

Short communication

Properties and application of lead–calcium–tin–aluminium–bismuth alloys for positive grids

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Abstract

The effects of bismuth addition less than 0.05 wt% on the electrochemical properties of lead–calcium–tin–aluminum alloys were investigated in detail. Passivation and corrosion phenomena were investigated by cyclic voltammetry, electrochemical impedance spectra, linear sweep voltammetry. The effect of bismuth on oxygen evolution and hydrogen evolution were also discussed. The experimental results show that the addition of bismuth leads to the decreases of the hydrogen overpotential and increase of the hydrogen evolution rate. Oxygen evolution rate increases with the increase of content of bismuth. The measurements of cyclic voltammetry suggested that bismuth may promote the formation of lead dioxide. A key result was that the presence of bismuth might have beneficial effect on the formation of Pb(II).

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1. Introduction

The effect of bismuth on the performance of lead–acid batteries has been the subject of considerable concern, but its true effect is not very clear. At present, many researches have indicated that the addition of bismuth has no ill-effect on the performance of lead–acid battery. Kelly and co-workers [1] investigated the effect of bismuth on Pb–Ca alloys by the cyclic voltammetry and the linear sweep voltammetry, the results show that the addition of bismuth reduces the anodic attack, and the addition of bismuth has similar advantages to antimony, but without ill-effect of antimony. Koop et al. [2] confirmed that addition of bismuth in the range from 0.03% to 0.05% had no significant effect on hydrogen evolution, but produced a marked improvement in battery cycle-life and raised the deep chargeability. The electrochemical properties of lead containing 0–5% bismuth have been studied by Rice and Manders [3], the experiment results show that bismuth could lead to the increase of hydrogen overpotential and improve the distribution of current on negative plates. It was also concluded that the bismuth on

the positive electrode, promotes the evolution of oxygen and inhibits the formation of lead dioxide from lead sulfate. The enhancement of lead sulfate nucleation was also investigated. Johnson et al. [4] examined the hydrogen evolution characteristics of lead–bismuth alloy, it was concluded that the presence of bismuth could lead to the increase of hydrogen evolution rate and the decrease of hydrogen overpotential in the range of 0–0.27%. However, when the content of bismuth is over 0.27%, the parameter values *a* and *b*, which indicate the rate of hydrogen gas formation, change a little. Recently, the influence of bismuth addition in the range of 0.006–0.086% on the metallurgical and electrochemical properties of Pb–Sb alloys has been reported by Lam et al. [5]. The results indicated that bismuth addition has no significant effect on the age-hardening behavior and the general microstructure or grain size of the alloy, but the corrosion rate of the grid decreases with the increasing of the bismuth content. A key discovery was that the addition of bismuth, up to 0.09 wt%, did not affect the self-discharge behavior. Prengaman [6] demonstrated that regions rich in bismuth and tin were formed in lead–calcium–bismuth alloy, and the aggregation of these elements consolidate the cohesion of the grids and active material.

At present, most of the researches have based on the lead–bismuth alloy. However, the properties of lead–bismuth

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binary alloy are not directly relevant to the properties of lead–calcium–tin–aluminum alloy that was commonly used as battery grids. In this article, the effects of bismuth addition less than 0.05 wt% on the properties of lead–calcium–tin–aluminum as positive grids were investigated in detail.

2. Experimental

The following five kinds of lead alloy rods, whose compositions were analyzed by inductively coupled plasma spectroscopy (ICP), have been prepared for our experiment.

Pb–0.09% Ca–0.98% Sn–0.011% Al.
 Pb–0.09% Ca–0.98% Sn–0.011% Al–0.0108% Bi.
 Pb–0.09% Ca–0.98% Sn–0.011% Al–0.0227% Bi.
 Pb–0.09% Ca–0.98% Sn–0.011% Al–0.0321% Bi.
 Pb–0.09% Ca–0.98% Sn–0.011% Al–0.0432% Bi.

The alloy rod was used as the tested electrode with the diameter of 7.0 mm, and one end of the alloy rod was welded with a copper wire as a current collector, and then, this rod was sealed in epoxy resin and polished to expose other side as the working electrode. A three-compartment electrolytic cell was used in the experiments with the electrolyte of 1.28 sp.gr. H₂SO₄ solution which diluted from 98 wt% H₂SO₄ (AR) with double-distilled water. The counter and reference electrode were a platinum plate (0.5 cm²) and Hg/Hg₂SO₄ (1.28 sp.gr. H₂SO₄ solution system), respectively. All potentials reported in this paper were referred to this electrode. The behavior of the electrode was influenced by the oxide on its surface, so before every experiment, the test electrode was held at a potential of –1.2 V for 10 min to reduce the oxide on the surface of the working electrodes.

Linear sweep voltammograms, cyclic-voltammetric measurements and electrochemical impedance spectra were performed with the potentiostat/galvanostat of PGSTAT30 (Autolab, Eco Chemie B.V. Company).

3. Results and discussion

3.1. Hydrogen evolution

Hydrogen evolution reaction rate was measured by linear sweep voltammograms between –1.2 and –1.7 V at the scan rate of 1 mV s^{–1}. The result of hydrogen evolution is shown in Fig. 1, which indicates the over potential of hydrogen evolution declines but reaction rate increase with the addition of bismuth. It can be concluded that bismuth promotes the evolution of hydrogen (Table 1).

Table 1
Tafel parameters for hydrogen evolution reaction at lower potentials on Pb–Ca–Sn–Al alloy electrodes with different bismuth content

| | 0.00 wt% | 0.0108 wt% | 0.02274 wt% | 0.0321 wt% | 0.0432 wt% |
|----------|----------|------------|-------------|------------|------------|
| <i>a</i> | –2.0057 | –1.9987 | –1.936 | –1.9089 | –1.9433 |
| <i>b</i> | –0.2732 | –0.2698 | –0.262 | –0.2582 | –0.2844 |

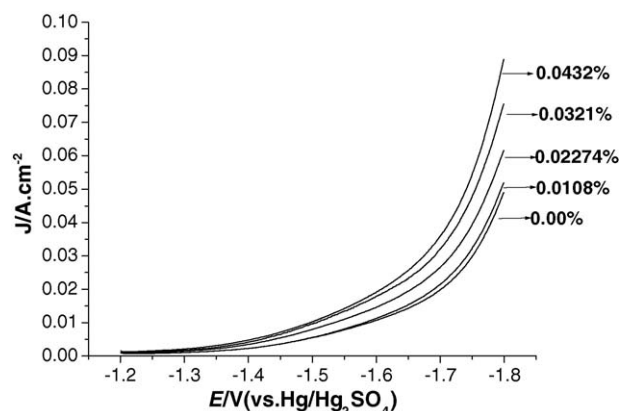


Fig. 1. Hydrogen evolution on Pb–Ca–Sn–Al alloy electrodes with different bismuth content; sweep rate = 1 mV s^{–1} in 1.28 sp.gr. H₂SO₄.

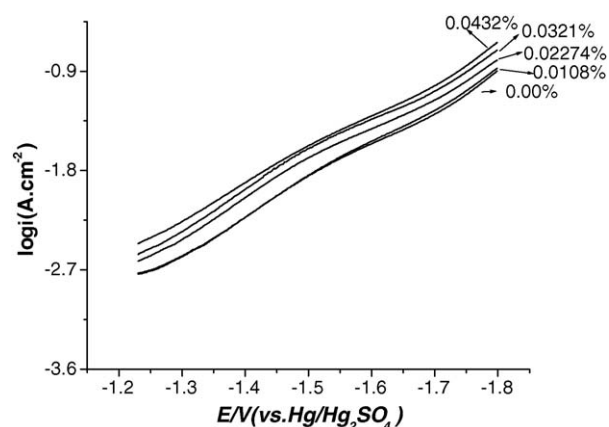


Fig. 2. Tafel plots of hydrogen evolution on Pb–Ca–Sn–Al alloy electrodes with different bismuth content.

According to Papageorgiou and Skyllas-Kazacos's view [7], hydrogen evolution reaction was related to electrode surface morphology and microstructure. Bismuth might insert into the lattice of lead and replace some atoms of lead, as a result, the grain size of lead alloy declined and more “active area” for hydrogen evolution reaction was produced.

The relative Tafel plots present in Fig. 2 indicate that two linear regions locate on lower and higher potential region, respectively (Figs. 3 and 4), and this results was also reported by Zhong et al. [8] and Lam et al. [9]. The kinetics parameters of two linear regions are presented in Tables 2 and 3.

3.2. Oxygen evolution

The rate of oxygen evolution was measured by linear sweep voltammograms. Because the rate of oxygen evolution

Table 2
Tafel parameters for hydrogen evolution reaction at higher potentials on Pb–Ca–Sn–Al alloy electrodes with different bismuth content

| | 0.00 wt% | 0.0108 wt% | 0.02274 wt% | 0.0321 wt% | 0.0432 wt% |
|----------|----------|------------|-------------|------------|------------|
| <i>a</i> | –2.1890 | –2.1499 | –2.1641 | –2.1410 | –2.0958 |
| <i>b</i> | –0.378 | –0.3579 | –0.3974 | –0.407 | –0.3804 |

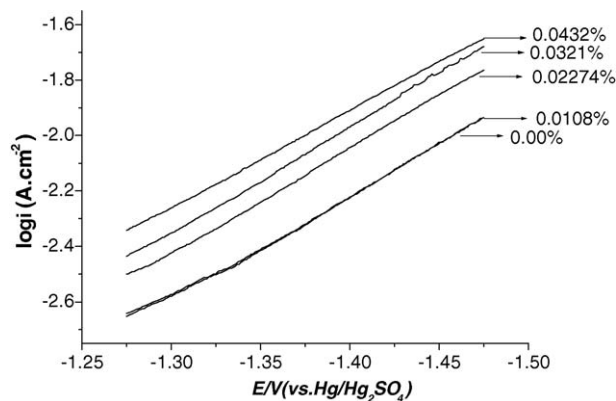


Fig. 3. Tafel plots of hydrogen evolution on Pb–Ca–Sn–Al alloy electrodes with different bismuth content at lower potentials.

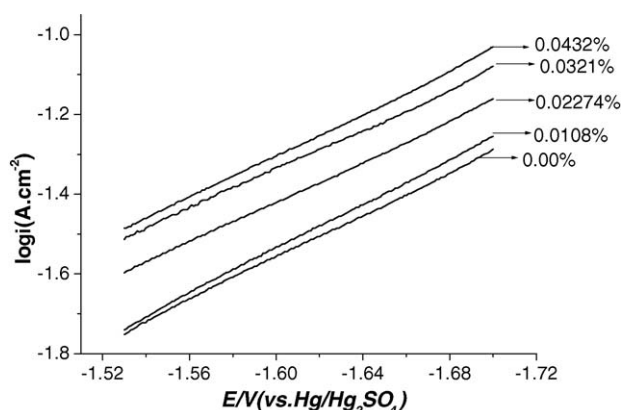


Fig. 4. Tafel plots of hydrogen evolution on Pb–Ca–Sn–Al alloy electrodes with different bismuth content at higher potentials.

is affected by the PbO_2 , oxygen evolution test was performed after the working electrode was held at a constant potential of 1.7 V for 40 min, to produce a steady film of PbO_2 , and then negative sweep was performed with 1 mV s^{-1} between 1.7 and 1.2 V. The result is shown in Fig. 5, it indicates that the addition of bismuth lightly affects on oxygen evolution when the potentials lower than 1.5 V. However, at the potentials higher than 1.5 V, the rate of oxygen evolution is proportional to the amount of bismuth addition. The addition of bismuth promotes the evolution of oxygen. It can be suggested that bismuth ions were absorbed onto the lead dioxide surface or insert into the crystal lattice of lead dioxide. The location of bismuth enhanced the discharge rate of water into hydroxyl group on the cathode, and by this way the evolution of oxygen was electrocatalyzed [10–13].

The corresponding Tafel plots between 1.5 and 1.65 V are presented in Fig. 6, and the kinetics parameters of oxygen evo-

Table 3
Tafel parameter values of oxygen evolution reaction on Pb–Ca–Sn–Al alloy electrodes and different bismuth content

| | 0.00 wt% | 0.0108 wt% | 0.02274 wt% | 0.321 wt% | 0.0432 wt% |
|-----|----------|------------|-------------|-----------|------------|
| a | 1.7902 | 1.7855 | 1.7835 | 1.7813 | 1.773 |
| b | 0.1055 | 0.1082 | 0.1107 | 0.1143 | 0.116 |

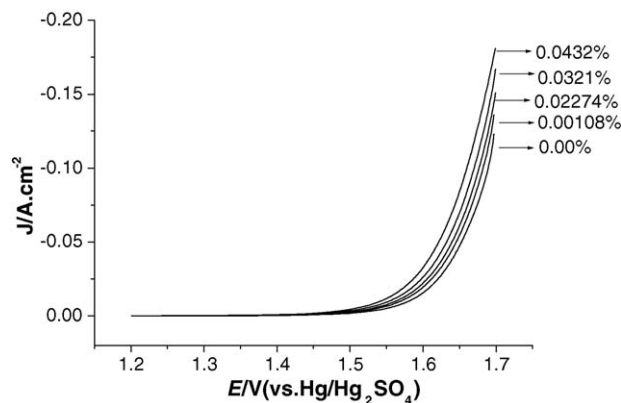


Fig. 5. Oxygen evolution rate on Pb–Ca–Sn–Al alloy electrodes with different bismuth additions; sweep rate = 1 mV s^{-1} in 1.28 sp.gr. H_2SO_4 .

lution reaction are list in Table 3, it can be seen that the value of a decreases slightly and the value of b increases with the bismuth additions.

3.3. Cyclic voltammetry

Figs. 7–9 give the cyclic-voltammetric curves between 800 and 1600 mV at different sweep rates. The formation of PbO_2 was related with the peak current of i_p . It can be seen that i_p increases with the increase of sweep rate but slightly increases with the addition amount of bismuth, the results suggest that bismuth may promote the formation of PbO_2 , which is considered to be responsible for the contribution of capacity. But the relationship between i_p and the addition amount of bismuth, as can be seen from Fig. 10, is not linear. This behavior is consistent with the results reported by Zhong et al. [14]. This phenomenon is explained that the change of the microstructure of the alloys and the morphology of PbSO_4 crystals due to the addition of bismuth accelerates the formation of PbO_2 from PbSO_4 .

3.4. Linear sweep voltammetry

The electrodes were anodized at 0.9 V for 15, 30, 60 min, and then swept to -1.2 V at a rate of 2 mV s^{-1} in 1.28 sp.gr.

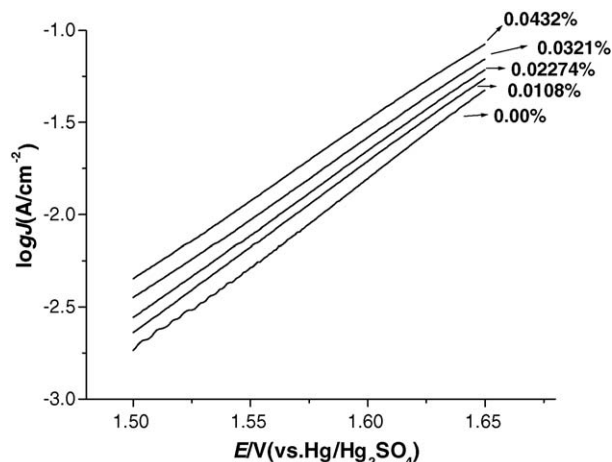


Fig. 6. Tafel plots of oxygen evolution on Pb–Ca–Sn–Al alloy electrodes with different bismuth additions.

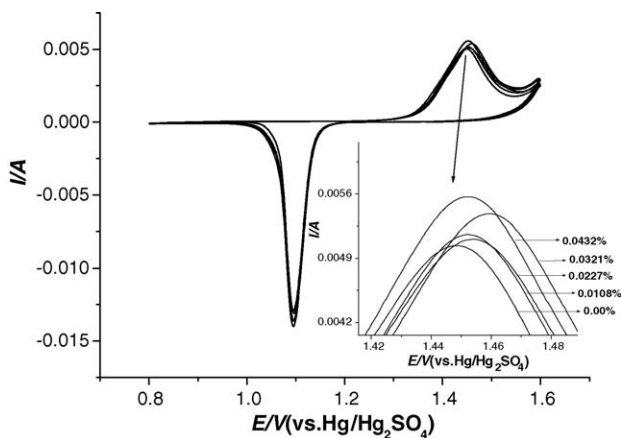


Fig. 7. Cyclic voltammograms of Pb–Ca–Sn–Al electrodes with different bismuth content (50th cycle); sweep rate = 5 mV s⁻¹.

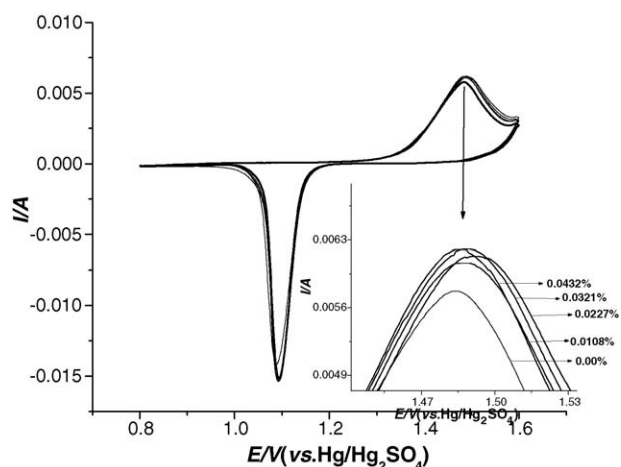


Fig. 8. Cyclic voltammograms of Pb–Ca–Sn–Al electrodes with different bismuth content (50th cycle); sweep rate = 10 mV s⁻¹.

H₂SO₄ solution. The reason for the potential of 0.9 V is it close to the potential in which the positive grids suffer from the deep discharge.

Figs. 11–13 show the voltammograms of anodic films of Pb–Ca–Sn–Al alloy on electrodes with different bismuth con-

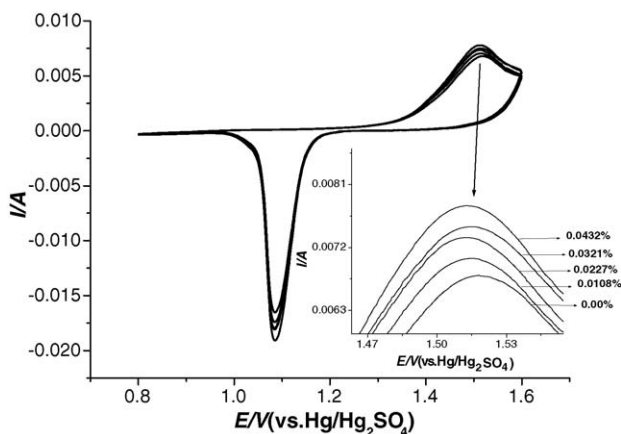


Fig. 9. Cyclic voltammograms of Pb–Ca–Sn–Al electrodes with different bismuth content (50th cycle); sweep rate = 20 mV s⁻¹.

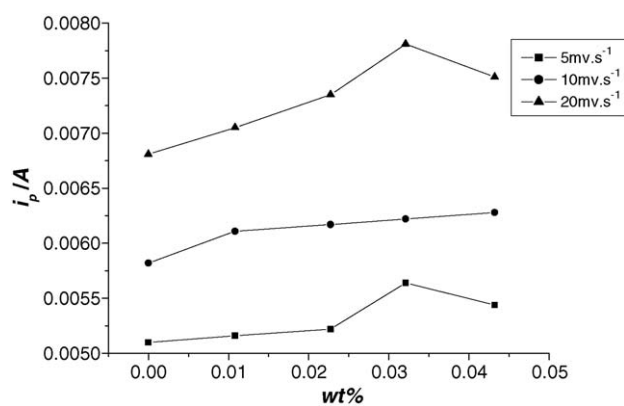


Fig. 10. i_p for the PbO₂ formation peak vs. Bi content.

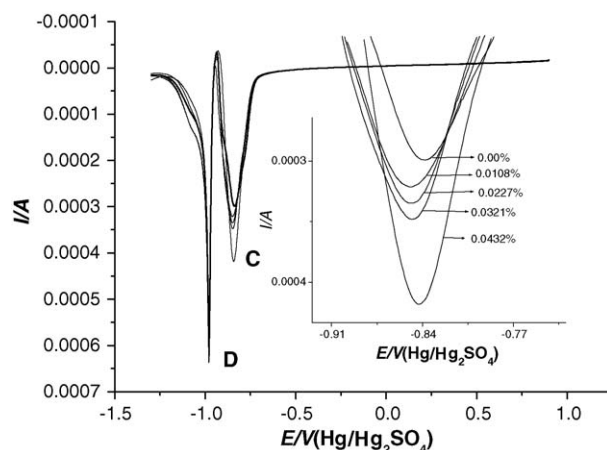


Fig. 11. Voltammograms of anodic films formed on Pb–Ca–Sn–Al with different percent bismuth electrodes at 0.9 V for 15 min in 1.28 sp.gr. H₂SO₄.

tent. The peak C correspond to the reduction of Pb(II) to Pb, the peak D correspond to the reduction of PbSO₄ to Pb. It can be seen from Figs. 11–13 that the effect of bismuth on the reduction of PbSO₄ to Pb is not obvious. The reduction charges for PbSO₄/Pb reaction do not vary significantly with polarization time and the addition amount of bismuth. Table 4 lists the reduc-

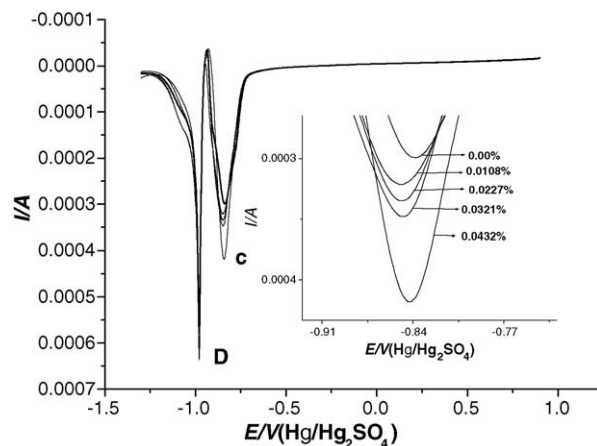


Fig. 12. Voltammograms of anodic films formed on Pb–Ca–Sn–Al with different percent bismuth electrodes at 0.9 V for 30 min in 1.28 sp.gr. H₂SO₄.

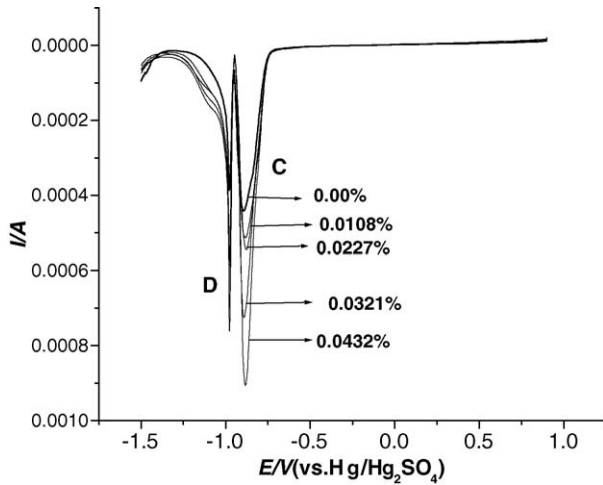


Fig. 13. Voltammograms of anodic films formed on Pb–Ca–Sn–Al electrodes with different content bismuth at 0.9 V for 60 min in 1.28 sp.gr. H₂SO₄.

tion charge of Pb(II)/Pb reaction for the Pb–Ca–Sn–Al electrode with different percent bismuth. The peak current and reduction charges of Pb(II)/Pb reaction increases with the oxidation time. The results also indicate that the peak current of Pb(II) to Pb reaction of Pb–Ca–Sn–Al–Bi electrodes is higher than that of the Pb–Ca–Sn–Al electrode, and with increase of the amount of bismuth addition, the peak current of Pb(II)/Pb increases. Hence, the addition of bismuth may promote the formation of Pb(II).

3.5. AC impedance

Impedance measurements were performed at different potentials in 1.28 sp.gr H₂SO₄ solution at 20 ± 1 °C, in the range of 10 MHz to 10 Hz with an AC voltage signal of 5 mV. As a pre-treatment, 10 cycles between 600 and 1600 mV were applied at the rate of 50 mV s⁻¹. The tested electrodes were held at 0.9 V for 1 h before measurements. Fig. 14 shows the Nyquist plots of impedance of electrodes. The corresponding bode plots are presented in Figs. 15 and 16. The Nyquist plot of impedance of electrodes shown in Fig. 14 consists of a semicircle and a straight line. The semicircle is related to charge transfer resistance and double layer capacitance. The straight line ascribes to Warburg impedance due to diffusion process. It can be observed that the diameter of the semicircle related with charge transfer resistance decrease with the addition amount of bismuth. It can be suggested that the addition of bismuth improved the conductivity of the Pb–Ca–Sn–Al alloy and reduced the reaction resistance.

Table 4
Reduction charges in the voltammograms for the Pb(II) films of Pb–Ca–Sn–Al alloy electrodes with different content bismuth

| Q ($\times 10^{-3}$ C) | 0.00 wt% | 0.0108 wt% | 0.02274 wt% | 0.0321 wt% | 0.0432 wt% |
|---------------------------|-------------|---------------|----------------|---------------|---------------|
| Q_{900s} | 4.067 | 4.818 | 5.091 | 5.290 | 5.559 |
| Q_{1800s} | 9.180 | 10.12 | 9.574 | 9.925 | 10.94 |
| Q_{3600s} | 17.87 | 18.19 | 19.17 | 25.41 | 27.03 |

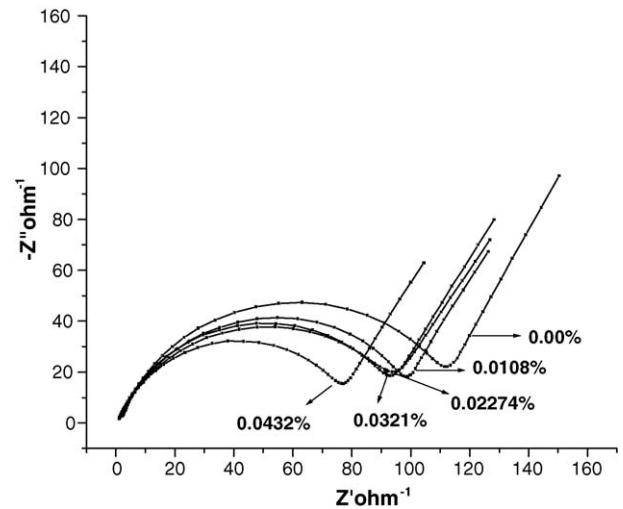


Fig. 14. Nyquist plots of Pb–Ca–Sn–Al and different percent bismuth electrodes at 0.9 V.

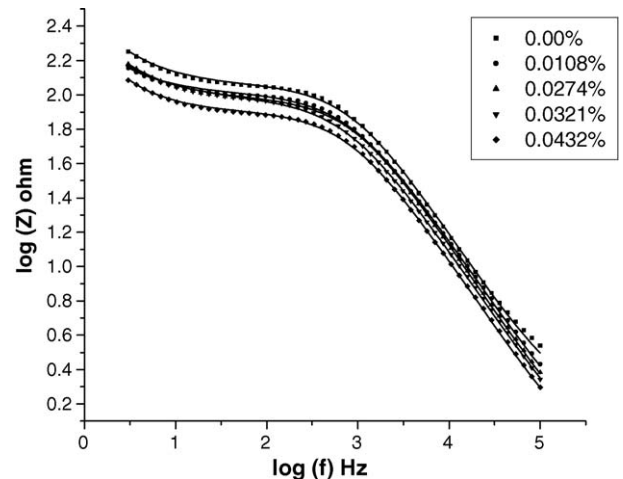


Fig. 15. Bode plots of Pb–Ca–Sn–Al and different percent bismuth electrodes at 0.9 V: modulus vs. logarithm of frequency.

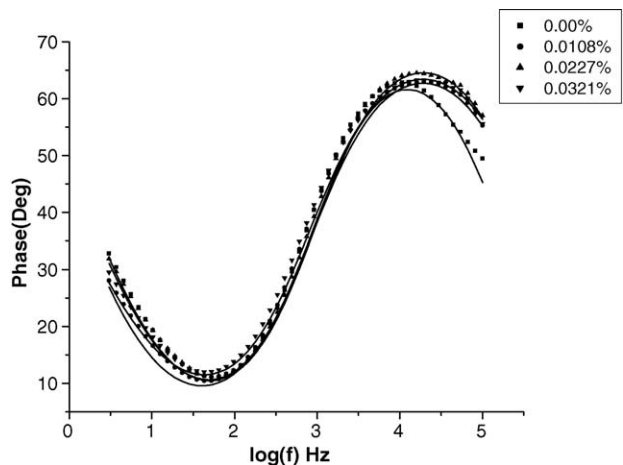


Fig. 16. Bode plots of Pb–Ca–Sn–Al and different percent bismuth electrodes at 0.9 V: phase vs. logarithm of frequency.

4. Conclusions

1. Both hydrogen and oxygen evolution on Pb–Ca–Sn–Al alloys are enhanced by addition of bismuth.
2. The presence of bismuth may have beneficial effect on the formation of lead dioxide, but the relationship between the peak current and the amount of bismuth is not linear.
3. The peak current of Pb(II)/Pb reaction increase with the increase of content of bismuth in Pb–Ca–Sn–Al alloys.

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