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Investigation on characteristics of anodic film formed on PbCaSnCe alloy in sulfuric acid solution

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Abstract

The electrochemical properties of the anodic films formed on PbCaSnCe and PbCaSn alloys at 0.9 V (versus Hg/Hg_2SO_4 electrode) in 4.5 mol/L sulfuric acid solution were investigated by linear sweeping voltammetry (LSV), ac voltammetry (ACV), electrochemical spectroscopy impedance (EIS), capacitance measurement and X-ray photoelectron spectroscopy (XPS) technology. Based on Mott–Schottky analysis, the effect of cerium on the semiconductor properties of anodic film is discussed as well in this paper. The experimental data shows that cerium can significantly decrease the impedance of the anodic film on PbCaSn alloy, and can improve the corrosion resistance of the alloy. It can be inferred from the capacitance measurement result that the passive film should be an n-type semiconductor. The addition of cerium can decrease the slope of M–S plot, which indicates the increasing of defect density in the film, and this can contribute to improve the conductivity of the anodic film on PbCaSn alloy. XPS results shows that the anodic film formed on PbCaSnCe alloy is consisted of PbO_{1+x} $(0<x<1)$ and $PbSO_4$, while for the anodic film formed on PbCaSn alloy, PbO and $PbSO_4$ are the major component. Considering the better conductivity of PbO_{1+x} $(0<x<1)$ than that of PbO, it is concluded that PbCaSnCe may serve as the candidate of the new grid material for maintenance-free lead acid battery.

Keywords: Electrochemical properties; PbCaSnCe alloy; Anodic films; Mott–Schottky analysis

1. Introduction

PbCa and PbSb alloys are widely used as the grid materials in lead acid battery industry [1,2]. PbSb alloy has a merit of high performance on the charge–discharge for the lead-acid battery because Sb can encourage the growth of PbO_2 in the anodic corrosion film. While the demerit of PbSb alloys is that it can decrease the over voltage of hydrogen evolution on the negative grid, and will cause increasing of hydrogen evolution on negative grid during charging process, and increasing the water loss in lead acid battery. With increasing the charge–discharge processes Sb may dissolve in the electrolyte, and will cause the deposit of metallic Sb on the negative electrode. Because of the low over-potential of hydrogen evolution on PbSb alloy, the gas evolution and self-discharge of battery may be accelerate, which lead to early excessive water loss and increase the self-discharge for batteries, and further to the premature loss of the battery capacity [3–5]. The over-potential of hydrogen evolution on PbCa alloy is higher than that on PbSb alloy for about 200 mV, which result in its lower rate of water consumption and a smaller rate of self-discharge, and then make the PbCa alloy more suitable for maintenance-free applications or valve regulates lead acid battery (VRLA). However, PbCa alloy has a unfavorable factor usually referred to as premature capacity loss (PCL), which is attributed to an high impedance barrier layer composed of PbO, and formed easily at the interface of the positive grid and the active material, which has an undesirable effect of increasing the anode impedance after storage for a certain period of time, and then the capacity of lead acid battery decreasing sharply [6–9].

In order to improve the conductivity of the passive layer and the charge–discharge performance of the batteries, Sn should be added into the PbCa alloys. According to Giess et al. [10], Sn suppresses the transformation of lead to α-PbO_2, and inhibits the growth of Pb(II) compound in the film. Although, the passive phenomena of the film cannot be thoroughly eliminated by adding Sn, and excessive Sn content may increase the self-discharge of the lead acid battery [11,12].

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A lot of new grid materials have been investigated in recent years for eliminating the effect disadvantages of PbSb and PbCa alloys on the performance of lead acid battery [13–15], but how to promote the maintenance-free property of the battery is still a key problem for developing the novel grid alloy. Adding alloy element into PbCaSn is obviously an effective means to solve the problem of 'PCL'. In our previous work, it was found that adding the rare-earth element, as Ce, into PbCaSn alloy can increase the conductivity of its anodic film [16]. The alloy containing high Sn and low Ca with the additive cerium was studied and it was concluded that the high Sn and low Ca alloy has better corrosion resistant and high stability than the alloy with high Ca and low Sn [17]. Therefore, the alloy with high Sn, low Ca and additive cerium is taken as the experimental material in this work, and the effect of cerium on the electrochemical properties of the anodic film formed on PbCaSn electrode at 0.9 V in 4.5 mol/L H_2SO_4 is investigated using linear sweeping voltage (LSV), ac voltammetry electrochemical impedance spectroscopy (EIS), and X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD).

2. Experimental

2.1. Material and sample

The experimental material was molten the mixtures of pure lead (99.99 wt.%), pure tin (99.99 wt.%), pure calcium (99.99 wt.%) and pure cerium (99.99 wt.%) according to the weight percent in a crucible of an electric furnace with nitrogen as protect gas. According to the phase diagram of PbCe system [18], Ce can melt into lead molten at 1000 K to form a compound of Ce_2Pb. So, the alloy elements Ca, Sn, Ce and Al were added into lead molten at 1000 K, in which the addition of Al can reduce oxidation of Ca and Ce and permitting the alloy better controlling of Ca and Ce contents. After adequate stiring for 10 min, and as the molten temperature dropped to 723 K, the molten alloy was poured into a copper mould of 500 K in the atmosphere to form the blank rod (Ø 20 mm × 200 mm), from which the experimental rod samples were machined in a form of wafer (Ø 10 mm × 5 mm). The composition of the casting alloys was determined by chemical analysis, and the result was listed in Table 1. One end surface of the sample exposed in the electrolyte acted as the working surface was polished with emery paper of successively decreasing grain size down to about 10 μm, while other surface were sealed with epoxy resin in the lower part of an L-shaped glass tube. The anodic corrosion films were prepared at 0.9 V (versus Hg/Hg_2SO_4 electrode) in 4.5 mol/L H_2SO_4.

Table 1
Chemical composition of the substrate alloys

Alloy	Mass content fraction (wt.%)				
	Ca	Sn	Ce	Al	Sn/Ca
PbCaSnCe	0.045	1.35	0.05	0.0013	30
PbCaSn	0.045	1.35	0.00	0.0013	30

2.2. Electrochemical experiments

All the electrochemical experiments were performed in a conventional three-electrode cell, the counter and reference electrodes were a platinum mesh and Hg/Hg_2SO_4 electrode, respectively. All the potentials mentioned in this paper are referred as the reference electrode.

The linear sweep voltammetry (LSV) was performed by EG&Gt model 273A electrochemical working station. The working electrode was first polarized at −1.2 V for 20 min to remove the oxidation formed on the electrode surface, then the anodic film on it was formed at 0.9 V for 0.5, 1, and 2 h in 4.5 mol/L H_2SO_4 solution, respectively. After the film formation, the working electrode was immediately scanned from 0.9 to −1.2 V with a rate of 2 mV/s.

A CH Instrument model 750 electrochemical working station with a frequency of 1000 Hz was used to record the change of the real part of the impedance (Z') for the anodic film with the voltage.

Capacitance measurement was also performed by CHI750 electrochemical working station with a scanning rate 10 mV, the scanning potential range from −0.4 to 1.0 V, and the measured frequency is 1000 Hz.

EIS apparatus is consisted of a Solartron Schlumberger 1250 frequency response analyzer and a Solartron 1286 electrochemical interface, the potential increases by 10 mV and the sweeping frequency is from 100 kHz to 100 Hz.

Surface analysis of X-ray photoelectron spectroscopy (XPS) was carried out with VGA Scientific MKII (ESCALAB), using Al Kα X-ray source. The X-ray power was 40 W, Pb 4f, S 2p, and O 1s binding energies were determined with C 1s (284.60 eV) reference.

XRD experiment was performed at Japan D/max-3C automatic X-ray diffration apparatus with Cu Kα X-ray source using an accelerating voltage of 40 kV and an current density of 40 mA cm^{-2}.

All experiments were carried out at room temperature (25 °C).

3. Results and analysis

3.1. Linear sweep voltammetry (LSV)

Fig. 1 shows the voltammograms of the anodic film formed on PbCaSnCe and PbCaSn electrodes at 0.9 V for 1 h, the potential 0.9 V is chosen for the anodic film growth, for it is in the growth potential of PbO [19–22]. Two reduction peaks can be observed in Fig. 1, in which peak a represents the reduction of Pb(II) (like PbO, $PbO{\cdot}PbSO_4$, $3PbO{\cdot}PbSO_4$, etc.) to Pb and peak 'b' is caused by the reduction of $PbSO_4$ to Pb [21]. The currents of two peaks for the film on PbCaSnCe electrode are evidently lower than those on PbCaSn electrode, from which it can be conclude that cerium may inhibit the growth of Pb(II) compound in the anodic film.

Fig. 2 lists the variations of the reduction charges for peaks 'a' and 'b' with oxidation time in the linear sweep voltammograms of the anodic films on two electrodes at 0.9 V. It can be found