Journal of Power Sources xxx (2015) 1–4

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Effect of various alkaline metal ions on electrochemical behavior of lead electrode in sulfuric acid solution

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HIGHLIGHTS

- The specific anodic oxidation peak appears in CV of Pb in H_2SO_4 + alkaline sulfate.
- Height of specific anodic oxidation peak varies with alkaline ions in the solution.
- Specific anodic oxidation peak increases with the concentration of alkaline ions.
- It is suggested that the alkaline ions in the passive film decrease the passivity.

ARTICLE INFO

Article history:
Received 24 October 2014
Received in revised form
11 March 2015
Accepted 9 April 2015
Available online xxx

Keywords:
Specific anodic oxidation
Lead acid battery
Cyclic voltammetry
Alkaline metal ions
Negative eletrode

ABSTRACT

The effect of various alkaline metal ions on electrochemical behavior of lead electrode in sulfuric acid solution has been investigated. It was found that "the specific anodic oxidation peak" appears at the cathodic scan in cyclic voltammogram of lead electrode in sulfuric acid solution containing Li_2SO_4, K_2SO_4, Na_2SO_4, Rb_2SO_4, or Cs_2SO_4. The height of the specific anodic oxidation peak varies with the alkaline sulfate in the solution; $K_2SO_4 >> Na_2SO_4 > Cs_2SO_4 > Rb_2SO_4 > Li_2SO_4$. It should be note that alkaline ions exist in lead sulfate formed on lead electrode in sulfuric acid solution containing potassium sulfate when the electrode was immersed in the solution at the rest potential for more than 1 h.

1. Introduction

Lead acid battery is one of the most popular secondary batteries all over the world because of its wide usable temperature range, reasonable cost, relatively high discharge capacity, and so on. In order to prevent short circuits across the separators due to the formation of metallic lead dendrites [1], alkaline sulfate or alkaline earth sulfate is sometimes added to the electrolyte. However, there have been some works that the addition of alkaline sulfate or alkaline earth sulfate to the electrolyte results in not only the prevention of the short circuits, but also the electrochemical behavior of the negative and positive electrode of lead acid battery [2–8]. We have already investigated the electrochemical behavior of the lead plate electrode, corresponding to the negative electrode of lead acid battery, in sulfuric acid solution with Na_2SO_4 [6]. In this paper, the addition effect of various alkaline sulfates (Li_2SO_4, K_2SO_4, Na_2SO_4, Rb_2SO_4, or Cs_2SO_4) on electrochemical behavior of lead electrode in sulfuric acid solution has been investigated.

2. Experimental

2.1. Cyclic voltammetry (CV)

Lead flat plates (apparent surface area: 1.54 cm^2) were used as a working electrode. A lead plate was also used as a counter electrode and an Hg/Hg_2SO_4 electrode was used as a reference electrode. The potential of the working electrode shown in this paper was referred to the reference electrode. Immediately after the electrolyte (4.35 M sulfuric acid solution (s.g. 1.25) with or without alkaline sulfate (Li_2SO_4, K_2SO_4, Na_2SO_4, Rb_2SO_4, or Cs_2SO_4)) was added into the electrochemical cell, the potential was kept at −1.2 V for more than 30 min in order to reduce native lead oxide already existed on the plate to metallic lead.

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http://dx.doi.org/10.1016/j.jpowsour.2015.04.047
0378-7753/© 2015 Published by Elsevier B.V.

Please cite this article in press as: N. Hirai, Y. Yamamoto, Journal of Power Sources (2015), http://dx.doi.org/10.1016/j.jpowsour.2015.04.047

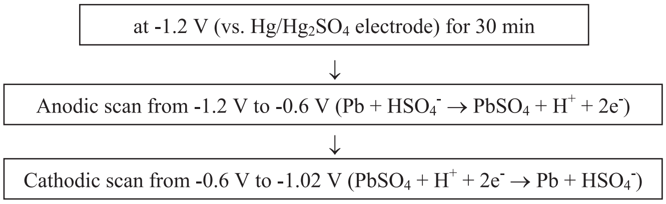

Fig. 1. Procedure of cyclic voltammetry (CV).

The procedure of cyclic voltammetry (CV) is shown in Fig. 1. The rest potential of the lead plates was about −1.03 V. All of the experiments were performed at room temperature and the electrolytes were not deaerated.

2.2. Immersion experiment

After immersing the lead plate (thickness: 1 mm) in 4.35 M sulfuric acid solution with or without 0.5 M alkaline sulfate (K_2SO_4, Na_2SO_4, or Rb_2SO_4), the surface of the plate was analyzed by SEM-EDX and XRD. The condition of XRD analysis was as follows; 2θ: 10–90°, scan speed: 4° min^{-1}, accelerating voltage: 40 keV, current: 20 mA.

3. Results

3.1. Cyclic voltammetry

Fig. 2 provides cyclic voltammograms of lead electrodes in 4.35 M sulfuric acid solution with or without 0.5 M K_2SO_4. Whether with or without K_2SO_4, an anodic current, corresponding to the discharge of negative electrode, and a cathodic current, corresponding to the charge of negative electrode, are observed at −0.98 V and −1.07 V respectively. However, an anodic current, called “specific” anodic one in this paper, is observed during cathodic scan at −1.02 V only when K_2SO_4 is dissolved in the solution.

Cathodic scans of CVs of lead electrodes in 4.35 M H_2SO_4 + x M K_2SO_4 solution (x = 0.50, 0.25, 0.050) are shown in Fig. 3. The peaks in the figure corresponds to the specific anodic oxidation. The height of the peaks increases with the concentration of K_2SO_4 in the solution.

Figs. 4 and 5 give cathodic scans of CVs of lead electrodes in 4.35 M H_2SO_4 + 0.5 M X_2SO_4 (X = K, Na, Cs, Rb, Li) or 1.0 M $MgSO_4$ solution. The height of the specific anodic oxidation peak, varying with the alkaline sulfate in the solution, is as follows; $K_2SO_4 >> Na_2SO_4 > Cs_2SO_4 > Rb_2SO_4 > Li_2SO_4$.

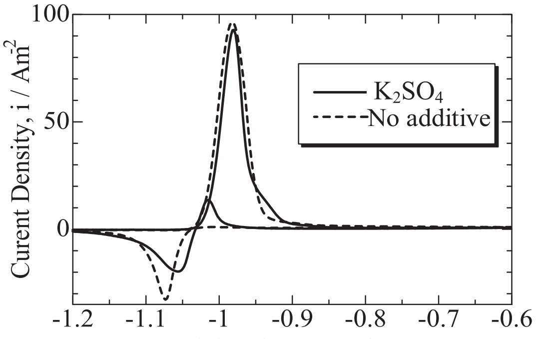

Fig. 2. Cyclic voltammograms (CVs) of lead electrodes in 4.35 M sulfuric acid solution with or without 0.5 M K_2SO_4.

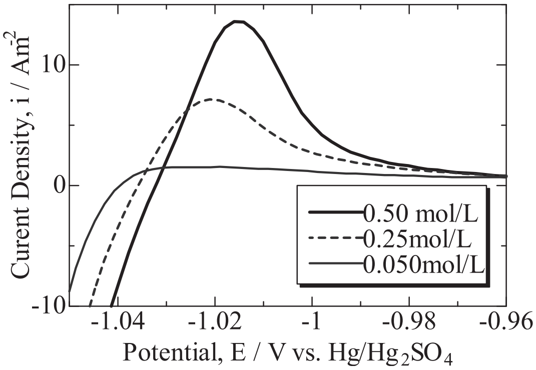

Fig. 3. Cathodic scans of CVs of lead electrodes in 4.35 M H_2SO_4 + x M K_2SO_4 solution (x = 0.50, 0.25, 0.050).

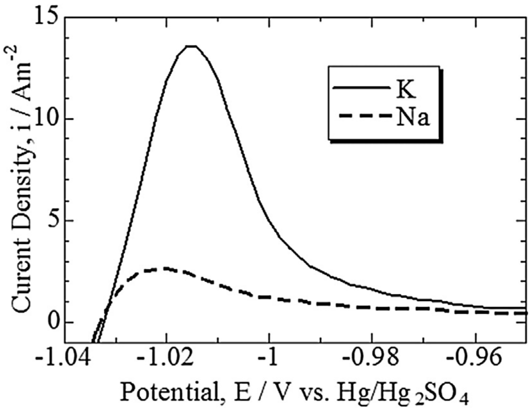

Fig. 4. Cathodic scans of CVs of lead electrodes in 4.35 M H_2SO_4 + 0.5 M X_2SO_4 solution (X = K, Na).

3.2. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDX)

After immersing the lead plates in 4.35 M H_2SO_4 + 0.5 M K_2SO_4 solution for 1 day or 5 weeks, the surfaces of the plates were analyzed by SEM-EDX, SEM images and the quasi-quantitative analysis, calculated from the obtained EDX spectra, are shown in

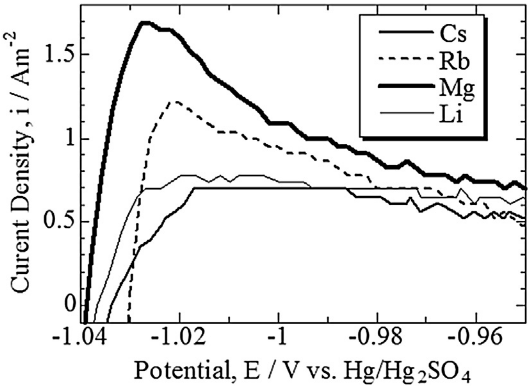

Fig. 5. Cathodic scans of CVs of lead electrodes in 4.35 M H_2SO_4 + 0.5 M X_2SO_4 (X = Cs, Rb, Li) or 1.0 M $MgSO_4$ solution.

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