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Effects of Sm and Y on the electron property of the anodic film on lead in sulfuric acid solution

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HIGHLIGHTS

- ► The growth of PbO in the anodic film on lead electrode at 1.28 V in sulfuric acid was inhibited by the addition of Sm or Y.
- ► The passive capacity of lead electrode in sulfuric acid was improved by the addition of Sm or Y.
- ► The numbers of point defect in the anodic films on lead electrode at 1.28 V, 1.5 V and 1.8 V increase with increasing Sm or Y.

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ABSTRACT

The influences of Sm and Y on the electron properties of the anodic films on lead at 1.28 V(vs.SCE), 1.5 V(vs.SCE) and 1.8 V(vs.SCE) in 4.5 mol L^{-1} sulfuric acid are investigated by using electrochemical impedance spectroscopy (EIS), Mott–Schottky plot, galvanic polarization and photo-electrochemical technique. The results show that Sm and Y can significantly decrease the resistances of the anodic films on lead electrode at 1.28 V, 1.5 V and 1.8 V, the oxygen and hydrogen evolutions of lead electrode covered by the anodic film decrease with the addition of Sm or Y. The anodic films on lead electrode at three potentials appear an *n*-type semi-conductive character, the addition of Sm or Y can decrease the slope of M–S plot of the anodic film, it implying the increment of the defect density within the anodic film, which is beneficial for improving the charge–discharge behavior of the lead acid battery.

1. Introduction

In recent twenty years, lead–antimony alloy have been replaced by lead–calcium alloy as the choice of the positive materials in lead acid battery for its high corrosion rate, high water loss and even to self-discharge [1]. The hydrogen evolution potential of calcium is higher than that of antimony in sulfuric acid, accordingly the water loss of lead–calcium alloy sharply decreases, and then the lead–calcium alloy can become the candidate of the positive grid for the maintenance-free lead acid battery. While for lead–calcium alloy, a serious problem is the anodic film with high impedance (about 10^{10} Ω cm^2) on its surface during charging and discharging, which is responsible for the so-called premature capacity loss "PCL" of lead acid battery [2–7]. The addition of Sn into lead–calcium alloy can effectively decrease the impedance of the anodic film by incorporated into the PbO lattice [8] or decreasing the thickness of PbO film [2], but excessive Sn may lead self-discharge for lead acid battery [9,10].

To better solve the "PCL", many rare earth elements such as Ce [11–13], Yb [14], La [15], Sm [16], Li [17] and Sr [18] are involved into lead–calcium–tin alloy, the results show that these rare earth elements can effectively decrease the resistance of the anodic film, and therefore the deep recycle property of the lead acid battery is improved. However, the above investigations are mainly focused on the electron property of the anodic film on lead alloy with or without rare earth element at 0.9 V (vs.Hg/Hg_2SO_4), and fewer papers report the rare earth element effect on the anodic films on lead alloy at the potentials above 0.9 V (vs.Hg/Hg_2SO_4). It is well known that the positive grid may be suffered from a large potential cycle during the factual operation, the anodic film formed at high potentials can affect the electron properties of the positive grid, and then to affect the application property of the lead acid battery. While up to now, there are no reports about this issue. The aim of this work is to determine the influences of Sm and Y on the electrochemical behaviors of the anodic films on lead–stannum

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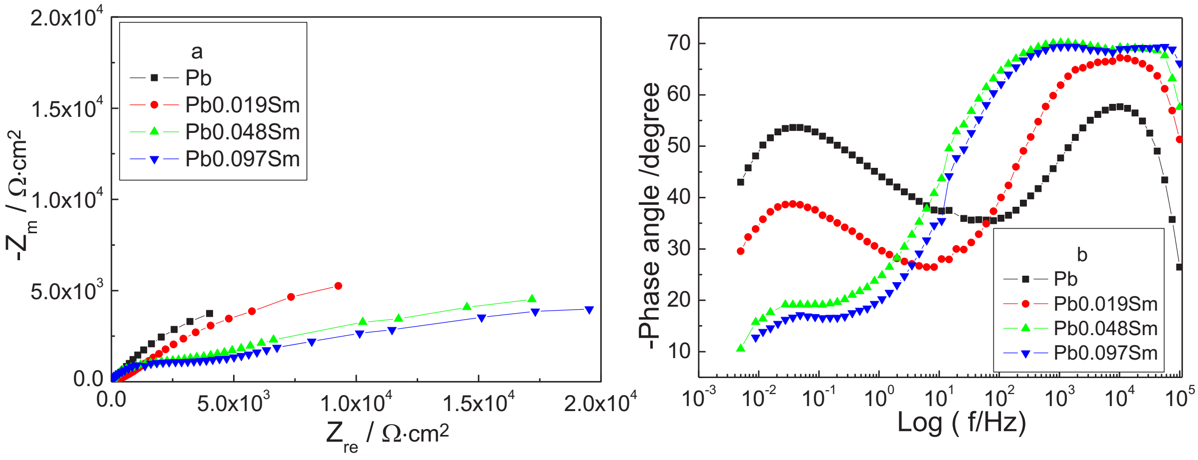

Fig. 1. EIS of the anodic films on Pb, Pb0.019%Sm, Pb0.048%Sm and Pb0.097%Sm alloys at 1.28 V for 3 h in 4.5 mol L^{-1} H_2SO_4 solution, a) Nyquist plot; b) corresponding Bode phase angle.

and lead–yttrium alloys at 1.28 V(vs.SCE), 1.5 V(vs.SCE) and 1.8 V(vs.SCE) in 4.5 mol L^{-1} H_2SO_4 solution.

2. Experimental

2.1. Material and sample

The experimental material is prepared by weighed mixture of pure lead (99.99 wt%), pure samarium (99.99 wt%) and pure yttrium (99.99 wt%) in an electric furnace with nitrogen as protect gas. Sm and Y are added into lead molten at 1000 K, after adequate stiring for 10 min. When the molten temperature drops to 723 K, the molten alloy is poured into a copper mold in the atmosphere to form the blank rod (Φ20 × 100 mm), and the rod samples are machined in a form of wafer (Φ10 × 5 mm). The compositions of the casting alloys are determined by chemical analysis, the result is listed as following: Pb, Pb0.019wt.%Sm, Pb0.048wt.% Sm, Pb0.097wt.% Sm, Pb0.018wt.%Y, Pb0.047wt.%Y and Pb0.095wt.%Y. One end surface of the sample exposed in the electrolyte acted as the working surface is abraded with 2000 grit SiC paper, polished with 0.5 *um* Al_2O_3 powder and then cleaned using double-distilled water, while other surfaces are sealed with epoxy resin in the lower part of an L-shaped glass tube.

2.2. Electrochemical experiments

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

EIS apparatus is consisted of EG&G instrument model 273A electrochemical working station with 5210 frequency response analyzer, the potential is increased by 10 mV and the sweeping frequency is from 100 kHz to 5 mHz.

Mott–Schottky plots of the anodic films are also carried out at EG&G instrument model 273A electrochemical working station with a 10 mV s^{-1} scanning rate, the scanning potential range is from 0 V to 2 V, and the measured frequency is 1000 Hz.

The photocurrent measurement is made of a conventional three electrode cell of 1-multi neck flash with a quartz window as a photon inlet, a 300W Xenon arc lamp is used as a light source, a monochromatic light with a wavelength from 200 nm to 800 nm is provided by a scanning digital monochromator controlled by a stepping

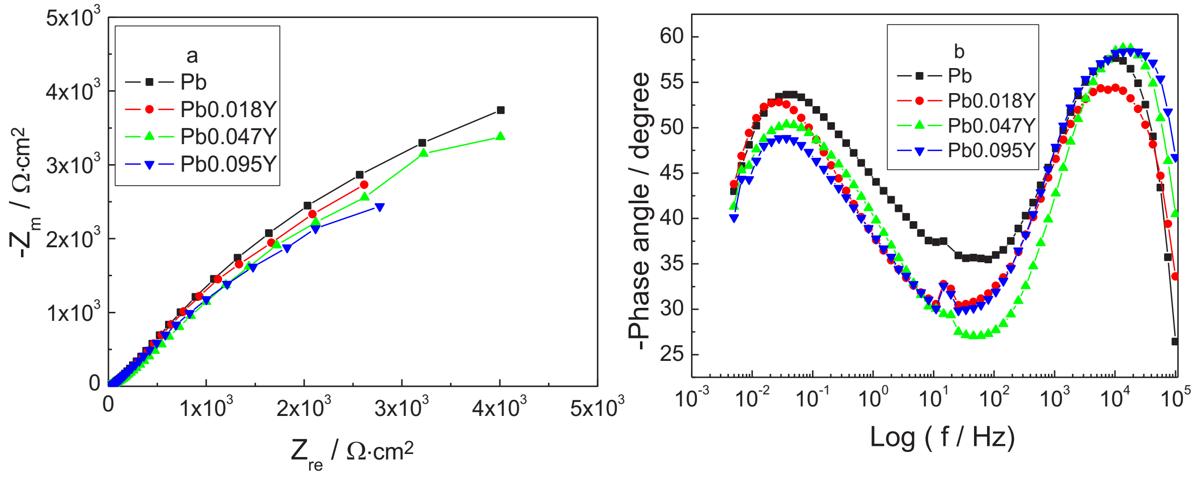

Fig. 2. EIS of the anodic films on Pb, Pb0.018Yt, Pb0.047Yt and Pb0.095Yt alloys at 1.28 V for 3 h in 4.5 mol L^{-1} H_2SO_4 solution, a) Nyquist plot; b) corresponding Bode phase angle.