

Electrochemical behaviour of lead electrode in sulfuric acid solution containing citric acid

Guo-Lin Wei*, Jia-Rong Wang

Department of Chemistry, Shanghai University of Science and Technology, Jiading, Shanghai 201800, China

Received 10 January 1994; accepted 31 March 1994

Abstract

The electrochemical behaviour of a lead electrode as the positive electrode (in PbO_2 form) and the negative electrode of a lead/acid battery in sulfuric acid solution containing different concentrations of citric acid has been studied by cyclic voltammetry. For the behaviour of lead as a positive electrode, a new layer of PbO_2 is formed in the presence of citric acid. It is difficult for this layer to be reduced and, therefore, the conductivity between the positive grid and the positive active material will be greater than that in pure sulfuric acid solution. The peak currents attributed to the formation and reduction of PbO_2 , and to the evolution of oxygen, increase with the concentration of citric acid. The limits of the effects are reached at about 2 g/l citric acid in 4.5 M H_2SO_4 . For the behaviour of lead as a negative electrode, the peak currents attributed to the oxidation of lead to PbSO_4 , and to the evolution of hydrogen gas also increase with the concentration of citric acid. In 4.5 M H_2SO_4 , the limits of these effects are reached at a citric acid concentration of 2 and 3 g/l, respectively. The observed behaviour is caused by the adsorption of citric acid on the PbO_2 , lead and PbSO_4 surfaces.

Keywords Lead electrodes, Sulfuric acid; Citric acid

1. Introduction

Many attempts have been made [1–11] during the last decade to understand the electrochemical behaviour of lead, as the positive electrode (in PbO_2 form) and/or the negative electrode of the lead/acid battery, in sulfuric acid solution containing various kinds of additives.

The purpose of these studies has been to find suitable additives for positive/negative electrodes and/or for the sulfuric acid electrolyte in order to modify the charge/discharge properties of the lead/acid battery. The additives that have been studied most often are inorganic ions in sulfate form, especially those that are also used as positive-grid alloying elements, e.g., Sb^{3+} , Sb^{5+} [1–3] and Sn^{2+} [4,5]. The number of organic additives that have been examined is relatively small [9–11]. In order to evaluate the practical effect of a solution additive on the operational characteristics of the lead/acid battery and to understand the dynamic mechanism, it is necessary to study the electrochemical behaviour of lead as both the positive and the negative electrodes in sulfuric acid solution containing the additive.

In our recent work, we found that the addition of citric acid to sulfuric acid solution was effective in increasing the capacity of the lead/acid battery. For a hand-made battery with a theoretical capacity of 8.6 Ah, when discharged at a current of 300 mA until the voltage reached 1.7 V, the capacity increased from 2.7 to 3.40 Ah when 0.80 wt.% citric acid was added, respectively, to 1.10 sp. gr. H_2SO_4 solution used for plate formation and to 1.28 sp. gr. H_2SO_4 solution used for discharge. The cycleability was also prolonged. In the present paper, an attempt has been made to estimate the effect as a whole, and to understand the mechanism. Cyclic voltammetry has been used and the potential limits have been extended into the oxygen- and hydrogen-evolution regions.

2. Experimental

In all experiments, a conventional 100 cm^3 capacity spherical cell was used. The working electrode with an apparent area of 0.28 cm^2 was made from pure lead (99.999 wt.%) set in a glass tube with epoxy. The electrode surface was in an upright direction so that the gas formed could escape from the electrode surface easily. The counter electrode was a platinum plate of

*Corresponding author

1 cm×1 cm geometric area. A Hg/Hg₂SO₄ electrode containing the same solution as that in the cell served as the reference electrode. All potentials are reported with respect to this electrode. The reference electrode was equipped with a luggin capillary. Before each experiment, the lead electrode was polished carefully with emery papers and then polarized at -1.2 V for 5 min in order to obtain a reproducible electrode surface. A 4.5 M H₂SO₄ solution was prepared from concentrated H₂SO₄ and doubly-distilled water. Solutions containing 0.4, 1.2, 2.0, 4.0 and 6.0 g/l citric acid were prepared by dissolving a certain amount of citric acid in 4.5 M H₂SO₄. It is difficult for citric acid to be dissolved completely when a quantity of more than 6 g/l is present. All reagents used were AR grade.

The instrumental equipment used in this work was a JH-2C potentiostat connected to a XFD-8A signal generator. Cyclic voltammograms were recorded on a LZ3-204 X-Y functional recorder. All experiments were carried out at 30±0.1 °C.

In the study of the electrochemical behaviour of lead as a positive electrode, the electrode was cycled between 900 and 1500 mV at a rate of 10 mV/s for 4 h. After that, the scanning potential range was extended to between 900 and 1700 mV with the scan rate being kept at 10 mV/s. A stabilized 'control' curve due to the evolution of oxygen gas and to the growth of the lead anodic film could be readily obtained in such a way.

As for the study of the electrochemical behaviour of lead as a negative electrode, the electrode was cycled between -750 and -1150 mV at 10 mV/s for 4 h before a 'control' curve was recorded. To obtain a constant voltammetric response due to hydrogen-gas evolution, the electrode had been cycled between -1100 and -1500 mV at 10 mV/s for 2 h before the linear potential sweep curve from -1100 to -1500 mV was recorded.

3. Results and discussion

3.1. Electrochemical behaviour of lead as a positive electrode

Cyclic voltammograms between 900 and 1500 mV for a lead electrode on the third cycle in the absence or presence of citric acid are presented in Fig. 1. When no or only 0.4 g/l citric acid is present in 4.5 M H₂SO₄, the cathodic current peaks appearing at 1120 and 1045 mV can be ascribed, respectively, to the reduction of β -PbO₂ and α -PbO₂ to PbSO₄ [12]. When the sulfuric acid solution contains about 1.2 to 6.0 g/l citric acid, a third reduction peak appears at 1020 mV due to the reduction of a new layer of PbO₂. The α -PbO₂ reduction peak shifts positively to 1065 mV, but the β -PbO₂

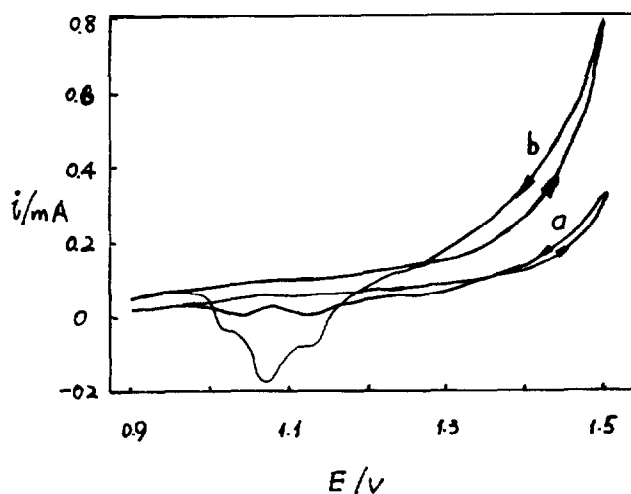


Fig. 1. Cyclic voltammograms for lead in 4.5 M H₂SO₄ with (a) 0, and (b) 2.0 g/l citric acid; scan rate 10 mV/s; cycle number 3.

reduction peak remains at 1120 mV. A similar effect was observed by Laitinen and Watkins [13] and Bullock and McClelland [14] when H₃PO₄ was added to sulfuric acid. The shift in the peak for α -PbO₂ is also demonstrated by the fact that the height of this peak increases with cycle number and eventually overlaps the peak for β -PbO₂ (see below). As for the new peak, when 1.2 g/l or more citric acid is present, neither the height nor the position changes with either the cycle number or the concentration of citric acid. This effect can be attributed to the adsorption of citric acid on the active sites of PbO₂. The citric acid adsorbs on the PbO₂ and causes the three-dimensional growth of PbO₂ to be inhibited and the two-dimensional growth to be enhanced. This results in the formation of a more dense layer of PbO₂. This new layer of PbO₂ formed in the presence of citric acid is more difficult to be reduced than that produced from pure sulfuric acid. Thus, when citric acid is present in sulfuric acid solution during plate formation and the operation of lead/acid batteries, the insulating sulfate layer between the positive grid and the active material will be replaced (at least partially) by a PbO₂ layer and the conductivity will become greater. This will be beneficial to the charge/discharge properties of the positive electrode as well as to the cycle life of lead/acid batteries.

It can be seen in Fig. 1 that the reduction peak currents of both β -PbO₂ and α -PbO₂ at cycle 3 are larger when H₂SO₄ is added with 2.0 g/l citric acid. The heights of these two peaks increase with cycle number and gradually they overlap to become one peak (Fig. 2). The overall currents peak appears at about 1060 mV. The plot of this peak current at cycle 60 (after cycling between 900 and 1500 mV for 4 h), I_{PbO_2} , as a function of citric acid concentration is shown by curve (a) in Fig. 3. The current increase is observed up to a concentration of 2 g/l and then remains constant.

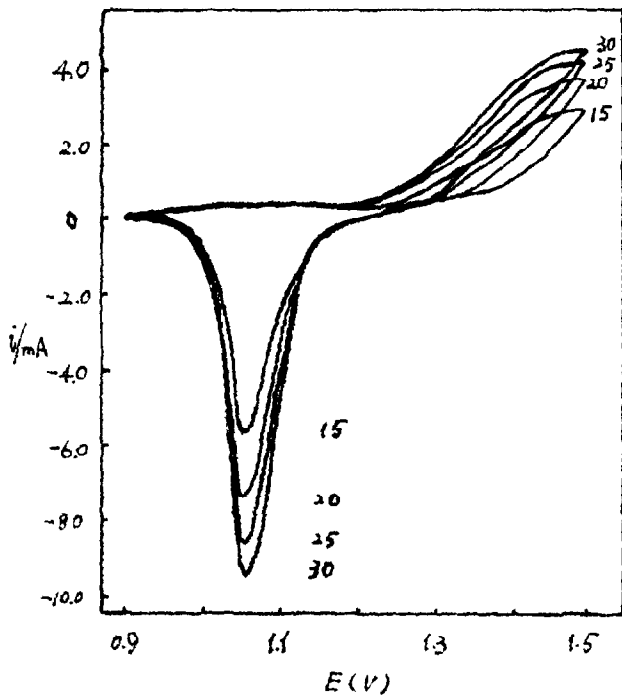


Fig. 2. Cyclic voltammograms for lead in 4.5 M H_2SO_4 with 2.0 g/l citric acid; scan rate: 10 mV/s. The number on the curve shows the cycle number.

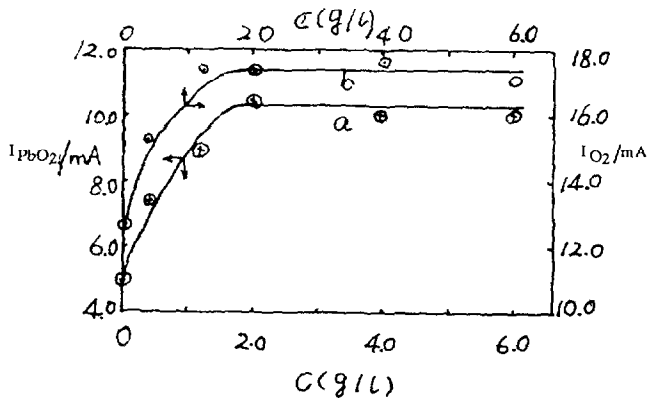


Fig. 3. Effect of citric acid concentration on electrochemical behaviour of lead as a positive electrode in 4.5 M H_2SO_4 ; curve (a) I_{PbO_2} , and (b) I_{O_2} .

In a cyclic voltammetric experiment between 900 and 1700 mV, an obvious oxidation current peak due to the formation of $\beta\text{-PbO}_2$ is observed (Fig. 4). This peak appears at 1490 mV when no or only 0.4 g/l citric acid is present, and at 1450 mV when 1.2 g/l or more citric acid is present. Hence, citric acid assists the formation of $\beta\text{-PbO}_2$. The corresponding reduction peak always appears at 1060 mV (Fig. 4), regardless of the presence of citric acid. The relationship between the formation and reduction peak currents of $\beta\text{-PbO}_2$ with the concentration of citric acid is similar to that of I_{PbO_2} shown by curve (a) in Fig. 3, i.e., the peak currents increase at first and then remain invariable. This phenomenon

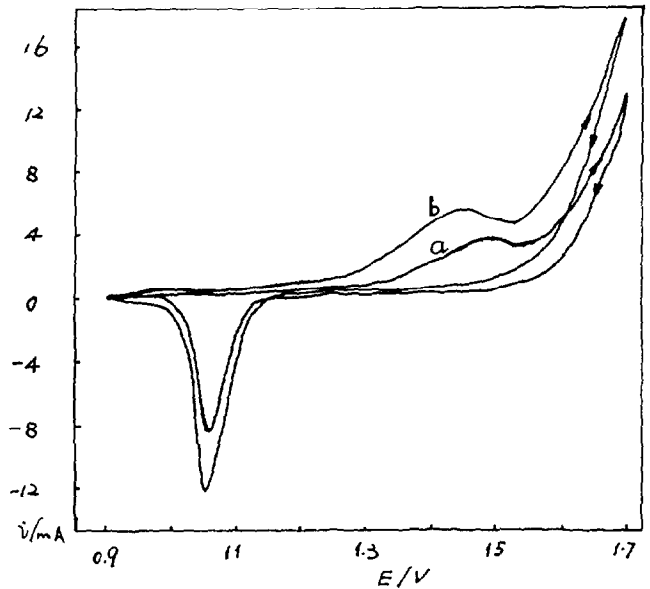


Fig. 4. Cyclic voltammograms for lead in 4.5 M H_2SO_4 with (a) 0, and (b) 2.0 g/l citric acid after cycling between 900 and 1500 mV for 4 h; scan rate: 10 mV/s.

may still be caused by the adsorption of citric acid. Citric acid acts as a surface-active agent. It will adsorb on the PbO_2 surface, especially on those sites that are growing at the fastest rate. PbO_2 formed in such a way has a greater surface area and will give a larger reduction peak currents. The resulting PbSO_4 that is formed in the presence of citric acid may also have a greater surface area. This will be beneficial to the formation of PbO_2 . Once the saturated adsorption of citric acid is reached, any increases in the concentration of citric acid will not enhance the effects further.

The sharp rise in the anodic current following the formation of $\beta\text{-PbO}_2$ is caused by the evolution of oxygen gas. The change in the current value at 1700 mV, I_{O_2} , with the concentration of citric acid is also given in Fig. 3 (curve (b)). I_{O_2} can be used as a measurement of oxygen-gas evolution. The behaviour is the same as that observed for I_{PbO_2} , curve (a). The increase in I_{O_2} with the concentration of citric acid may be caused by the increase in the amount of PbO_2 that has been formed and/or by the decrease in the overpotential required for the oxygen-gas evolution process when citric acid is present.

3.2. Electrochemical behaviour of lead as negative electrode

Fig. 5 presents the cyclic voltammograms for a lead electrode after being cycled between -750 to -1150 mV for 4 h. The anodic current peak is caused by the oxidation of lead to PbSO_4 . The peak position shifts from -920 mV when no citric acid is present to -900 mV when even 0.4 g/l citric acid is added to 4.5 M H_2SO_4 . The passivation caused by the oxidation process

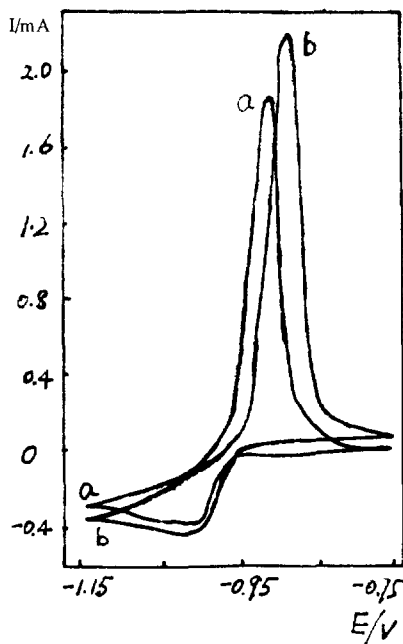


Fig 5 Cyclic voltammograms for lead electrode after being cycled between -750 to -1150 mV for 4 h in 4.5 M H₂SO₄ with (a) 0, and (b) 2.0 g/l citric acid; scan rate: 10 mV/s

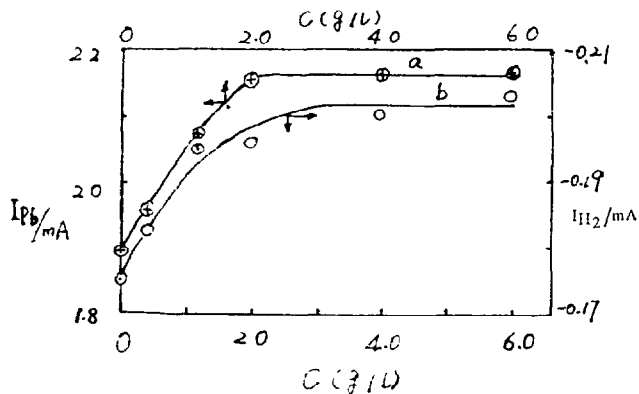


Fig 6 Effect of concentration of citric acid on electrochemical behaviour of lead in 4.5 M H₂SO₄; curve (a) I_{pb} , and (b) I_{H_2}

of lead to PbSO₄ is inhibited by citric acid. This will assist the discharge process of the negative plate of the lead/acid battery. The anodic current peak value, I_{pb} , is greater when citric acid is added. The dependence of I_{pb} on the concentration of citric acid is shown by curve (a) in Fig. 6. It increases with concentration up to 2 g/l, but does not change further from 2 to 6 g/l. An enhancement in the I_{pb} value is also observed when a lead electrode is cycled first in pure H₂SO₄ and then in H₂SO₄ containing citric acid (e.g., 4 g/l).

The above experimental procedure is similar to that reported by Mahato [11], in an evaluation of the expander activity of lead/acid battery negative electrodes. Citric acid will adsorb on lead sulfate during the oxidation of lead to PbSO₄. This results in the formation of a porous layer of PbSO₄ that will inhibit passivation

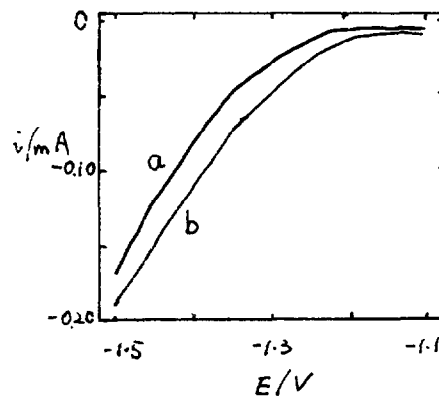


Fig. 7. Stabilized linear potential sweep curves for hydrogen evolution on a lead electrode in 4.5 M H₂SO₄ with (a) 0, and (b) 2.0 g/l citric acid, scan rate 10 mV/s

of the lead surface. During the reduction of PbSO₄, citric acid may also adsorb on the electrode surface and the resulting lead will have a larger surface area and will give a greater capacity than that produced in pure H₂SO₄. Thus, the presence of citric acid will be beneficial to both the charge and the discharge process of the lead/acid negative electrode. The limits of these effects are reached when the adsorption of citric acid on the lead or PbSO₄ surfaces reaches a saturation level.

Stabilized linear potential sweep curves due to the evolution of hydrogen on a lead electrode are shown in Fig. 7. The current value at -1500 mV, I_{H_2} , can be used as a measurement of the hydrogen evolution. The value increases with the concentration of citric acid from -0.175 mA in pure 4.5 M H₂SO₄ to -0.202 mA in 4.5 M H₂SO₄ with 3 g/l citric acid and then levels off at 3 to 6 g/l. The observed increase in I_{H_2} can be attributed to a lowering of the hydrogen overpotential in the presence of citric acid. Taking I_{H_2} as a measurement of charge inefficiency [1], it is possible for citric acid to decrease the charge efficiency of the lead electrode in a lead/acid battery. This requires further demonstration with a real battery.

4. Conclusions

With respect to the electrochemical behaviour of lead as the positive electrode of the lead/acid battery, a new layer of PbO₂ is formed in the presence of citric acid. This layer is difficult to be reduced and this will be beneficial to the operation of a lead/acid battery. The peak currents associated with the formation and reduction of PbO₂ and with evolution of oxygen increase with increase in the concentration of citric acid. The limits of these effects are reached at a citric acid concentration of 2 g/l in 4.5 M H₂SO₄.

Concerning the electrochemical behaviour of lead as the negative electrode of the lead/acid battery, the

passivation caused by the formation of PbSO_4 is inhibited by the presence of citric acid. The peak currents due to the oxidation of lead to PbSO_4 and to the evolution of hydrogen both increase with the concentration of citric acid up to 2 and 3 g/l, respectively, but do not increase further with concentrations up to 6 g/l.

The influence of citric acid on the oxidation and reduction process of lead as the positive and negative electrodes of the lead/acid battery is caused by the adsorption of citric acid on the surface of PbO_2 , lead and PbSO_4 . The presence of citric acid in H_2SO_4 is beneficial to the charge/discharge processes of the lead/acid battery, but may decrease the charge efficiency by enhancing the gas-evolution process.

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