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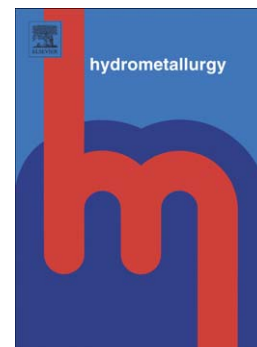
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The Role of Silver in Enhancing the Electrochemical Activity of Lead and Lead-Silver Alloy Anodes

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Abstract

The role of silver as an alloying additive to reduce the overpotential of the oxygen evolution reaction on lead anodes used in the electrowinning of zinc has not previously been established. This paper summarizes the results of a detailed study of the mechanism of the action of silver both as an additive to the alloy and in solution. The presence of Ag_2O_2 in the oxide layer was confirmed on Pb electrodes anodised in sulphuric acid electrolytes containing silver ions. The enhanced electrochemical activity of PbAg alloy anodes over Pb is attributed to the presence of Ag_2O_2 in the corrosion layer.

1. Introduction

Although PbAg alloys have been used as anodes for zinc electrowinning for many years the mechanism by which silver causes a reduction in potential is not well understood. When silver is alloyed with lead it is reported to inhibit the oxidation of PbO to PbO₂ and to induce the formation of β -PbO₂ not only at the oxide / solution interface but also at the metal / oxide interface (Pavlov and Rogachev, 1986). Other work has also shown that increasing the amount of Ag in PbAg alloys increases the β -PbO₂ / α -PbO₂ ratio (Monahov et al., 2000; Taguchi, 1996; Tikkanen and Hyvarinen, 1969). However the β -PbO₂ / α -PbO₂ ratio does not affect the oxygen overpotential (Monahov et al., 2000) as the potential for the oxygen evolution reaction on α -PbO₂ is similar to that on β -PbO₂ (Taguchi et al., 1996). Silver is more effective in reducing the overpotential for the oxygen evolution reaction (OER) when introduced from the electrolyte rather than from the alloy (Zuborovskii, 1977b). However, silver added to the electrolyte has negligible effect on the corrosion rate of lead (Pavlov and Rogachev, 1986).

It is also thought that silver reduces the OER overpotential by reducing the charge transfer resistance. The presence of PbO at the interface between the PbAg alloy and the PbO₂ outer layer is considered to have the greatest influence on the charge transfer resistance and it is considered that the presence of Ag₂O, evidenced by XPS, increases the conductivity of PbO and thus decreases the charge transfer resistance for oxygen evolution (Taguchi, 1996). Other authors have proposed that PbO₂ formed via the

electrochemical oxidation of lead and lead alloys has a gel-crystal structure (Pavlov and Monahov, 1996). In this model the OER occurs in the gel layer. Silver has been found to change the nature and increase the number of active centres in the gel zone (Monahov et al., 2000), however it is not clear how this occurs. These authors also found that Ag in PbAg alloys increases the gel layer/crystal ratio (Monahov et al., 2000), however, there is no clear evidence in the literature that increasing this ratio affects the overpotential for oxygen evolution.

Taguchi et al (1996) prepared Pb-Ag bi-electrodes by embedding silver wire into a Pb electrode and observed that OER occurs preferentially on Ag wire in preference to the Pb host metal. They concluded that, in PbAg alloy anodes, oxygen evolution occurs preferentially on the Ag rich portions on the alloy surface. However silver metal itself is a poor anode for the OER in sulphuric acid, with a potential approximately 120 mV higher than that of pure lead when operated galvanostatically at 500 A m^{-2} in $100 \text{ g L}^{-1} \text{ H}_2\text{SO}_4$ at 25°C (Zuborovskii, 1977c). From this, it has been inferred that the OER does not occur at sites of metallic silver on PbAg alloys. Furthermore metallic silver is not observed in the oxide layer, whereas silver oxidation products are present, suggesting that these are responsible for the lower OER overpotential (Zuborovskii, 1977a). This has been supported by SIMS analyses which reveal that silver ions are evenly distributed throughout the thickness of the oxide layer on PbAg alloys anodized at 500 A m^{-2} in sulphuric acid electrolyte (180 g L^{-1}) with $55 \text{ g L}^{-1} \text{ Zn}$, in the absence and presence of $5 \text{ g L}^{-1} \text{ Mn}^{2+}$ (Cachet et al., 1996). The role of metallic silver and the nature of silver oxidation products and their role warrant further investigation.

Since the mechanism by which silver causes a reduction in potential is not well understood, an experimental program was conducted with the aim of increasing the understanding of the role of silver in the performance of PbAg alloy anodes. In order to ascertain whether metallic silver was acting as sites for the oxygen evolution reaction, the electrochemical behaviour of silver anodes was also evaluated. The effects of aqueous silver on the oxygen evolution reaction on pure lead anodes were also studied, as it was also considered that silver ions may play a role.

2. Experimental

2.1 The anodic behaviour of silver metal

All tests employed a circular silver anode (99.9% Ag, 4.25 mm diameter) mounted on a brass stub and encased in epoxy resin. Tests were conducted in either 170 g L⁻¹ H₂SO₄ (H₂SO₄) or 170 g L⁻¹ H₂SO₄ + 5 g L⁻¹ Mn²⁺ (H₂SO₄/Mn). Electrolytes were prepared using AR grade sulphuric acid, manganese metal flakes and deionised water. The electrochemical studies were carried out using a conventional three-electrode system with stationary and vertically oriented working electrodes. Currents and potentials were supplied to the anodes using a PAR Model 173 Potentiostat / Galvanostat fitted with a PAR Model 376 Logarithmic Current Converter. The counter electrode was a platinum wire and the reference was a Hg|Hg₂SO₄ (saturated K₂SO₄) reference electrode. All potentials are reported with respect to the normal hydrogen electrode (NHE) using E(Hg

| $\text{Hg}_2\text{SO}_4, \text{K}_2\text{SO}_4$ (sat'd)) = 0.645 V versus NHE. Salt bridges containing saturated K_2SO_4 were used to prevent the sulphuric acid electrolyte contaminating the reference electrodes. Anode potentials were logged using a data acquisition system controlled by LabVIEW software. The electrochemical cell was a 75 mm x 50 mm x 21 mm rectangular glass box constructed from microscope slides. The cathode was a platinum wire. Temperature control was provided via a hotplate – stirrer fitted with a temperature probe.

Video images of anode surfaces during anodisation were obtained using an Optem Zoom 70 lens (Model: 29-65-15), attached to an Optem TV Tube 2x (Model: 29-90-80) which was fitted to a Sony ExwaveHAD colour video camera. The camera/lens system was mounted on an electrically controlled stage which facilitated focussing and enabled the surface of the anode to be easily scanned. Digital video images were captured using VirtualDub 1.7.7 software on a computer via a Belkin Hi-Speed USB 2.0 DVD Creator.

2.2 Electrochemical studies of PbAg alloys and of Pb in sulphuric acid with soluble silver

Electrochemical tests of the effect of soluble silver on Pb anodes were conducted using a Pb rotating disc electrode (4.2 mm diameter) in $170 \text{ g L}^{-1} \text{H}_2\text{SO}_4$ at 40°C in the presence and absence of silver. Electrolytes were prepared using AR grade sulphuric acid and 1000 ppm AgNO_3 (AAS standard solution) or AgNO_3 (AR). Once the temperature of the electrolyte was stable at 40°C the electrodes were placed into the electrolyte and a

constant current or potential was applied within a few minutes. Electrodes were rotated at 1200 rpm in all tests. Analyses of the silver in electrolytes were performed using atomic absorption spectrometry and ICP-MS.

Electrochemical studies of PbAg anodes were conducted using the following anodes, PbAg(0.42%)-rolled, PbAg(0.63%)-rolled and PbAg(0.75%)-cast, which were polished with 1200 grit SiC paper prior to use. Tests were conducted in $170 \text{ g L}^{-1} \text{ H}_2\text{SO}_4$ at 40°C and the electrodes were rotated at 1200 rpm.

2.3 Determination of silver in the oxide layers of Pb and PbAg anodes

In order to determine the amount of silver in the oxide layer formed on PbAg alloys, the alloys (dimensions = 77 mm x 40 mm x 9 mm) were operated anodically at 500 A m^{-2} for 24 hours in $170 \text{ g L}^{-1} \text{ H}_2\text{SO}_4$ at 40°C . Each anode was the central electrode in a cell with two lead cathodes. The following anodes were used: PbAg(0.42%)-rolled, PbAg(0.63%)-rolled and PbAg(0.75%)-cast. Prior to use the anodes were sandblasted with 30/60 mesh garnet grit. Duplicates of each anode were tested concurrently. Immediately after anodisation each anode was removed from its cell and the oxide layer removed by gently scrubbing the anode faces with a nylon brush, while rinsing with deionised water. The filtered oxide residues were washed with two 5 mL aliquots of deionised water and left to dry in air at room temperature. The filtrates were collected and analysed for silver by ICP-MS. The air-dried oxide residues were analysed for Ag and Pb by ICP-MS.

2.4 Preparation of silver oxide for XRD analysis

To prepare silver oxide coated Pb anodes, stationary Pb anodes (30 mm x 30 mm x 1.3 mm) were anodised in Ag-containing sulphuric acid at constant potentials using a cell with a central anode and two Pb cathodes (84 mm x 55 mm x 1.3 mm). In order to prevent electrodeposition of silver at the cathodes, the anolyte (170 g L⁻¹ H₂SO₄ + 200 ppm Ag) and catholyte (170 g L⁻¹ H₂SO₄) were separated by a battery separator membrane. The volume of the anolyte compartment was 90 mL and that of the catholyte compartment was 200 mL. Both the catholyte and anolyte were recirculated between reservoirs, each containing 700 ml of electrolyte. A Hg|Hg₂SO₄ (saturated K₂SO₄) electrode with a salt bridge containing saturated K₂SO₄ was used to monitor the potential of the anode which was maintained at a set value by using LabVIEW software to control the current output from an Agilent E3633A Power Supply. Immediately following anodisation the Pb anodes were quickly removed from the cell, rinsed with deionised water and dried under a flow of air.

X-ray diffraction was performed on anodised Pb anodes using an 'Enhanced Mini-Materials Analyser' x-ray diffractometer (GBC Scientific Equipment) with Cu K α radiation over the 2 θ range of 20° – 70° at a scan rate of 0.25°/min and with a step size of 0.04°.

3. Results and Discussion

3.1 Behaviour of a silver anode in sulphuric acid in the absence and presence of manganese

3.1.1 Cyclic voltammetry

Figure 1 shows the current - potential plot for a linear potential sweep from 0 V to 2.20 V and back to 0 V of metallic silver in 170 g L⁻¹ H₂SO₄ in the absence and presence of 5 g L⁻¹ Mn. The anodic peak at approximately 0.7 V versus NHE is due to the oxidation of Ag to Ag₂SO₄. The nearly constant current observed at potentials between ~ 0.8 V and 1.97 V is due to the simultaneous oxidation of Ag to Ag₂SO₄ and the dissolution of Ag₂SO₄. It was found in subsequent tests at constant potential that increasing the agitation of the electrolyte increased the current density, indicating that increasing the dissolution rate of Ag₂SO₄ increased the rate of oxidation of Ag to Ag₂SO₄. Hence a silver anode is passivated in sulphuric acid solutions at potentials between 0.8 and 1.97 V. However the passivating layer, Ag₂SO₄, is itself soluble in sulphuric acid and as it gradually dissolves fresh Ag metal is exposed to the electrolyte and is able to be oxidized to Ag₂SO₄. The overall rate is therefore governed by the rate of dissolution of Ag₂SO₄ in this potential region, and this concurs with the observations of Grishina and Rumyantsev (2001).

At potentials greater than 1.93 V, video images collected during the CV scans show the formation of black deposits and oxygen evolution at many of these sites. The onset of

oxygen evolution occurred at approximately 1.97 V and video microscopy revealed it was accompanied by the formation of isolated and roughly circular black deposits on which the reaction occurred. The black deposits are most probably silver oxide (Ag_2O_2) (Dugdale et al., 1961). Note: Ag_2O_2 is not a silver (II) oxide but rather a mixed silver (I, III) oxide, Ag(I)Ag(III)O_2 (Tudela, 2008). After the simultaneous formation of black particles and oxygen evolution upon these particles on the anode surface, the rate of oxygen evolution gradually decreased. This is thought to be due to oxidation of silver oxide to silver oxysulphate, on which oxygen evolution is inhibited (Dugdale et al., 1961). However it may also be that insulating Ag_2SO_4 formed between the metal and the oxygen-evolving Ag_2O_2 regions, as video images showed that over extended periods of anodisation the black deposits easily flaked off the surface. On the reverse scan from 2.2 V to 0 V, the cathodic peak at 0.61 V is due to the reduction of Ag_2SO_4 to Ag. This change was also visible under the optical microscope as the silver electrode changed from dull grey to shiny grey at this potential.

3.1.2 Potentiostatic tests

The potential of $\text{PbAg}(0.63\%)$ anodes operating at 500 A m^{-2} (typical of that used in the electrowinning of zinc) in $170 \text{ g L}^{-1} \text{ H}_2\text{SO}_4$ is 1.99 V. To determine the effect of silver metal on the current density at this potential, a silver anode was operated at 1.99 V in $170 \text{ g L}^{-1} \text{ H}_2\text{SO}_4$ in the absence and presence of manganese (5 g L^{-1}).

In the absence of manganese, the initial rise in current (Figure 2) is likely due to the sum of the oxidation of Ag to Ag_2SO_4 , the oxidation of Ag_2SO_4 to Ag_2O_2 and the oxidation of water to oxygen on Ag_2O_2 . During the initial 30 seconds rapid oxygen evolution was observed, via optical video microscopy, on the black (Ag_2O_2) deposits. However after about 1.5 minutes the rate of bubble evolution on these sites had almost ceased. After about 4 minutes the black deposits that were previously sites of bubble formation began to spall from the surface and appeared to dissolve in the electrolyte. The increase in current density observed after 12 minutes was accompanied by an increase in the number of black spots (Ag_2O_2) on the electrode surface and an increase in the rate of bubble formation. Removal of the majority of the black deposits by flushing the anode surface with a gentle stream of electrolyte resulted in the current density decreasing to approximately 100 A m^{-2} . This confirmed that the current density was due to a combination of oxygen evolution on Ag_2O_2 and the oxidation of Ag to Ag_2SO_4 , and that the black deposit (Ag_2O_2) adheres weakly to the electrode.

It appears that an insulating layer forms beneath the black deposit (Ag_2O_2) initially produced on the silver surface. It is possible that this insulating layer is Ag_2SO_4 (Briggs et al., 1961; Grishina and Rumyantsev, 2001; Grishina and Noskov, 2003) or silver peroxysulphate (Briggs et al., 1961; Wales and Burbank, 1959). The structure of this so-called silver peroxysulphate is not known (Briggs et al., 1961; Wales and Burbank, 1959). This layer prevents charge transfer to the Ag_2O_2 layer, and hence inhibits the oxygen evolution reaction on this layer. Ag_2O_2 does not adhere to the “ Ag_2SO_4 / peroxysulphate” and thus is easily detached, a fact also observed by Jones and Thirsk

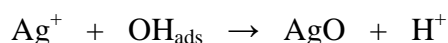
(1954). The detachment of Ag_2O_2 from “ Ag_2SO_4 / peroxy sulphate” is probably facilitated by the dissolution of Ag_2SO_4 .

In the presence of 5 g L^{-1} of manganese ions the silver anode immediately began to lose its shiny lustre, possibly due to formation of Ag_2SO_4 . The high current due to rapid evolution of oxygen observed in the absence of manganese was not observed in the presence of manganese (see inset of Figure 2). After 120 ms bubbles and tiny black spots were observed and bubble evolution occurred at the sites of the black spots. In addition, a faint purple colouration, indicative of permanganate, was observed concomitantly with the evolution of oxygen and was observed to form at the sites of oxygen evolution. This suggests that either Ag_2O_2 or intermediates in the oxygen evolution reaction, such as the hydroxyl radical, are necessary for the oxidation of Mn(II) to Mn(VII). Although bubble evolution ceased after five minutes the current density remained constant at approximately 110 A m^{-2} (Figure 2) due to oxidation of Ag to Ag_2SO_4 , with the current density determined by the rate of dissolution of Ag_2SO_4 .

These results confirm earlier experimental work (Dugdale et al., 1961; Jones and Thirsk, 1954) that oxygen evolution occurs on Ag_2O_2 but not on Ag metal, silver sulphate or silver peroxy sulphate.

A possible reaction mechanism for the oxidation of silver ions to AgO has been proposed by Dugdale et al (1961).





Although it has been claimed (Taguchi et al., 1996) that oxygen evolution occurs on silver metal when a Pb-Ag bielectrode (silver wire embedded in lead) is anodised in sulphuric acid, optical video microscopy of a Pb-Ag bielectrode anodised in sulphuric acid in the presence and absence of manganese revealed that the OER does not occur preferentially on silver metal but rather at the junction of the two metals.

3.2 The effects of soluble silver on the oxidation of Pb anodes in sulphuric acid

In the absence of silver ions, the current density at a Pb anode operated at 1.95 V in 170 g L⁻¹ H₂SO₄ at 40°C was 17 A m⁻². The addition of silver ions significantly increases the current density (Figure 3). The increase in current density is unlikely to be due to the direct oxidation of silver ions at the electrode surface as the current density was observed to increase gradually with time (Figure 3), whereas a catalytic effect involving solely aqueous species would be expected to result in a rapid increase in current density. Linear voltammetric sweeps of the surface oxidation products from 1.95 V to 1.5 V revealed the presence of PbO₂ (1.60V) and an additional peak at 1.77-1.80 V, attributable to Ag₂O₂ (see next section). As the concentration of silver in the electrolyte increased, the mass of Ag₂O₂ on the anode increased and the mass of PbO₂ decreased, as shown in by the areas under the peaks for reduction of Ag₂O₂ and PbO₂ (Figure 4).

A positive correlation was observed between current density and the density (mmol/mm^2) of Ag_2O_2 on the electrode surface (Figure 5) which was obtained from the charge associated with the cathodic peaks for the reduction of Ag_2O_2 . The observed gradual increase in current density (Figure 3) in the presence of Ag is probably due to the gradual formation of Ag_2O_2 on the electrode surface.

As an aside, given the high electrocatalytic activity of silver ions toward the oxygen evolution reaction, one may be tempted to consider using Pb alloys without silver in zinc electrowinning and to add silver ions to the electrolyte. However, silver would be lost as it would co-deposit with zinc on the cathodes and it would also reduce the current efficiency because hydrogen evolution occurs more readily on silver than on zinc.

3.2.1 Evidence for Ag_2O_2 on Pb anodes

In order to further substantiate the origin of the peaks observed at 1.77 – 1.80 V during linear voltammetric sweeps of the surface oxidation products of Pb electrodes polarised in sulphuric acid containing Ag (see Figure 4), a platinum electrode was scanned over the same potential range after polarisation in sulphuric acid with 100 ppm Ag. It also exhibited a peak (see Figure 4) at the same potential, confirming the peak is attributable to a silver oxidation product.

The silver oxidation product that formed on both Pb and Pt anodes was considered to be Ag_2O_2 as the observed reduction potentials (1.77 - 1.794 V) are close to the standard equilibrium potential of 1.80 V [17] for the reduction of Ag_2O_2 to silver ions. The presence of Ag_2O_2 was confirmed (ICDD-PDF 00-022-0472) by XRD analysis spectrum of a Pb sheet (30 mm x 30 mm x 1.3 mm) that had been anodised at 1.95 V in $170 \text{ g L}^{-1} \text{H}_2\text{SO}_4 + 200 \text{ ppm Ag}$ at room temperature for 7.5 hours, rinsed with deionised water and air dried. The x-ray diffraction spectrum also showed peaks attributable to Ag_2SO_4 (ICDD-PDF 00-027-1403), Pb (ICDD-PDF 00-004-0686) and PbO_2 (ICDD-PDF 00-011-0549) (see Figure 6). The XRD trace did not show any peaks attributable to PbSO_4 . The absence of PbSO_4 was expected as, immediately following anodisation, the anode was quickly rinsed with deionised water and dried under a flow of air. This inhibited oxidation of the Pb substrate by PbO_2 . XRD peaks due to Ag_2O_3 , which has a reduction potential of 1.670 V, were not observed.

3.2.2 *The effect of Pb and PbO_2 surfaces on the electrocatalytic activity of soluble silver*

Figure 7 compares the current density – time transients of (i) a Pb electrode operated in the presence of 2 ppm Ag (Test I) and (ii) of a Pb electrode operated initially in Ag-free sulphuric acid (170 g L^{-1}) and then in the presence of 2 ppm Ag (Test II). The difference in these two scenarios is the nature of the initial electrode / electrolyte interface. In Test I

the initial interface was Pb / 170 g L⁻¹ H₂SO₄ + 2 ppm Ag, whereas in Test II the initial interface was PbO₂ / 170 g L⁻¹ H₂SO₄ + 2 ppm Ag.

In both cases the maximum current density attained was similar (approximately 150 A m⁻²). However, whereas this was attained in 22 hours on a Pb anode, it was attained within only 2 hours on a PbO₂ anode. The increase in electrode activity is not due to the oxidation of Ag⁺(aq), since the charge supplied far exceeds the charge required to oxidise all of the silver ions. The possibility that Ag⁺(aq) are oxidised to Ag³⁺(aq) or a silver oxide which reacts with water to regenerate Ag⁺(aq) was also discounted as the rate of increase in current density is too slow to be due solely to aqueous species (see inset of Figure 7).

Since the increase in electrocatalytic activity is most probably due to the formation of increasing amounts of Ag₂O₂ on the electrode surface as demonstrated in Figure 5, the results indicate that the oxidation of Ag⁺ to Ag₂O₂ occurs more rapidly on a PbO₂ anode than on a Pb anode. This is reasonable because, on a PbO₂ electrode, there would be more sites for the oxygen evolution reaction and hence a greater surface concentration of hydroxyl radicals to oxidise Ag⁺(aq) to Ag₂O₂.

These results support earlier work (Zuborovskii, 1977c) in which the potential of a PbO₂ anode decreased more rapidly than that of a Pb anode when a constant current of 500 A m⁻² was applied in sulphuric acid electrolytes containing silver ions.

3.2.3 Evidence for Ag_2O_2 on PbAg anodes and its electrocatalytic activity

Voltammetric sweeps of PbAg anodes after polarisation in Ag-free sulphuric acid exhibited the same cathodic peak as that observed on Pb anodes anodised in Ag-containing sulphuric acid electrolytes (see Figure 10). Since Ag_2O_2 is formed at the surface of Pb anodised in sulphuric acid electrolytes containing soluble silver, it is reasonable to conclude that Ag_2O_2 is also produced at the surface of PbAg anodes anodised in Ag-free sulphuric acid. The following experiment was used to ascertain the electrocatalytic activity of Ag_2O_2 toward the oxygen evolution reaction.

A PbAg (0.63%) alloy was polarised at 2.0 V versus NHE in $170 \text{ g L}^{-1} \text{ H}_2\text{SO}_4$ at 40°C until the current density stabilised. After attaining a stable current density, the potential electrode was scanned (A in Figures 8, 9 and 10) at a rate of 5 mV/s from 2.0 V to 1.66 V, held at this potential for 2 seconds and then returned instantly to 2.0 V. The plot of the current versus potential for this scan (Figure 10) shows the presence of a peak at 1.72 V, similar to that observed on Pb anodes anodised in Ag-containing sulphuric acid electrolytes (Figure 4) and thus indicative of Ag_2O_2 . The anode was held at 2.0 V for a further 43 minutes and then another similar scan was performed (B in Figures 8, 9 and 10). After a further 10 minutes at 2.0 V, a final scan (C in Figures 8, 9 and 10) was performed from 2.0 V to -1 V. The reduction of Ag_2O_2 at “A” resulted in the current density being reduced from 550 A m^{-2} to 160 A m^{-2} , when 2.0 V was subsequently applied to the anode (Figure 8). Hence the activity of the anode towards oxygen

evolution is dependent upon the presence of Ag_2O_2 on the anode surface. Increased anode activity (higher current density) at *A* compared with *B* is due to the presence of more Ag_2O_2 on the anode at *A* than at *B*.

3.2.4 Relationship between Ag_2O_2 and current density on PbAg anodes

For various PbAg alloys operated at the same potential in sulphuric acid, a linear relationship was observed between the percentage of Ag as Ag_2O_2 in the oxide layer of PbAg alloys and the current density (Figure 11). The %Ag was calculated using

$$\% \text{Ag} = \frac{m(\text{Ag}) \text{ as } \text{Ag}_2\text{O}_2}{m(\text{Ag}_2\text{O}_2) + m(\text{PbO}_2)}$$

The masses of Ag_2O_2 and PbO_2 were determined from the cathodic charge for the reduction of Ag_2O_2 and PbO_2 , respectively, measured during cathodic potential sweeps. Rolled PbAg anodes (Ag = 0.63%, 0.42%) exhibited higher current densities than a cast PbAg(0.75%) anode. This may be due to more silver being available at the surface of rolled anodes than at the surface of cast anodes, allowing more silver to be oxidised to Ag_2O_2 .

3.3 Silver content in the oxide layers of Pb and PbAg anodes

The silver content in the oxide layers formed on PbAg anodes during operation at 500 A m^{-2} in 170 g L^{-1} at 40°C was also determined by collection of the oxide layer,

followed by dissolution and analysis for Ag and Pb. The results of these analyses were similar to those obtained from the charge during cathodic potential scans (see Table 1). Table 1 also shows that the concentrations of silver in the oxide layers of the PbAg alloys were all similar to the concentrations of Ag in the alloys. That the concentrations of silver in the oxide layer are similar to the concentration of silver in the alloy indicates that very little silver dissolves from a PbAg anode under these conditions. The similarity between the results obtained from voltammetry and chemical analysis also indicates that silver is present mainly as Ag_2O_2 . Considering the fact that Ag_2O_2 readily dissolves in sulphuric acid, it appears that Ag_2O_2 formed on PbAg alloy anodes is somehow stabilised, perhaps by incorporation into the PbO_2 matrix.

3.4 Discussion on the role of silver in reducing the corrosion rate of PbAg alloys

PbAg alloys have lower corrosion rates than pure lead metal anodes when polarised in sulphuric acid electrolytes (Rey et al., 1938). Studies of the corrosion mechanism of lead metal at potentials sufficient for oxygen evolution suggest that the mechanism by which lead metal is oxidised proceeds via attack from hydroxyl radicals, which are intermediates in the oxygen evolution reaction (Ai et al., 2004; Ai et al., 2005; Cong and Wu, 2007). Using the findings from this study it is postulated that during polarisation of PbAg anodes at the oxygen evolution potential, Ag in the PbAg alloy is oxidised to Ag_2O_2 and that Ag_2O_2 catalyses the oxidation of H_2O to O_2 . The higher rate of conversion of H_2O to O_2 likely results in a decreased lifetime of the hydroxyl radical

intermediate. Thus the concentration of hydroxyl radicals in the oxide layer on a PbAg anode is likely to be decreased relative to the case of a pure Pb anode, resulting in comparatively less oxidation of the PbAg substrate.

4. Conclusions

Oxidation of Ag anodes in $170 \text{ g L}^{-1} \text{ H}_2\text{SO}_4$ at 40°C at 1.99 V in the absence of manganese ions resulted in the initial formation of localized areas of Ag_2O_2 which acted as sites for the oxygen evolution reaction for a short period ($\sim 100 \text{ s}$). At longer times these sites appeared to become inactive which is thought to be due to the formation of a non-conducting layer of Ag_2SO_4 or silver peroxysulphate at the interface between the silver metal substrate and Ag_2O_2 . Eventually these inactive Ag_2O_2 regions spalled from the anode or dissolved in the electrolyte. In the presence of $5 \text{ g L}^{-1} \text{ Mn}$, the oxygen evolution reaction occurs in the first few minutes but thereafter is completely inhibited, probably because Ag_2O_2 is no longer able to be formed.

The presence of Ag_2O_2 on Pb electrodes anodised in sulphuric acid electrolytes containing silver was suggested by linear voltammetry and confirmed by x-ray diffraction. In the presence of increasing concentrations of silver ions, the potentiostatic anodisation of Pb anodes in sulphuric acid resulted in an increase in the current density,

and to a corresponding increase in the mass of Ag_2O_2 and a decrease in the mass of PbO_2 on the anode surface.

Voltammetric sweeps suggest that Ag_2O_2 was also formed on PbAg alloys anodised in sulphuric acid. As the concentration of Ag_2O_2 in the oxide layer on the surface of the PbAg anode increases so does the current density at anodes oxidised at the same potential. The superior performance of PbAg alloy anodes over Pb anodes is attributed to the presence of Ag_2O_2 in the PbO_2 layer on the metal substrate.

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The Role of Silver in Enhancing the Electrochemical Activity of Lead and Lead-Silver Alloy Anodes

Authors: J.J. McGinnity and M.J. Nicol

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- 1 table

Table 1 Ag concentrations in the oxide layers of PbAg alloys oxidised at 500 A m⁻²

Anode	Rolled/Cast	Duration (hrs)	Potential vs NHE (V)	% Ag in Alloy	% Ag in Oxide Layer (%)	
					via chemical assay	via voltammetric scan
Pb-0.42% Ag	Rolled	24.2	1.995	0.42	0.40	
		24.3	1.987		0.66	

Pb-0.63% Ag	Rolled	24.2	1.991	0.63	0.78	
		24.3	1.988		1.33	
		24.5	1.989			0.60
		4.62	1.997			0.98

Pb-0.75% Ag	Cast	24.3	1.992	0.75	0.63	
		24.3	1.983		0.64	

The Role of Silver in Enhancing the Electrochemical Activity of Lead and Lead-Silver Alloy Anodes

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- Figure Captions
- Figures and Tables (11 figures, 1 table)

Figure Captions

Fig. 1. Voltammetry of silver metal in $170 \text{ g L}^{-1} \text{ H}_2\text{SO}_4$ (H_2SO_4) and $170 \text{ g L}^{-1} \text{ H}_2\text{SO}_4 + 5 \text{ g L}^{-1} \text{ Mn}$ ($\text{H}_2\text{SO}_4 + \text{Mn}$) at 40°C . Forward scan rate: 50 mV/s . Reverse scan rate: 20 mV/s

Fig. 2. Current density on a silver anode in $170 \text{ g L}^{-1} \text{ H}_2\text{SO}_4$ with and without $5 \text{ g L}^{-1} \text{ Mn}$ at

Fig. 3. Effect of increasing silver concentration on the current density at a Pb anode at 1.95 V in H₂SO₄ at 40°C.

Fig. 4. Linear voltammetric sweeps of platinum and lead anodes after polarisation at 1.95 V in sulphuric acid at 40°C. Note: Scan rate = 5 mVs⁻¹

Fig. 5. Effect of Ag₂O₂ surface density on current density at a Pb anode at 1.95 V in H₂SO₄ with 0-40 ppm Ag at 40°C

Fig. 6. XRD spectrum of the surface of a Pb sheet after anodisation at 2.0 V in 170 g L⁻¹ H₂SO₄ + 200 ppm Ag

Fig. 7. Comparisons of the electrocatalytic activity of 2 ppm Ag on electrodes with an initial surface of (I) Pb and (II) PbO₂, at 1.95 V in 170 g L⁻¹ H₂SO₄ at 40°C.

Inset: Comparisons of the electrocatalytic activity in the first five minutes

Fig. 8. Current density and potential versus time plots for a PbAg (0.63%) alloy in 170 g L⁻¹ at 40°C.

Fig. 9. Expanded view of current density and potential versus time plot from Figure 8.

Fig. 10. Voltammetric scans of surface oxidation product on a PbAg alloy anode after 239 min (A), 43 min (B) and 10 min (C) oxidation at 2.0 V in 170 g L⁻¹ sulphuric acid at 40°C

Fig. 11. Effect of Ag concentration in the oxide layer on the current density at various PbAg anodes at 2.0 V in 170 g L⁻¹ H₂SO₄ at 40°C. Note: The times for which the anodes were held at constant potential are given alongside each data point.

ACCEPTED MANUSCRIPT

Figures and Tables

Figure 1.

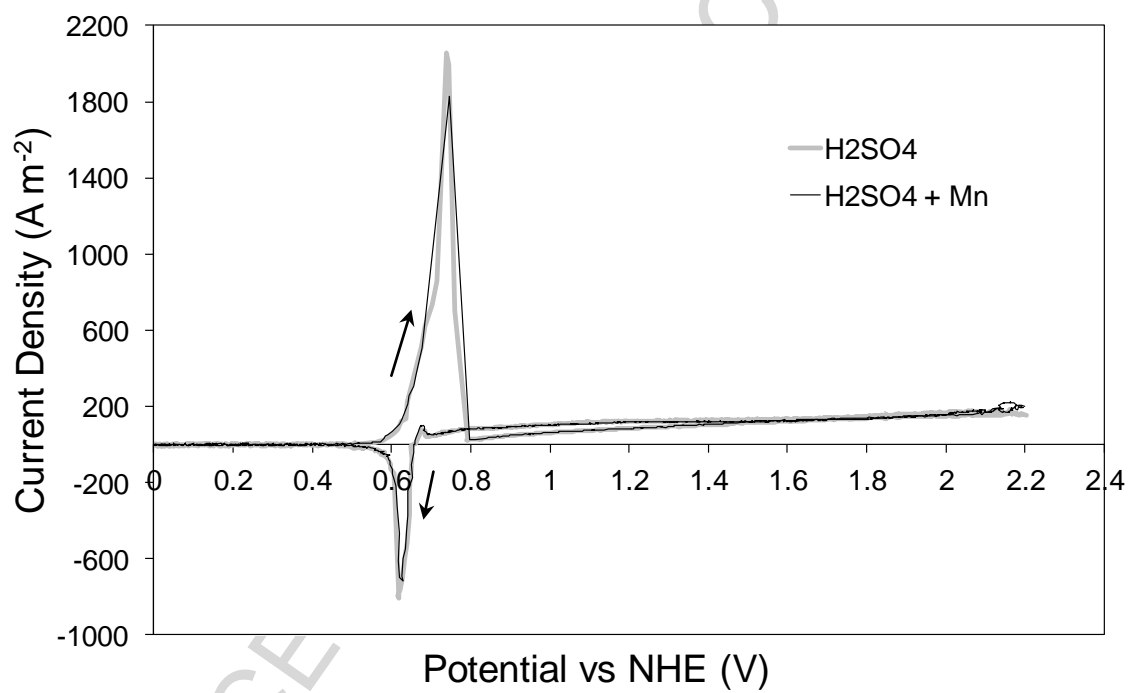


Figure 2.

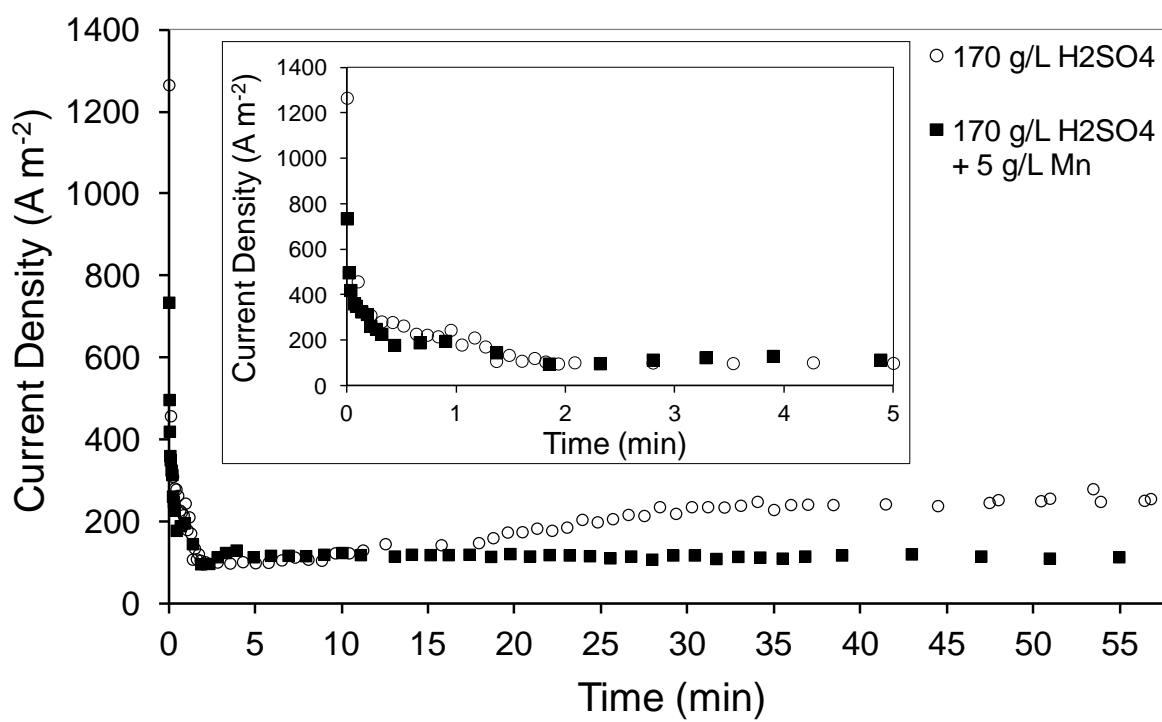


Figure 3.

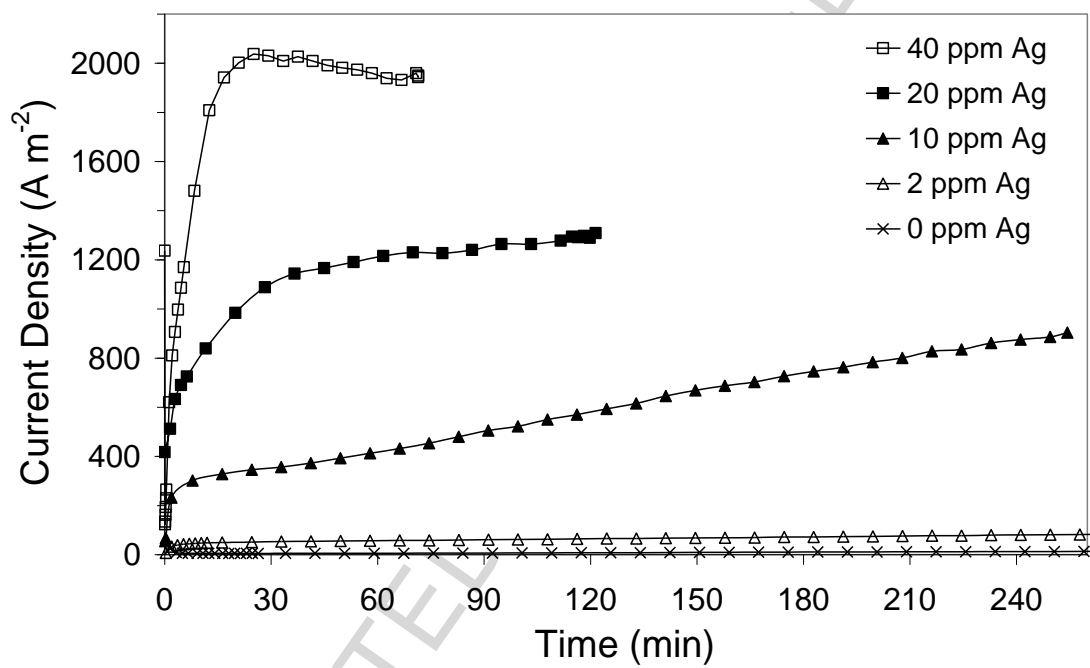


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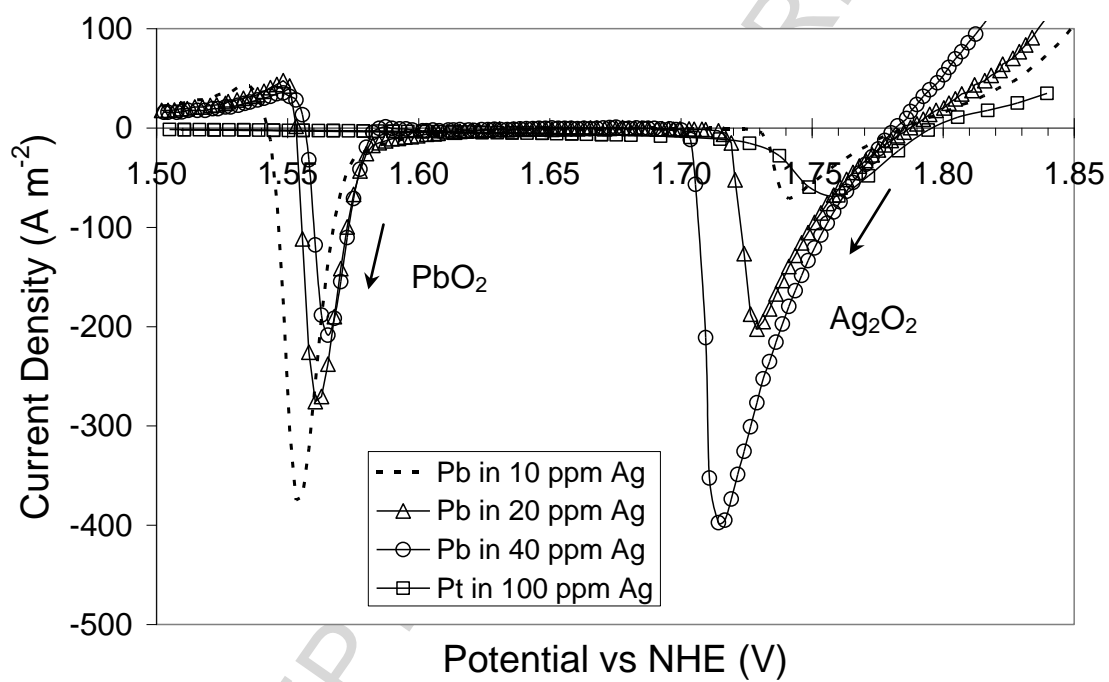


Figure 5.

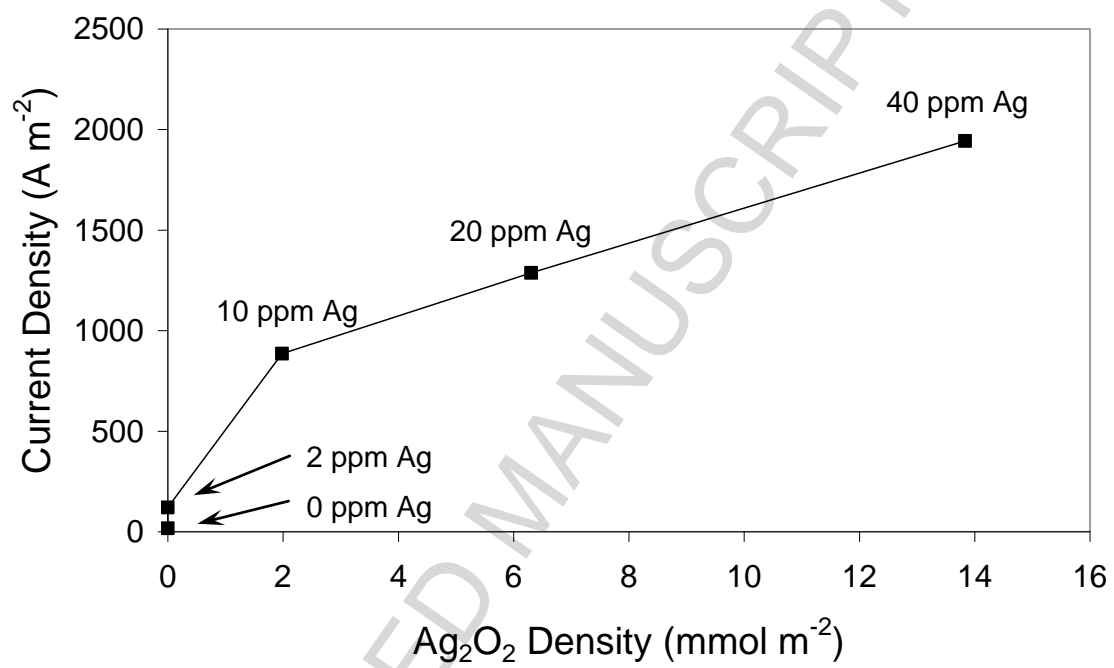


Figure 6.

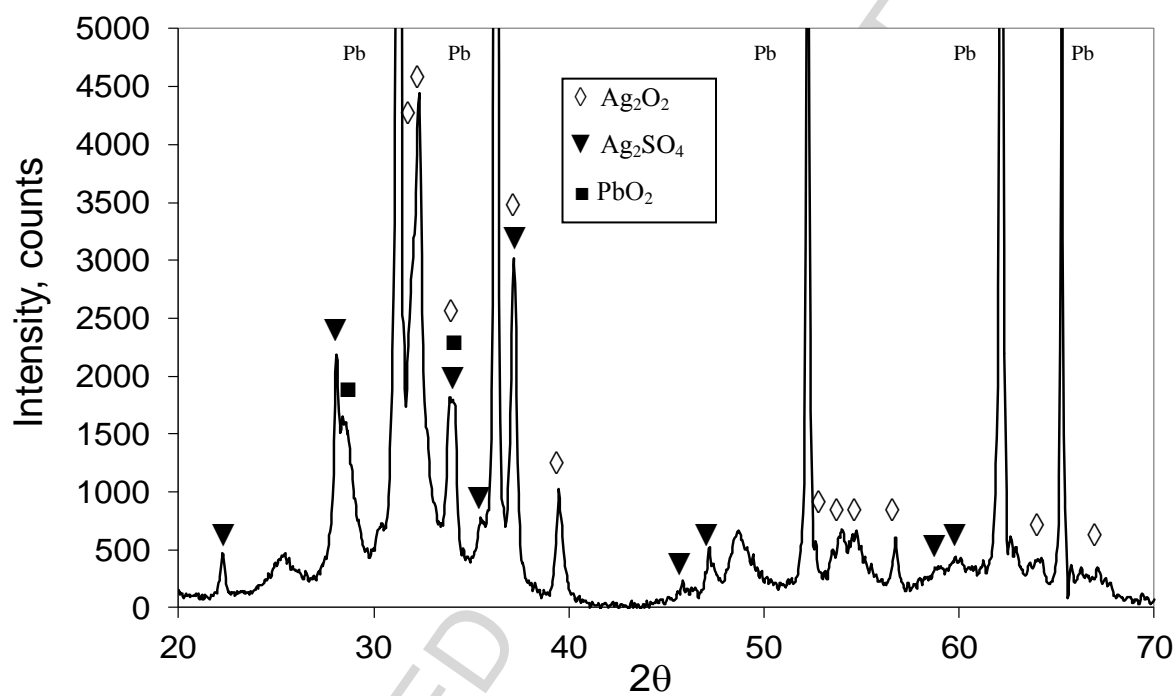


Figure 7.

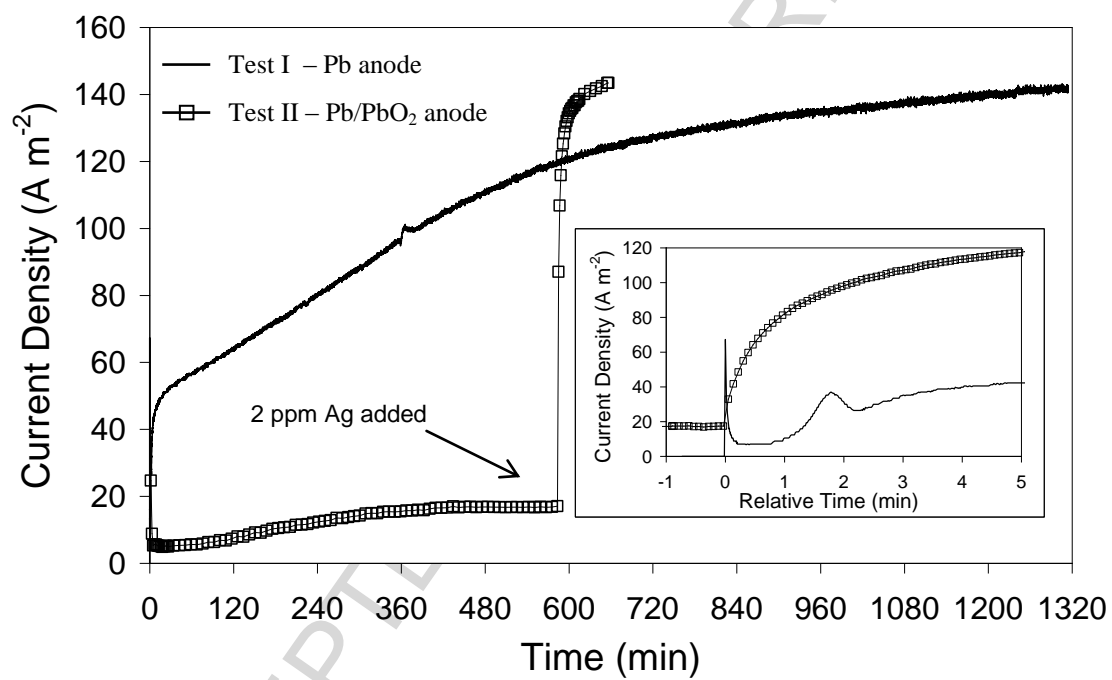


Figure 8.

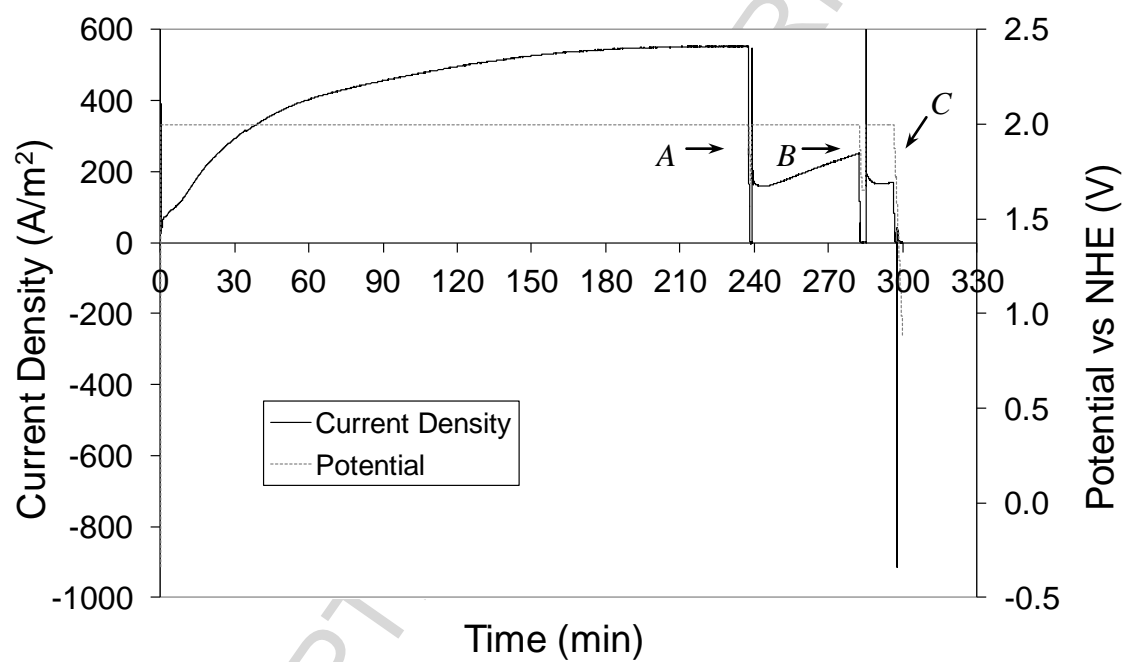


Figure 9.

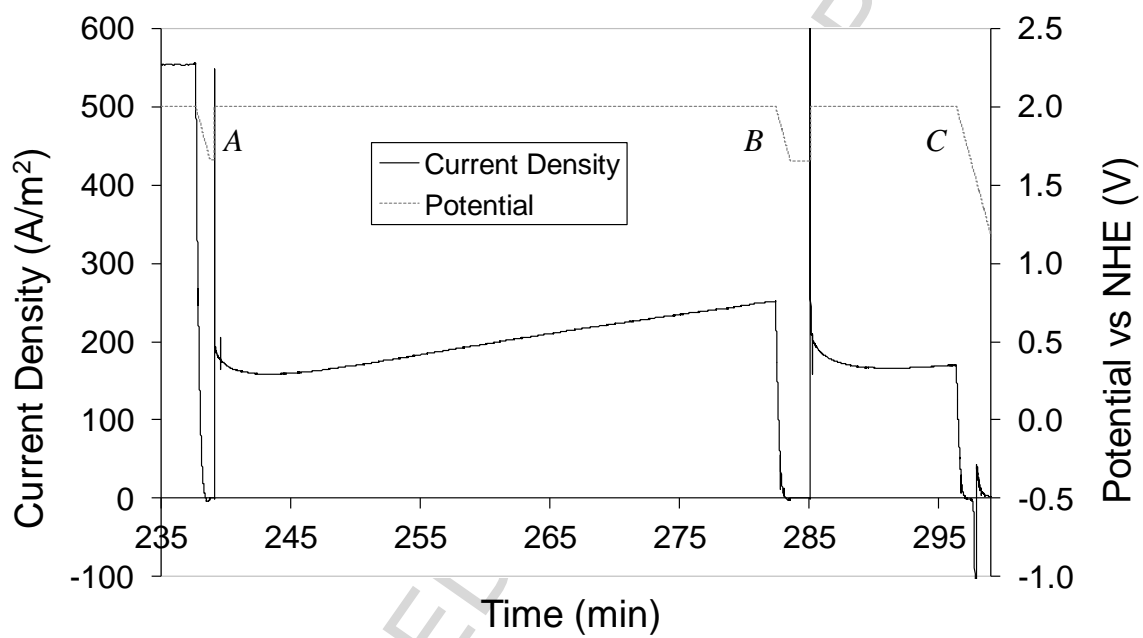


Figure 10

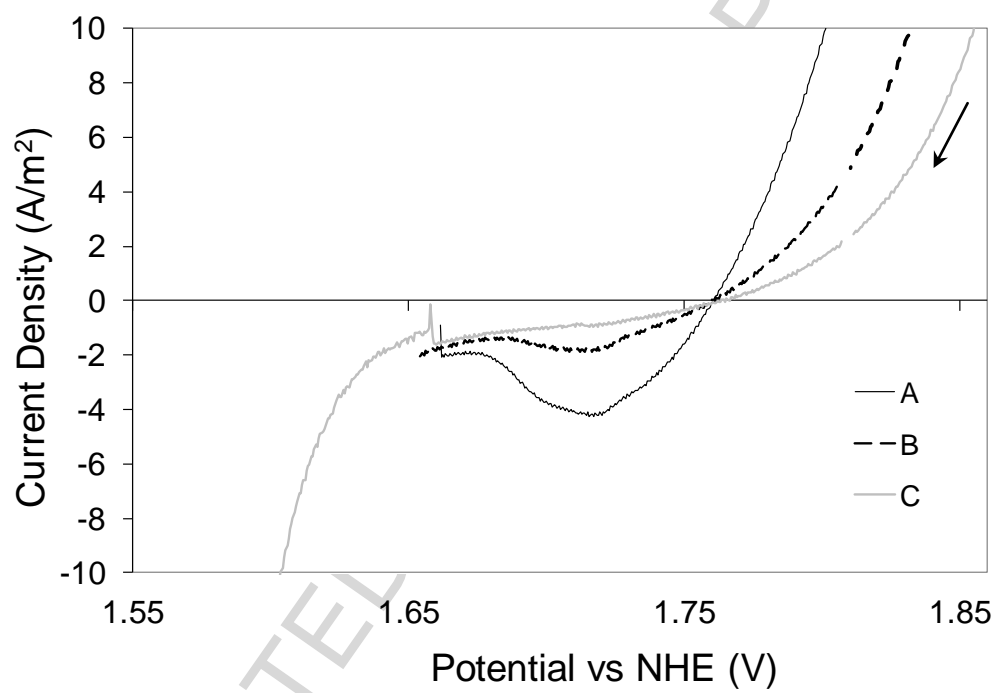
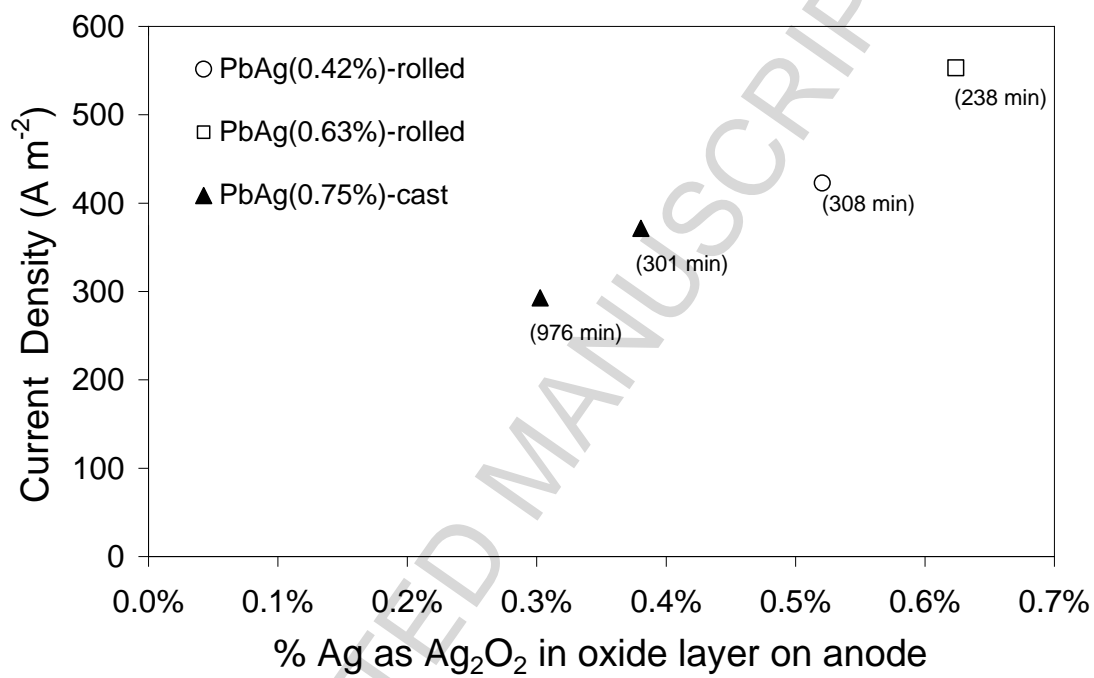


Figure 11.



Highlights

- Studied the role of silver in PbAg alloys in reducing the overpotential of the OER
- Ag_2O_2 was observed on Pb anodes in sulphuric acid containing silver ions
- Evidence given for presence of Ag_2O_2 on PbAg anodes in sulphuric acid
- The enhanced electrochemical activity of PbAg alloy anodes is attributed to Ag_2O_2