10) electrolyte at 1.8 and 2.0 V. Several studies have reported that lower potentials and high Mn(II) concentrations favour the formation of Mn(III)<sup>4,5)</sup>. However, in our studies, oxidation of Pb-Ag electrode from the BMn(1) electrolyte at 2.0 V resulted in the highest concentration of Mn(III). Fig. 3-(C) together with the highest concentration of Mn(III) in the BMn(1) electrolyte at 2.0 V suggests that the following disproportionation reaction of Mn(III) is responsible for the coverage of the whole electrode surface by MnO<sub>2</sub> and that the MnO<sub>2</sub> layer is electrically disconnected from the electrode.



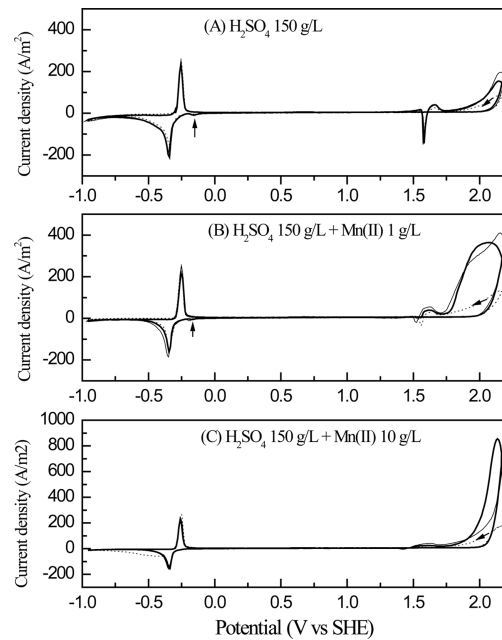
The fact that the whole surface of the electrode was covered by MnO<sub>2</sub> during oxidation in the BMn(1) electrolyte at 2.0 V implies that a critical concentration ratio of Mn(III) to Mn(II) is necessary for the disproportionation reaction of Mn(III) to occur. However, the occurrence of the peak for MnO<sub>2</sub> reduction in Fig. 3-(A) and (B) suggests that either direct electrochemical oxidation of Mn(II) to MnO<sub>2</sub> or the following reaction step is responsible for the formation of MnO<sub>2</sub> at the oxidation potential of 1.8 and 1.9 V<sup>2,4)</sup>.



In our experimental setup, the counter electrode was housed in a glass tube that was separated from the bulk solution by a glass frit. Hence there is no possibility that oxidized Mn species such as Mn(III) and Mn(IV) is reduced at counter electrode during oxidation reaction.

### 3.2. Rotation speed

Fig. 4 shows the effect of rotation speed on the cyclic voltammograms (CV) of Pb-Ag electrode in various sulfuric acid solutions. The sweeps were initiated to the positive direction from the open circuit potential at a sweep rate of 10 mV/sec. An anodic peak, corresponding to the oxidation of Pb to PbSO<sub>4</sub>, appears at -0.3 V during the positive sweep and no anodic peak appears before anodic current begins to increase rapidly at 2.0 V. The rapid increase in anodic current at these potential indicates that PbO<sub>2</sub> formation and oxygen evolution reaction occur together<sup>13)</sup>. Since these two reactions are



**Fig. 4.** Effect of rotation speed on the cyclic voltammograms of Pb-Ag electrode. Sweeps initiated in a positive direction from OCP at a scan rate of 10 mV/sec. (---- : without rotation, — : 500 rpm, — : 1000 rpm)

mass transport controlled, the maximum of the anodic current in each solution depends on the rotation speed. Comparison of Fig. 4-(A), (B), and (C) indicates that the Mn(II) in the electrolyte promotes the oxygen evolution reaction.

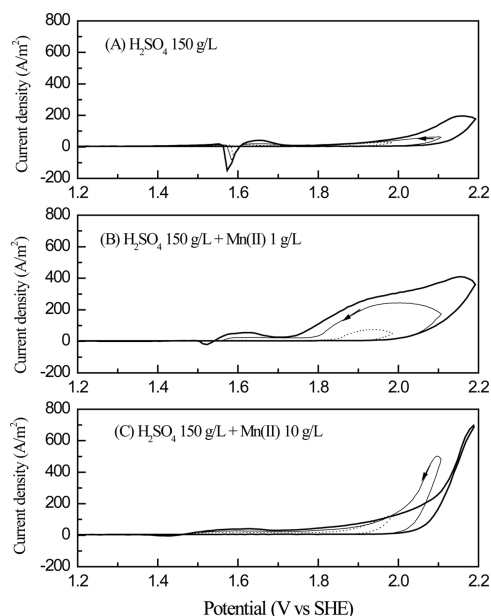
A remarkable feature of the CVs shown in Fig. 4 is an increase in anodic current during reduction sweep after reversing the potential sweep at 2.2 V and this is the most pronounced in the BMn(1) electrolyte. Similar CVs of lead and Pb-Co<sub>3</sub>O<sub>4</sub> electrode during reduction sweep have been reported<sup>14,15</sup>. Pavlov ascribed this phenomenon to the delay of the sweep potential through the PbO and PbO<sub>2</sub> layer owing to the complexity of the layer<sup>15</sup>. An alternative explanation is that oxidation of Mn(II) is more rapid on a PbO<sub>2</sub> surface produced at the higher potentials.

A small anodic peak appears at around 1.6 V during reduction sweep in all our experiments and this may be related to the oxidation of lead exposed to the electrolyte during reduction sweep. A peak for PbO<sub>2</sub> reduction appears at around 1.55 V in the B and BMn(1) electrolyte. The chemical reduction of PbO<sub>2</sub> by Mn(II) explains the decrease in the intensity of PbO<sub>2</sub> reduction with increasing Mn(II) concentration.

In the BM and BMn(1) electrolyte, a very small reduction peak (indicated by  $\uparrow$ ) appears before the peak for PbSO<sub>4</sub> reduction. This peak is responsible for the reduction of PbO to Pb. However, there is no such peak in the BMn(10) electrolyte. Mn(II) concentration and rotation speed had a negligible effect on the peak intensity for PbSO<sub>4</sub> reduction in our experimental ranges.

### 3.3. Sweep rate

Fig. 5-(A), (B), and (C) are the CVs of Pb-Ag electrode obtained by varying sweep rate at a rotation speed of 500 rpm. The initial sweep was started to the positive direction from the open circuit potential. Sweep rate affected little the oxidation and reduction behaviour of Pb-Ag in the potential range of -0.5 to -0.3 V. Therefore, the part of CV obtained in the potential range of 1.2 to 2.2 V is shown in Fig. 5. For each electrolyte, the anodic current obtained after switching the potential to negative at 2.2 V decreases with the decrease in sweep



**Fig. 5.** Effect of scan rate on the cyclic voltammograms of Pb-Ag electrode at a rotation speed of 500 rpm. (---- : 1 mV/sec, — : 5 mV/sec, — : 10 mV/sec)

rate. This supports the explanation for the occurrence of such an anodic current<sup>15</sup>. The intensity of reduction peak increases with increasing sweep rate in the B electrolyte. In the BMn(1) and BMn(10) electrolyte, a broad reduction peak appears when the sweep rate is 10 mV/sec.

## 4. Conclusions

Experiments involving constant potential oxidation followed by reduction sweeps were employed to investigate the oxidation reactions occurring on Pb-Ag anodes in sulfuric acid solutions containing Mn(II) in the potential range of 1.8 to 2.0 V. The reaction path for MnO<sub>2</sub> formation in our studies seemed to be dependent on the oxidation potential. At 1.8 and 1.9 V, electrochemical oxidation of Mn(II) is responsible for the formation of MnO<sub>2</sub>. However, the disproportionation reaction of Mn(III) accounts for the deposition of MnO<sub>2</sub> on the electrode at a potential of 2.0 V. Low initial concentrations of Mn(II) and high potentials results in higher concentrations of Mn(III) during potentiostatic

oxidation. At a potential of 1.8 V, insignificant amount of PbO<sub>2</sub> was formed as evidenced by the absence of a cathodic peak during the reverse sweep in the BMn(1) and BMn(10) electrolyte. The amount of PbO<sub>2</sub> formed during oxidation decreased as a result of chemical reduction with Mn(II) ions at 1.9 and 2.0 V. Cyclic voltammograms obtained by varying rotation speed and sweep rate showed an anodic peak in the potential range of 1.5 to 1.7 V during the negative sweeps. The complexity of the structure of the anode and the oxide layers on its surface as well as the many anode reactions involved during the electrowinning of zinc requires more extensive work to elucidate its electrochemistry.

### Acknowledgements

This work was supported by the Global Excellent Technology Innovation of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (No. 20165010100810).

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