# Effect of bismuth on hydrogen evolution reaction on lead in sulfuric acid solution

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## Abstract

The effect of bismuth on hydrogen evolution on lead in sulfuric acid solution is investigated by linear potential sweep, alternating current (ac) impedance, X-ray diffraction (XRD) and hydrogen-collection experiments. First, hydrogen evolution behaviour on commercial lead with and without bismuth and on pure bismuth is compared. It is found that the hydrogen evolution reaction takes place more easily on bismuth than on lead, but that the commercial lead with 50 ppm bismuth has a slower hydrogen evolution than the commercial lead without bismuth. Next, the effect of bismuth is studied. Bismuth is added to lead at 0–7.33 wt.% to make lead–bismuth alloys, or is deposited chemically on the surface of lead to form a bismuth-containing lead. The results from X-ray diffraction show that the prepared lead–bismuth alloys have the same crystal structure as pure lead, i.e., the added bismuth enters into the lead crystals. Apparently, chemically-deposited bismuth does not enter into the lead crystals, but is independent of but contact electronically with the lead. The results, obtained from linear potential sweep, ac impedance and hydrogen evolution volume measurements, show that the rate of hydrogen evolution depends on the amount of bismuth in or on the lead. It is concluded that bismuth accelerates the hydrogen evolution reaction on lead, irrespective of whether it enters the lead crystals or not. By contrast, the hydrogen evolution reaction is less dependent on bismuth in lead–bismuth alloys than on bismuth that is chemically deposited on lead and the effect of bismuth can be neglected if the alloy electrode is not taken to a very negative potential.
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## 1. Introduction

The hydrogen evolution reaction occasionally takes place on negative electrodes in lead–acid batteries. In valve-regulated lead–acid (VRLA) batteries it reduces the amount of water and may lead to battery failure [1]. The battery industry has been making every effort to inhibit the hydrogen evolution reaction, especially for VRLA batteries to which water cannot be added after use. Since bismuth is a metal on which the hydrogen evolution reaction has a lower overpotential than on lead, its existence in the lead alloys used for battery grids is believed to be detrimental. It is difficult, however, to remove bismuth from lead because of the chemical similarity of the two metals. Much work has been performed to understand the effect of bismuth on battery performance [2–10].

Rice [2] and Johnson et al. [3] have suggested that bismuth can enhance the hydrogen evolution overpotential for lead alloys with 0–5 wt.% bismuth in 0.05 M $H_2SO_4$ solution. Lam et al. [4] reported that the effect of bismuth on hydrogen evolution depends on the electrode potential. They found that the effect of bismuth can be neglected for the lead alloys with 0.05–0.06 wt.% bismuth at potentials from $-1.2$ to $-1.5$ V (versus $Hg|Hg_2SO_4$), but bismuth enhances the hydrogen evolution rate when the potential is more negative than $-1.5$ V. Papageorgiou and Skyllas-Kazacos [6] showed that

the effect of bismuth on the kinetics of hydrogen evolution is related to the surface state of the lead alloy. For instance, the hydrogen evolution overpotential decreases with increasing content of bismuth on non-etched lead–bismuth alloys, but is dependent on the surface state rather than the content of bismuth on etched alloy–bismuth alloys. Apparently, the role bismuth plays in lead–bismuth alloys is not well understood. The purpose of this paper is to understand the effect of bismuth on the hydrogen evolution reaction on lead by studying the behaviour on pure lead, pure bismuth, lead–bismuth alloys, and lead with chemically-deposited bismuth.

## 2. Experimental

### 2.1. Electrode preparation

Commercial lead (99.99 wt.%) metal, commercial bismuth-bearing (50 ppm) lead metal and a bismuth (99.999 wt.%) metal were used. The compositions of the commercial lead and the bismuth-bearing lead are listed in Table 1. Electrodes were prepared as follows: metals, single or double, were melted at 460 °C, mixed by stirring, cast as cylinders and sealed with epoxy resin to leave a disc with a diameter of 6.18 mm. The lead electrode with chemically-deposited bismuth was prepared by dipping a lead electrode in 2 mM $Bi_2(SO_4)_3$ solution for a set time. The content of bismuth in the prepared lead–bismuth alloys was determined by means of ICP (P-4010, Hitachi). The crystal structures of the alloys were determined by X-ray diffraction (XRD; D/MAX2100PC, Rigaku) and the cell constant for a cubic crystal was calculated according to:

$$d = \frac{a}{(h^2 + l^2 + k^2)^{1/2}} \tag{1}$$

where $d$ is the distance between the crystal planes, ($h, k, l$) is the crystal plane index, and $a$ is the cell constant.

### 2.2. Electrochemical measurements

Linear potential sweep and alternating current (ac) impedance experiments were performed with a PGSTAT-30 instrument (Autolab, Eco Echemie B.V. Company) and a three-electrode cell. The prepared electrodes were used as working electrodes. A platinum electrode with a large area was used as the auxiliary electrode. The reference electrode was $Hg|Hg_2SO_4|1.28g.cm^{-3}$ $H_2SO_4$. All potentials are reported with respect to this reference electrode. Before

each experiment, the working electrode was polished with a silicon carbide paper of 1200 grit, washed with deionized and double-distilled water, degreased with ethanol, and pre-polarized at −1.2 V for 10 min. The working surface was perpendicular to the solution surface during experiment. In the measurement of ac impedance, the frequencies employed were between $10^5$ and 0.5 Hz and the amplitude of the ac voltage was 10 mV. In the application of an equivalent circuit, a constant phase element (CPE) was used. The impedance ($Z$) of a CPE can be obtained via the following relationship [11–13]:

$$Z = [Q(j\omega)^n]^{-1} \tag{2}$$

where $\omega$ is the frequency of the alternating current, $Q$ is a combination of properties related to both the surface and the electroactive species, and the exponent $n$ is the slope of the impedance–frequency Bode plot. The CPE has the properties of a capacitance when $0.5 < n < 1$. With the values of $Q$ obtained by fitting experimental data with a Randle equivalent circuit, the double layer capacitance ($C$) at different potentials can be obtained by [14,15]:

$$C = Q(\omega'')^{n-1} \tag{3}$$

where $\omega''$ is the frequency at which the imaginary part of impedance is at a maximum.

### 2.3. Hydrogen collection

Hydrogen-collection experiments were performed at constant potentials with a potentiostat/galvanostat (Model 363, EG&G) in a three-electrode cell. The auxiliary electrode and the reference electrode were the same as in electrochemical measurements described above. Hydrogen evolved on the working electrode was collected and its volume was measured. The electrolyte was 4.79 M $H_2SO_4$ solution, which was prepared with de-ionized and double-distilled water and analytic grade $H_2SO_4$. All experiments were conducted at ambient temperature.

## 3. Results and discussion

### 3.1. Commercial lead and bismuth-bearing lead

The cathodic polarization curves shown in Fig. 1 are for an electrodes made from commercial lead, (denoted as the 'Pb electrode'), and a commercial bismuth-bearing lead, denoted as the 'Bi–Pb electrode'. Current densities on both electrodes

Table 1
Composition of commercial lead

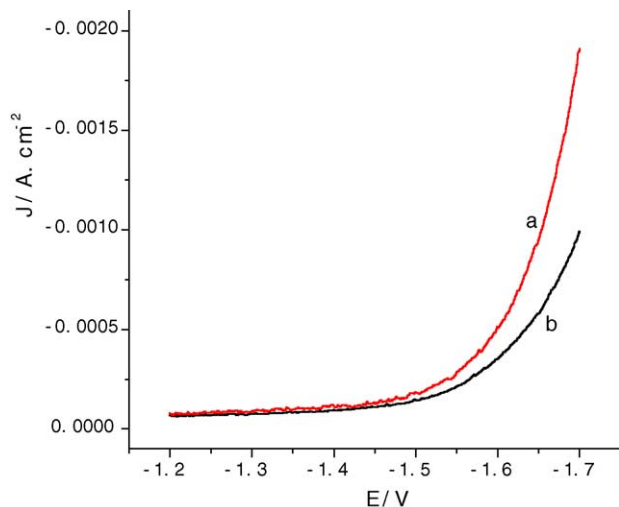| | Element (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Ag | Zn | Fe | Cu | Sb | Sn | Bi | As |
| Lead | 0.65 | 0.42 | 1.14 | 3.26 | 1.21 | 0.96 | 2.00 | 0.95 |
| Bismuth-bearing lead | 10.00 | 2.00 | 0 | 1.00 | 1.00 | 2.00 | 50.00 | 10.00 |

Fig. 1. Cathodic polarization curves of: (a) Pb and (b) Bi–Pb electrodes in 4.79 M $H_2SO_4$ solution; scan rate = 2 mv s$^{-1}$.

change little at potentials from $-1.2$ to $-1.3$ V, which indicates that it is difficult for the hydrogen evolution reaction to take place on both electrodes. As the potential becomes more negative, the current densities on both electrodes increase. The current on Pb electrode is larger than that on Bi–Pb electrode at the same potential and the difference in current density between two electrodes becomes more and more significant with increasing negative potential. Apparently, hydrogen evolution reaction takes place on a Pb electrode more easily than on a Bi–Pb electrode.

The variation in hydrogen evolution volume with time on Pb and Bi–Pb electrodes in 4.79 M $H_2SO_4$ solution at $-1.4$ and $-1.5$ V is shown in Fig. 2. It is found that hydrogen can be collected, which indicates that hydrogen evolution takes place on both electrodes at these potentials. The hydrogen evolution volume on Pb is larger than that on Bi–Pb at the same potential and the difference in hydrogen evolution volume between two electrodes becomes more significant with increasing negative potential. This is in agreement with the results obtained from cathodic polarization experiment.

Nyquist plots for Pb and Bi–Pb electrodes at $-1.5$ V are presented in Fig. 3. The characteristic semicircle indicates that a hydrogen evolution reaction is taking place on both electrodes is controlled by a charge-transfer step. The diameter of the semicircle is the reaction resistance for hydrogen evolution. The reaction resistance obtained by fitting with a Randle equivalent circuit is 95.5 and 484.1 $\Omega$ cm$^2$ for Pb and Bi–Pb electrodes, respectively. The larger reaction resistance for hydrogen evolution on Bi–Pb demonstrates that the hydrogen evolution reaction on Pb is far easier than that on Bi–Pb.

From the results shown in Figs. 1–3, it is concluded that the hydrogen evolution reaction takes place less easily on a bismuth-bearing lead electrode than on a lead electrode. It appears that bismuth can inhibit the hydrogen evolution reaction. The composition of the bismuth-bearing lead is,
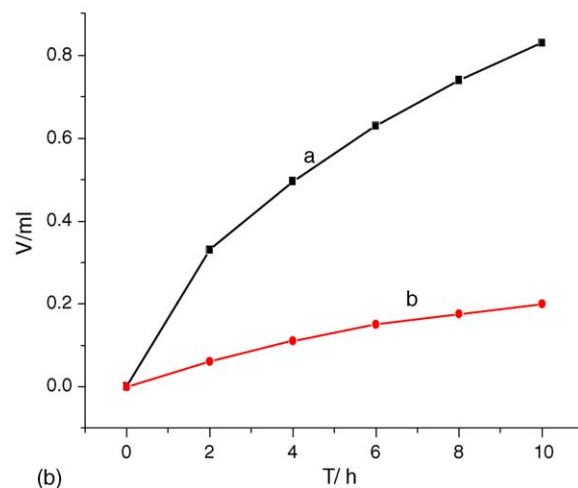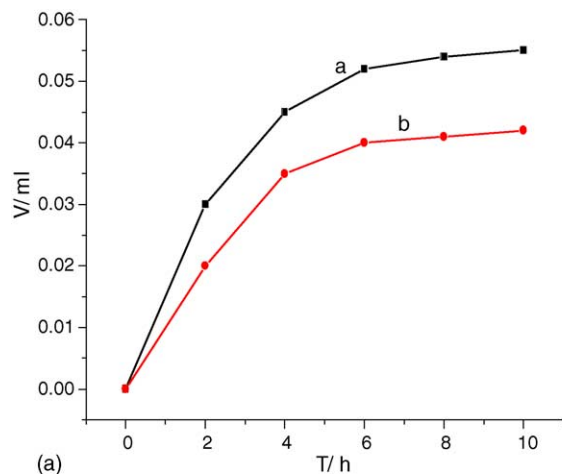


Fig. 2. Variation in hydrogen evolution volume with time on: (a) Pb and (b) Bi–Pb electrodes in 4.79 M $H_2SO_4$ solution at (A) $-1.4$ V and (B) $-1.5$ V.
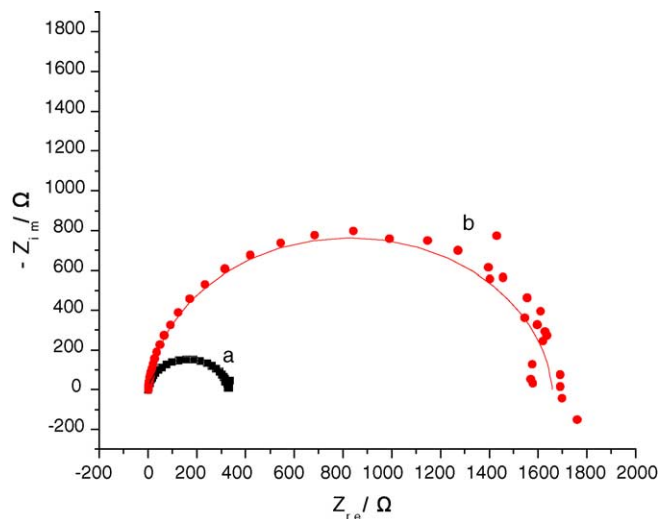


Fig. 3. Nyquist plots for: (a) Pb and (b) Bi–Pb electrodes in 4.79 M $H_2SO_4$ solution at $-1.5$ V.
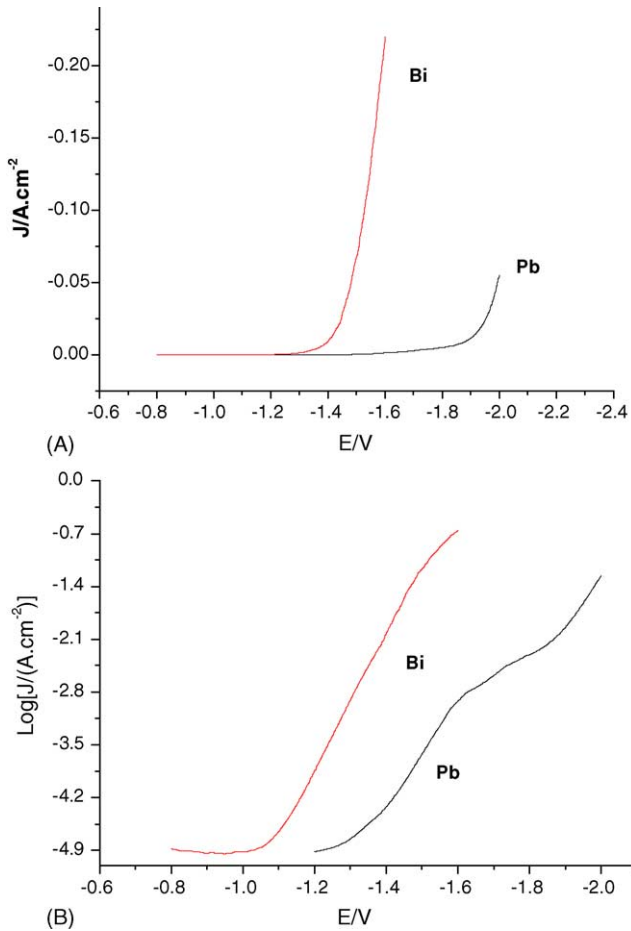
Fig. 4. Cathodic polarization curves for lead and bismuth electrodes in 4.79 M $H_2SO_4$ solution. (A) $E - J$ and (B) $E - \mathrm{Log}\, J$ relationship. Scan rate = 0.76 mV s$^{-1}$.

however, different from that of lead as is the content of bismuth, as seen in Table 1. Thus, the difference in the extent of the hydrogen evolution reaction on commercial lead and commercial bismuth-bearing lead cannot be ascribed to the effect of bismuth. Furthermore, it cannot be concluded that 55 ppm of bismuth in lead does not improve significantly the hydrogen evolution reaction on lead.

### 3.2. Lead and bismuth

Cathodic polarization curves for lead and bismuth electrodes in 4.79 M $H_2SO_4$ solution are given in Fig. 4(A). To reach a steady state, a low potential sweep rate of 0.76 mV s$^{-1}$ was used. Cathodic current appears at a potential of −1.2 V for the bismuth electrode. The collection of hydrogen confirms that the cathodic current can be ascribed to the hydrogen evolution reaction, as shown in Fig. 5. At the same potential, the current density and the hydrogen evolution volume on the bismuth electrode are both far larger than those on the lead electrode. Apparently, the hydrogen evolution reaction takes place more easily on bismuth than on lead. Nyquist plots for lead and bismuth electrodes in 4.79 M $H_2SO_4$ solu-
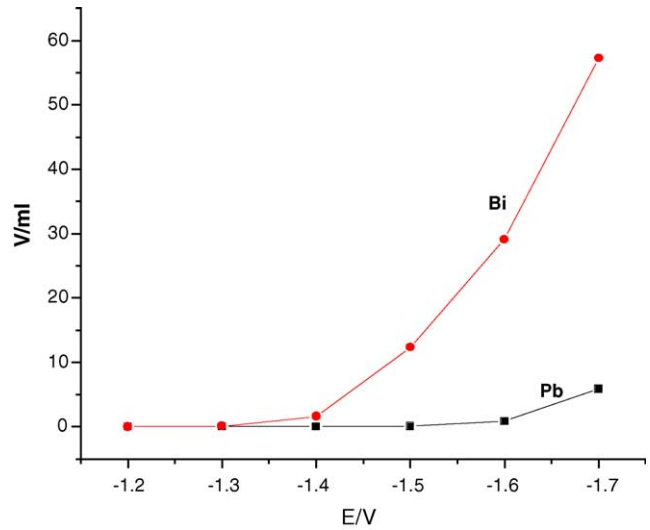


Fig. 5. Variation of hydrogen evolution volume with potential on lead and bismuth electrodes in 4.79 M $H_2SO_4$ solution for 2 h.



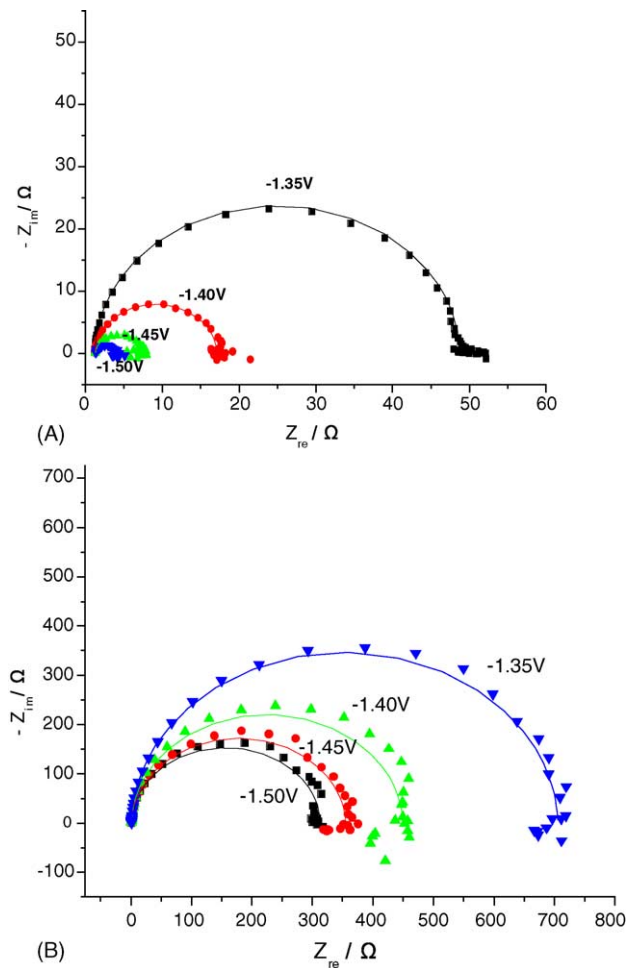Fig. 6. Nyquist plots for: (A) bismuth and (B) lead electrodes in 4.79 M $H_2SO_4$ solution at different potentials.

Table 2
Parameters for hydrogen evolution reaction on lead and bismuth in 4.79 M $H_2SO_4$ solution

| Electrode | Open-circuit potential (V) | Potential range for Tafel relation (V) | Constant $a$ (V) | Constant $b$ (V) |
|---|---|---|---|---|
| Pb | −0.97 | −1.3 to −1.6 | −2.00 | −0.14 |
|  |  | −1.9 to −2.0 | −2.18 | −0.14 |
| Bi | −0.47 | −1.1 to −1.5 | −1.62 | −0.10 |

tion at different potentials are presented in Fig. 6. As in the case of lead, hydrogen evolution on bismuth is controlled by a charge-transfer step.

To obtain more information about the reaction kinetics of hydrogen evolution on the two electrodes, the relation of potential with logarithmic current density ($J$) is shown in Fig. 4(B). The kinetics on bismuth are very different from those on lead. Two linear Tafel regions between −1.3 and −1.6 V and −1.9 and −2.0 V appear for lead, but only one for bismuth between −1.1 and −1.5 V. The Tafel constants obtained by fitting these linear relationship with the Tafel Eq. (4) are listed in Table 2. The constant $a$ is the overpotential for the hydrogen evolution reaction when the current density equals to $1\,A\,cm^{-2}$, and it represents the difficulty for the reaction to take place. The constant $b$ is the slope of the linear Tafel plot and represents the dependence of the reaction rate on potential.

$$\eta = a + b \log J \qquad (4)$$

The two Tafel plots for lead have the same slope, namely −0.14 V, which indicates that the hydrogen evolution reaction over these ranges of potential take place via the same mechanism. The non-linear relation of potential with logarithmic current density at potentials between two linear regions is ascribed to the zero charge potential of lead [16]. Bismuth has a more positive open-circuit potential than lead in sulfuric acid solution, as shown in Table 2, i.e., bismuth is nobler than lead. Bismuth has a more negative constant $a$ than lead, which shows that the hydrogen evolution reaction takes place on bismuth ahead of the reaction on lead. Bismuth has a more positive constant $b$ than lead, and therefore the hydrogen evo-

lution reaction rate on bismuth can be improved by changing the potential more significantly than that on lead.

### 3.3. Lead with chemically-deposited bismuth

As indicated in Section 3.2, bismuth has a more positive open-circuit potential than lead. Thus, bismuth can be thermodynamically deposited from solution on to lead by a displacement reaction. In fact, this happens when dipping lead in the solution containing bismuth ions. The lead electrode has the same open-circuit potential as the bismuth electrode after immersion in 2 mM $Bi_2(SO_4)_3$ solution for different times, as shown in Tables 2 and 3, which demonstrates that bismuth has been deposited on the surface of lead chemically.

Cathodic polarization curves for lead electrodes with and without chemically-deposited bismuth are given in Fig. 7. The results show that the hydrogen evolution current can be enhanced dramatically by chemically-deposited bismuth and that this effect intensifies with increase in the period of immersion of lead in the bismuth-containing solution. Nyquist plots for these lead electrodes are presented in Fig. 8, and these reveal that the hydrogen evolution reaction is controlled by charge-transfer step irrespective of whether the lead electrode has deposited bismuth or not. Nevertheless, there is a difference in the details of the reaction kinetics for hydrogen evolution on these electrodes, as shown by the parameters listed in Table 3.

The data in Table 3 show that the resistance to hydrogen evolution becomes smaller as the time for bismuth deposition increases and the polarized potential becomes more negative. The $\omega''$ value is the frequency at which the imaginary part of

Table 3
Some kinetic parameters of hydrogen evolution on lead electrodes in 4.79 M $H_2SO_4$ solution, as well as electrodes with chemically-deposited bismuth from 2 mM $Bi_2(SO_4)_3$ solution for different immersion times

| Deposition time (s) | Open-circuit potential (V) | Polarized potential (V) | Reaction resistance ($\Omega\,cm^2$) | $Q$ ($s^n\,\Omega^{-1}$) | $n$ | $\omega''$ (Hz) | Double-layer capacitance ($F\,cm^{-2}$) |
|---|---|---|---|---|---|---|---|
| 0 | −0.97 | −1.80 | 16.44 | $0.4655 \times 10^{-5}$ | 0.9835 | 572 | $1.4 \times 10^{-5}$ |
|  |  | −1.75 | 24.32 | $0.4470 \times 10^{-5}$ | 0.9778 | 447 | $1.3 \times 10^{-5}$ |
|  |  | −1.70 | 36.56 | $0.4801 \times 10^{-5}$ | 0.9676 | 273.4 | $1.3 \times 10^{-5}$ |
|  |  | −1.60 | 63.22 | $0.4632 \times 10^{-5}$ | 0.9814 | 130.8 | $1.4 \times 10^{-5}$ |
| 15 |  | −1.80 | 0.77 | $0.4204 \times 10^{-5}$ | 0.9921 | 13980 | $1.3 \times 10^{-5}$ |
|  |  | −1.75 | 1.71 | $0.4121 \times 10^{-5}$ | 0.9842 | 6690 | $1.2 \times 10^{-5}$ |
|  | −0.47 | −1.70 | 3.95 | $0.4077 \times 10^{-5}$ | 0.9830 | 2501 | $1.2 \times 10^{-5}$ |
|  |  | −1.60 | 11.71 | $0.3989 \times 10^{-5}$ | 0.9743 | 935 | $1.2 \times 10^{-5}$ |
| 120 |  | −1.80 | 0.65 | $0.5563 \times 10^{-5}$ | 0.9955 | 13980 | $1.8 \times 10^{-5}$ |
|  |  | −1.75 | 1.20 | $0.5246 \times 10^{-5}$ | 0.9875 | 6690 | $1.6 \times 10^{-5}$ |
|  | −0.47 | −1.70 | 2.36 | $0.4932 \times 10^{-5}$ | 0.9736 | 4090 | $1.4 \times 10^{-5}$ |
|  |  | −1.60 | 4.86 | $0.4926 \times 10^{-5}$ | 0.9818 | 1955 | $1.5 \times 10^{-5}$ |
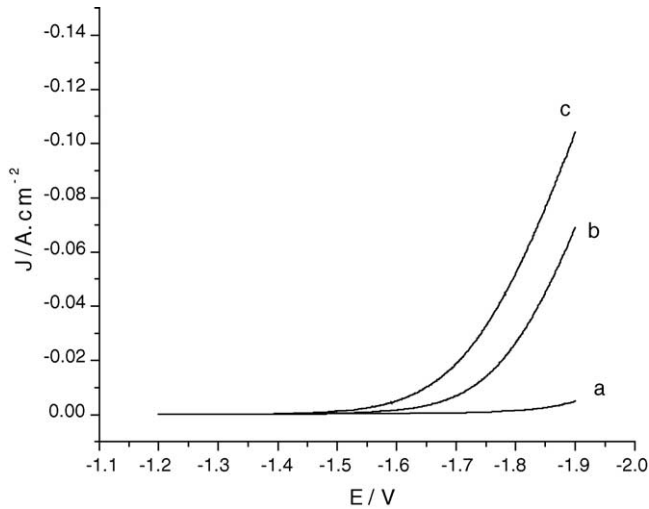
Fig. 7. Cathodic polarization curves for: (a) lead electrodes in 4.79 M H$_2$SO$_4$ solution, and for electrodes with chemically-deposited bismuth after immersion in 2 mM Bi$_2$(SO$_4$)$_3$ for (b) 15 s and (c) 120 s.

impedance is at a maximum and reflects the dependence of hydrogen evolution on the charge-transfer step; it increases as the potential becomes more negative and is larger for the electrode with deposited bismuth than that without deposited bismuth at the same potential. A negative increase in potential must assist a reaction that is controlled by a charge-transfer step. The larger $\omega''$ value of the electrode with deposited bismuth indicates hydrogen evolution reaction on it is less dependent on the control by charge transfer step. The $\omega''$ value is almost independent of the time for bismuth deposition, which indicates that the kinetics of hydrogen evolution are independent of the amount of bismuth deposited on lead. The double-layer capacitance is of the order of $1 \times 10^{-5}$ F cm$^{-2}$ for electrodes with and without deposited bismuth, and is independent of the amount of bismuth. This suggests that the electrode surface area is virtually unchanged by the presence and the amount of the deposited bismuth. The enhancement of the rate of hydrogen evolution is not attributed to an increase in surface area but to the existence and the amount of deposited bismuth.

Chemical deposition of bismuth on lead may occur in practice. Compared with lead, which is not easy to dissolve in sulfuric acid solution due to the formation of insoluble lead sulfate, bismuth when polarized may dissolve due to the solubility of bismuth sulfate. The chemical deposition of bismuth from solution on to lead can take place by a displacement reaction only if there are bismuth ions in the solution. In this case, bismuth can improve the hydrogen evolution reaction on lead.

### 3.4. Lead–bismuth alloy

Metal lead with different amounts of metal bismuth was melted and then lead–bismuth alloy electrodes with different contents of bismuth were prepared. The contents, determined
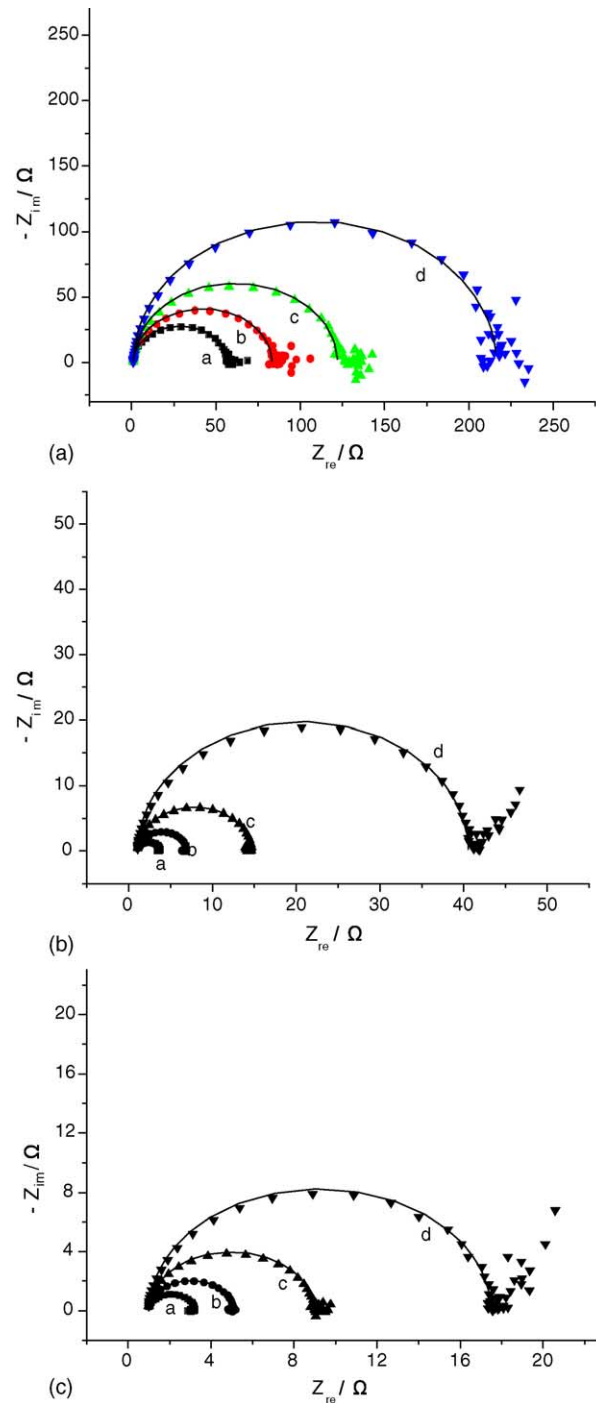


Fig. 8. Nyquist plots for (A) lead electrodes in 4.79 M H$_2$SO$_4$ solution at potential: (a) −1.8 V, (b) −1.75 V, (c) −1.7 V, and (d) −1.6 V, and for electrodes with chemically-deposited bismuth from 2 mM Bi$_2$(SO$_4$)$_3$ solution after (B) 15 s and (C) 120 s.

by ICP, are listed in Table 4. X-ray diffraction patterns for the alloys are given in Fig. 9. All the alloys have a characteristic of cubic crystal structure, i.e., the same as lead. Thus bismuth does not change the crystal structure of lead and enters into the lattice. The cell constants of the alloys were calculated by Eq. (1) and are listed in Table 4. The lattice of lead is enlarged

Table 4
Bismuth content, cell constant and impedance parameters of lead–bismuth alloys in 4.79 M $H_2SO_4$ solution at $-1.75$ V

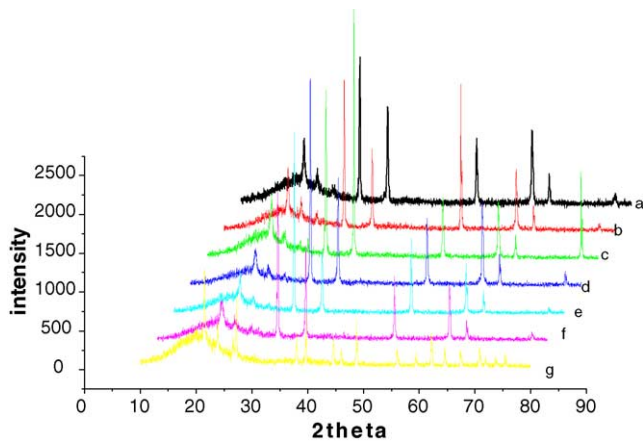| Bismuth content (%) | Cell constant $a$ (Å) | OCP (V) | Reaction resistance ($\Omega\,cm^2$) | $\omega''$ (Hz) |
|---|---|---|---|---|
| 0.00 | 4.944 | $-0.97$ | 24.32 | 447 |
| 0.10 | 4.951 | $-0.97$ | 12.44 | 1196 |
| 0.35 | 4.935 | $-0.97$ | 7.55 | 1955 |
| 0.83 | 4.920 | $-0.97$ | 6.24 | 3200 |
| 7.33 | 4.917 | $-0.966$ | 3.87 | 4090 |



Fig. 9. XRD patterns for lead–bismuth alloys with bismuth contents of: (a) 0.00, (b) 0.03, (c) 0.10, (d) 0.35, (e) 0.83 and (f) 7.33 wt.% and for (g) bismuth.

at a bismuth level of 0.1 wt.% and is then remains constant as the content increases.

Cathodic polarization curves for lead–bismuth alloy electrodes in 4.79 M $H_2SO_4$ solution are shown in Fig. 10. The open-circuit potentials of the alloys are the same as that of lead, as shown in Table 4. This suggests that the surface of the
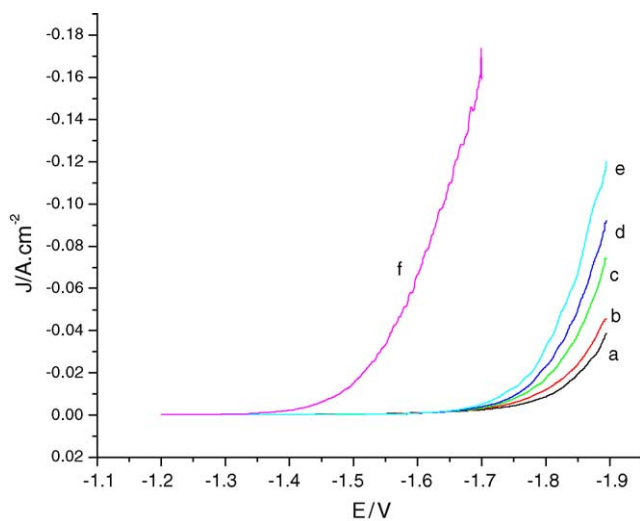


Fig. 10. Cathodic polarization curves for lead–bismuth alloy electrodes in 4.79 M $H_2SO_4$ solution, (Sweep rate = 2 mV s$^{-1}$), with bismuth content of (a) 0.00, (b) 0.10, (c) 0.35, (d) 0.83 and (e) 7.33 wt.% and for (f) bismuth.
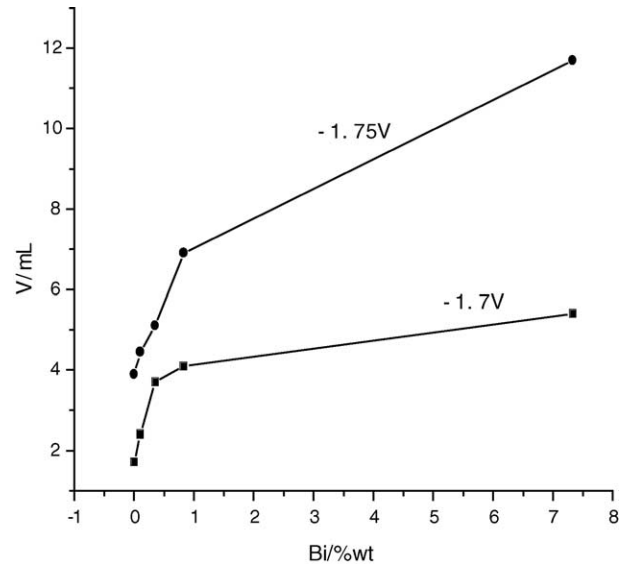


Fig. 11. Variation of hydrogen evolution volume with bismuth content for lead–bismuth alloys in 4.79 M $H_2SO_4$ solution.

alloys is characteristic of that of lead. The addition of bismuth into lead lattice does not change the cathodic polarization behaviour of lead at potentials more positive than $-1.60$ V. At potentials more negative than $-1.60$ V, however, the current density of the alloy electrodes increases with increasing bismuth content. The current is attributed to hydrogen evolution, as shown in Fig. 11, and the reaction is controlled by a charge-transfer step, as shown in Fig. 12. The $\omega''$ value obtained by fitting impedance data, as shown in Table 4, increases with increasing bismuth content. Apparently, bismuth in lead–bismuth alloy affects the kinetics of hydrogen evolution reaction only when the electrode potential is negative
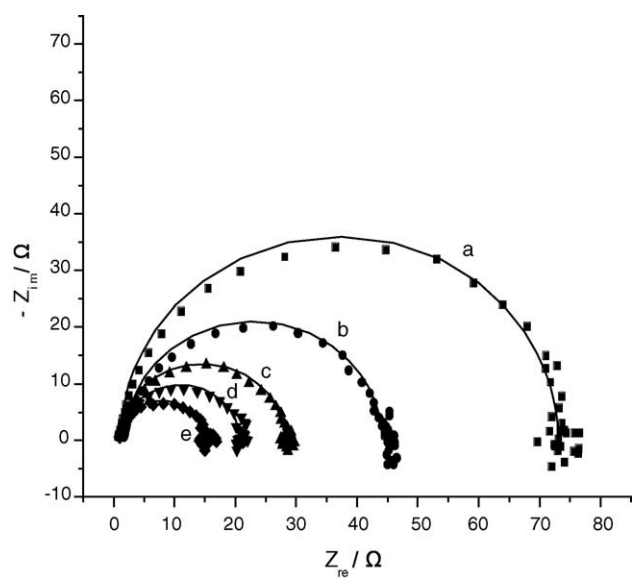


Fig. 12. Nyquist plots for lead–bismuth alloy electrodes in 4.79 M $H_2SO_4$ solution at 1.75 V, with bismuth content of (a) 0.00, (b) 0.10, (c) 0.35, (d) 0.83 and (e) 7.33 wt.%.

enough. This effect of bismuth can be neglected in the practical application of a lead–acid battery because the potential more negative than −1.6V for the negative of a lead–acid battery is hard to be reached even if the battery is overcharged. In this case, bismuth is not detrimental to valve-regulated lead acid battery.

In contrast to the behaviour of lead with chemically-deposited bismuth, which is similar to that of bismuth but not lead, the behaviour of lead–bismuth alloys is similar to that of lead but not bismuth. This may due to a difference in the mechanism for hydrogen evolution. In acidic solution, hydrogen evolution on a metal (M) may involve the following reactions:

$$H^+ + e^- \rightarrow MH \tag{5}$$

$$MH + MH \rightarrow H_2 \tag{6}$$

$$H^+ + MH + e^- \rightarrow H_2 \tag{7}$$

Reactions (5) and (7) involve charge transfer. Based on the Nyquitst plots, all the hydrogen evolution reactions on the electrodes examined in this study are controlled by reaction (5) and/or (7). On pure lead, reaction (5) is too slow for hydrogen to evolve even if reactions (6) and (7) are rapid. On pure bismuth, reaction (5) is faster than that on lead. Nevertheless, it is still a slow reaction and therefore reaction (7) is also slow. Hydrogen evolution is easier on pure bismuth than pure lead due to the rapid reaction (6). In the case of lead–bismuth alloys, their similarity to lead but not to bismuth can be attributed to the slow reaction (7) on bismuth. On alloys, bismuth hydride is formed before lead hydride. Reaction (6) cannot take place, however, because neighbouring bismuth almost are not available on lead–bismuth alloys.

## 4. Conclusions

Compared with lead, bismuth is a metal that favours hydrogen evolution. In sulfuric acid solution, bismuth has faster kinetics for hydrogen evolution than lead. The Tafel constants $a$ and $b$ in 4.79 M $H_2SO_4$ solution are −2.00 and −0.14 V for lead, and −1.62 and −0.10 V for bismuth, respectively. Lead with chemically-deposited bismuth behaves like bismuth, i.e., the chemically-deposited bismuth significantly accelerates the hydrogen evolution reaction on lead. In this case, bismuth is detrimental to the life of VRLA batteries. Chemical deposition of bismuth on lead must occur if bismuth ions exist in solution because the open-circuit potential of bismuth is far more positive than that of lead in sulfuric acid solution, namely, −0.47 V for bismuth and −0.97 V for lead in 4.79 M $H_2SO_4$ solution. By contrast, bismuth in lead alloys hardly affects the hydrogen evolution reaction; the alloys behave like lead. The cathodic polarization of alloys is the same as that of lead at potentials more positive than −1.60 V, even though the content of bismuth in the alloys is over 7 wt.%. In this case, bismuth is not detrimental to the performance of VRLA batteries.

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