Journal of Asian Electric Vehicles, Volume 5, Number 2, December 2007

Surface Morphology of Pb and PbO_2 Electrodes during Charge and Discharge in Sulfuric Acid Electrolyte Containing Some Additives

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Abstract

The ITE Battery Research group has developed a new organic battery activator for new and used lead-acid batteries. The chemical composition of the activators is a mixture of the soluble organic polymer such as polyvinyl alcohol and inorganic salts (metal ions). The detail morphological study are required for the formation of $PbSO_4$ *on the electrode. This paper summarizes the effects of the organic activator and metal ions in the activator during the charge and discharge. The chemical redox reactions were carried out for Pb and* PbO_2 *powders with* H_2O_2 *in sulfuric acid. It is considered that these reactions give useful information for the electrode processes of lead-acid batteries. The experimental results support the basic concepts for life extension of lead-acid batteries by ITE activator.*

Keywords

lead-acid battery, electrode surface, morphology, organic polymer activator, metal ion, $PbSO_4$

1. INTRODUCTION

Lead-acid batteries account for the largest segment of battery market. These batteries find applications in cars, trucks, and busses for starting, lighting, and ignition, motive power for fork lift trucks and golf carts, for energy storage in UPS and utility applications. The total worldwide market is approximately $20 billion and is expected to grow significantly in the future as the economies of China, India and other countries approach that of North America, Europe, and Japan. The lead-acid battery has a price advantage over several other battery systems with competitive performance [Kozawa, 2007].

It has been well confirmed that the lead-acid batteries deteriorate by a so-called sulfation on the negative electrode. The authors have reported the recovery from the sulfation by polyvinyl alcohol (PVA) as a main component of organic polymer activators [Minami et al., 2004; Kozawa et al., 2006]. The main action of the polymers is to produce fine particles of $PbSO_4$ on the negative electrode. Such a $PbSO_4$ is also charged to fine particles of Pb because the reactive sites with higher surface are produced on the electrode surface. It is possible to reuse the deteriorated batteries after the addition of the activators to the electrolyte [Tachibana et al., 2003]. Moreover, when the activators are added to the electrolyte of new batteries, the battery life may be extended [Nakagawa et al., 2006].

Since the morphological observations are insufficient in a series of studies on the lead-acid batteries [Sugawara et al., 2003], the authors have studied the effects of organic polymer activators on the morphology of electrode surface after the charge-discharge cycles of model cell [Nakagawa et al., 2006]. Also, the ITE activator is a mixture of organic polymer and inorganic salts (metal ions). It is necessary to study the effect of metal ions on the morphology of the electrode surface [Mori et al., 2007].

Moreover, the effects of PVA as organic polymer activators on the morphology of $PbSO_4$ formed in the oxidation of Pb powder by H_2O_2 as a model of discharge of anode. The reaction as a model of cathode was carried out for the reduction of PbO_2 by H_2O_2 [Hattori et al., 2007]. The results on the surface morphology are summarized in this paper.

2. EXPERIMENTAL

2.1 Observation of Surface morphology of Pb and PbO_2 *electrodes during charge and discharge*

The Pb negative electrode was lead plate of 2 cm^2 and pretreated by chemical polishing in CH_3COOH-H_2O_2 before use. The same lead plate was oxidized in 5 M H_2SO_4 at 6 mA/cm^2 for 120 min, and used as the PbO_2 positive electrode. The two electrodes were placed in a 50 ml beaker, and then the electrolyte of 5 M H_2SO_4 was added to be used as a model cell. The organic polymers used were polyvinyl alcohol (PVA) and PVA based ITE's activator (P000, PN30 and PNH2). The charge-discharge tests were carried out by a TOSCAT-3000 (Toyo

System Co., Ltd.). The model cell was charged was at 2 mA for 1 min, and then discharged to 1.8 V at 10 mA. The electrode surface after the 2000th discharge was characterized by XRD (Shimazu XD-D1) and SEM (JEOL JSM-5200).

2.2 Effect of metal ions on surface morphology

The working electrode (1 x 1 cm^2) was prepared from a Pb foil (purity: 99.9%, thickness: 0.2 mm). The Pb electrode was chemically polished in CH_3COOH- H_2O_2 solution for 10 s, and then washed with pure water [6]. The electrolyte was a 5 M H_2SO_4 containing Ag^+, Cu^{2+}, Ni^{2+}, In^{3+}, and Sn^{2+}, which were added as sulfates. The Pb electrode was first subjected to cyclic voltammetry (CV) measurements. The metal ion concentration was 2 x 10^{-4} M, and ITE organic polymer activators (P000) were also tested for comparison with the metal ions. The working Pb electrode was cycled at a sweep rate of 20 mV/s between -1.4 and 0 V vs. Hg/Hg_2SO_4. After 20 cycles, the electrode was washed with pure water and subjected to SEM measurements.

2.3 Depsition of $PbSO_4$ on Pb and PbO_2 with chemical reaction

The Pb powder (2 g) was added to 50 mL of 5 M H_2SO_4 containing PVA (0, 0.5, and 1%), and magnetically stirred. Then 10 mL of 1 M H_2O_2 as an oxidizing agent for Pb was added to the solution all at once. After 5 min and 60 h, the powder was filtered off and dried in a desiccator with silica gel. The similar procedure was tried for the formation of $PbSO_4$ on PbO_2. The H_2O_2 and Na_2SO_3 were used as the reducing agents for PbO_2. The Pb and PbO_2 powders were characterized by XRD and SEM.

3. RESULTS AND DISCUSSION

3.1 Electrode surface morphology during charge and discharge

Figure 1 shows the charge-discharge curve at 100th cycle in 5M H_2SO_4. The purpose of the charge-discharge cycle test is to prepare the sample for the observation of surface morphology. The charge was carried out at 2 mA for 1 min, and the discharge conditions at 10 mA to 1.8 V were selected. These conditions gave the nearly equal electricity for the charge and discharge. The similar charge-discharge curves were observed over the whole cycles, and the electrode after 2000th cycle was subjected to the morphology observation.

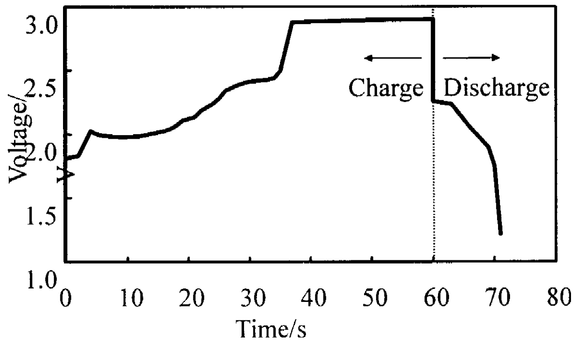


Fig. 1 Charge-discharge curve of the model cell at 100th cycle

Since the charge and discharge were not deep, the discharge capacity was nearly kept constant up to 2000th cycle. Also, no significant difference in the charge-discharge cycle tests was observed for the electrolyte with and without organic polymers. It is considered that the deteriorations of positive and negative electrodes were negligible small. Consequently, these electrodes after 2000th cycle were subjected to the observation of surface morphology.

Figure 2 shows the XRD patterns of the positive and negative electrodes surfaces after the discharge at 2000th cycle in 5 M H_2SO_4. The similar XRD patterns were obtained for the electrodes in the electrolytes with organic polymers. The diffraction signals of $PbSO_4$ with Pb and PbO_2 were observed for the positive electrode. The negative electrode showed the signals of $PbSO_4$ with Pb, and hence indicated the progress of the charge and discharge reactions in this model cell.

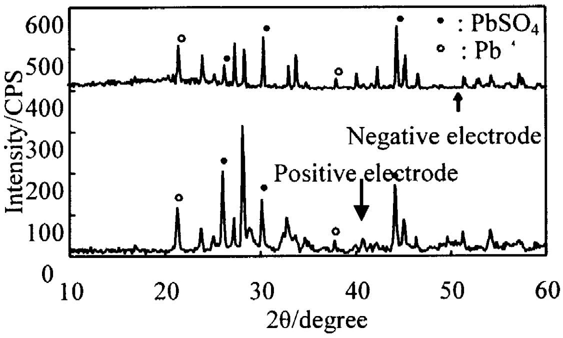
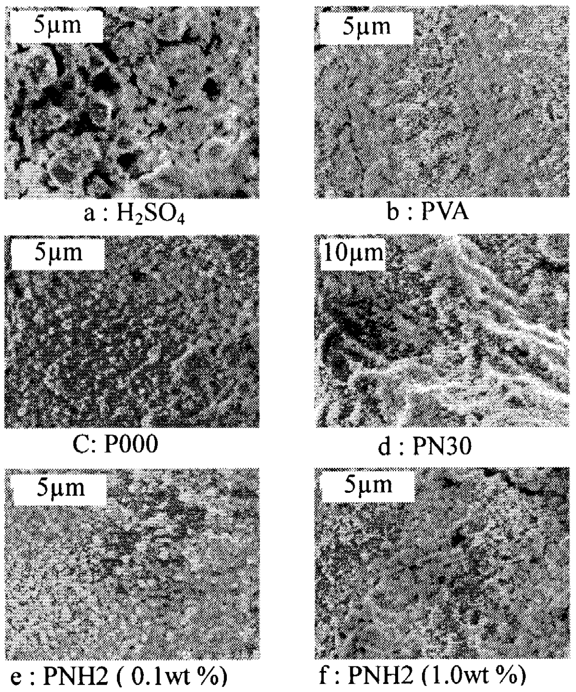


Fig. 2 XRD patterns of positive and negative electrode after charge-discharge cycles

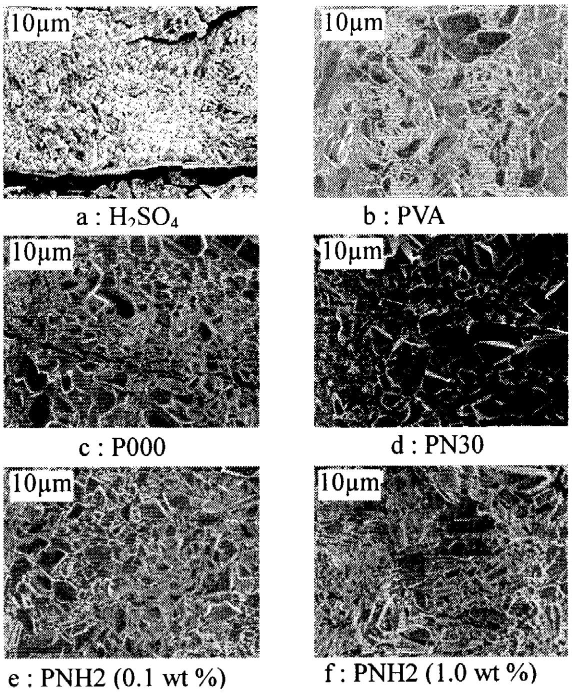
Figure 3 shows the effect of organic polymers on the morphology of negative electrode surface after 2000 cycles. The $PbSO_4$ formed on Pb in 5 M H_2SO_4 was the aggregation of the particles with the size of 3-5 μm as shown in Figure 3a. When PVA was added to the 5 M H_2SO_4 electrolyte, the particle size of $PbSO_4$ was below 1 μm and uniformly covered the electrode surface (Figure 3b). Other activators (P000, PN30, and PNH2) gave the same results for the surface morphology as shown in Figure 3c-Figure 3f. These results indicate that the organic polymers take part in the formation of the $PbSO_4$ with fine particles.

The $PbSO_4$ formation in the discharge of negative elec-



a : H_2SO_4 b : PVA
C: P000 d : PN30
e : PNH2 (0.1wt %) f : PNH2 (1.0wt %)

Fig. 3 SEM images of negative electrode surface after charge-discharge cycles



a : H_2SO_4 b : PVA
c : P000 d : PN30
e : PNH2 (0.1 wt %) f : PNH2 (1.0 wt %)

Fig. 4 SEM images of positive electrode surface after charge-discharge cycles

trode is considered as follows. The lead ions (Pb^{2+}) formed on Pb diffuse to bulk in the first step, and produce $PbSO_4$ on the Pb electrode combined with sulfuric acid in the second step. When the organic polymer is added to the H_2SO_4 electrolyte, the formation of $PbSO_4$ is supposed to occurs in the adsorbed layer of the polymer. Accordingly, the Pb^{2+} is concentrated in the adsorbed layer and reacts with H_2SO_4, which diffuse from the bulk to the electrode surface. The resulting $PbSO_4$ is expected to be fine particles, and becomes more active for the charge and discharge reaction. It has been considered that the batteries deteriorate by the passivation film of $PbSO_4$ with larger size of crystals. This phenomenon is a so-called sulfation, which can be depressed by the addition of organic polymer to the H_2SO_4 electrolyte.

Figure 4 shows the effect of organic polymers on the morphology of positive electrode surface after 2000th cycle. When the polymer was added to the electrolyte, the surface of the electrode was covered with slightly larger particles than that formed in H_2SO_4 electrolyte. This result indicates that the $PbSO_4$ formation slowly proceed in the polymer containing electrolytes. The Pb^{2+} is formed in the first step by the reduction of PbO_2 on the positive electrode, and then reacts with H_2SO_4 to produce $PbSO_4$ on the electrode in the 2nd step. The diffusion of H_2SO_4 is slower than that in negative electrode because the diffusion species are H_2SO_4 molecules in the concentration of battery electrolyte. Moreover, the adsorbed organic polymer layer disturbs the diffusion of H_2SO_4, the formation of $PbSO_4$ slowly proceed to produce the larger size of precipitates on the electrode. However, there was the slight effect of organic polymers on the particle sizes compared to that in the negative electrode. It seems reasonable to conclude that the deterioration of lead-acid batteries is caused by the sulfation on the negative electrode.

3.2 Effect of metal ions on surface morphology

Figure 5 shows the cyclic voltammograms of the Pb electrode in 5 M H_2SO_4 containing Ag^+ ions as an example. The redox couple of $Pb/PbSO_4$ was observed around -1.1 V. The current below -1.7 V shows hydrogen evolution. The addition of Ag^+ increased the current at the redox couple, and hence the Ag^+ ion activates the formation of $PbSO_4$. The hydrogen evolution deviated to a

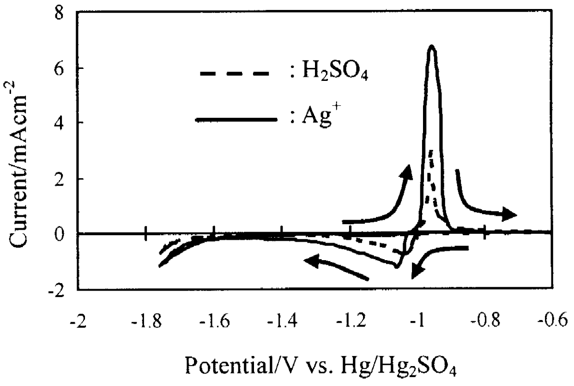


Fig. 5 Cyclic voltammograms of Pb in H_2SO_4 with and without Ag^+ at 20 mV/s

more positive potential than that in H_2SO_4 without Ag^+. The deposition of Ag on Pb may decrease the hydrogen evolution potential. The effect of Cu^{2+} gave the same result as that of Ag^+ in the current and shift in the hydrogen evolution potential.

The addition of In^{3+} slightly decreases slightly the current of the redox couple of $Pb/PbSO_4$, and the hydrogen evolution potential shifts to the negative region due to the deposition of In with a higher hydrogen overpotential on Pb. The Ni^{2+} and Sn^{2+} resulted in a decreased current and shift in the hydrogen evolution potential to the positive region compared to that in the H_2SO_4 electrolyte.

Figure 6 shows the relationships of the CV peak current and the standard electrode potential (E°) of metal ions for metal. The added metal ions may be classified in two groups of A (Cu^{2+} and Ag^+) and B (In^{3+}, Ni^{2+}, and Sn^{2+}). The group A with higher E° values increased the redox current of $Pb/PbSO_4$, and the other ions with lower E° values had a little effect on the redox current. Since the E° values of the A group are higher than that of $Pb/PbSO_4$, the deposition of Ag and Cu occurs in the redox region of $Pb/PbSO_4$. On the other hand, the deposition of metal and dissolution of metal ions are considered to occur during the CV measurement for the of group B added ions.

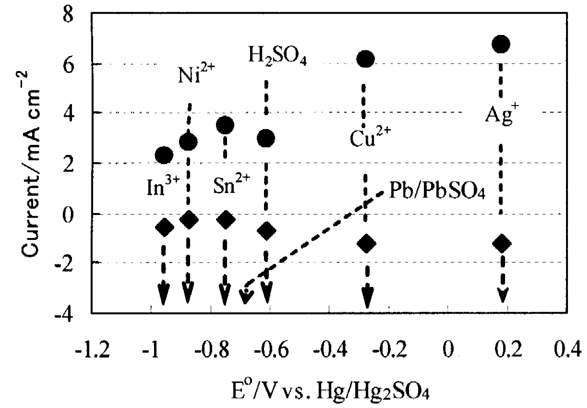


Fig. 6 Relationship between peak current and standard electrode potential (E°) of M^{n+}/M (M^{n+}: metal ion); ●: anodic current, ◆: cathodic current.

Figure 7 shows SEM images of electrode surface covered with the $PbSO_4$ particles. The surface was covered with the $PbSO_4$ particles of 2-3 μm in 5 M H_2SO_4 without metal ions (Figure 7a). When Ag^+ and Cu^{2+} were added to H_2SO_4 electrolyte, the $PbSO_4$ particle size became small (Figure 7b and Figure 7c). This effect of additives on the surface morphology corresponds to that of an organic polymer as shown in Figure 7f. On the other hand, there was a significant effect with the addition of Sn^{2+}, Ni^{2+} and In^{3+} on the surface morphology (Figure 7d, Figure 7e, and Figure 7f).

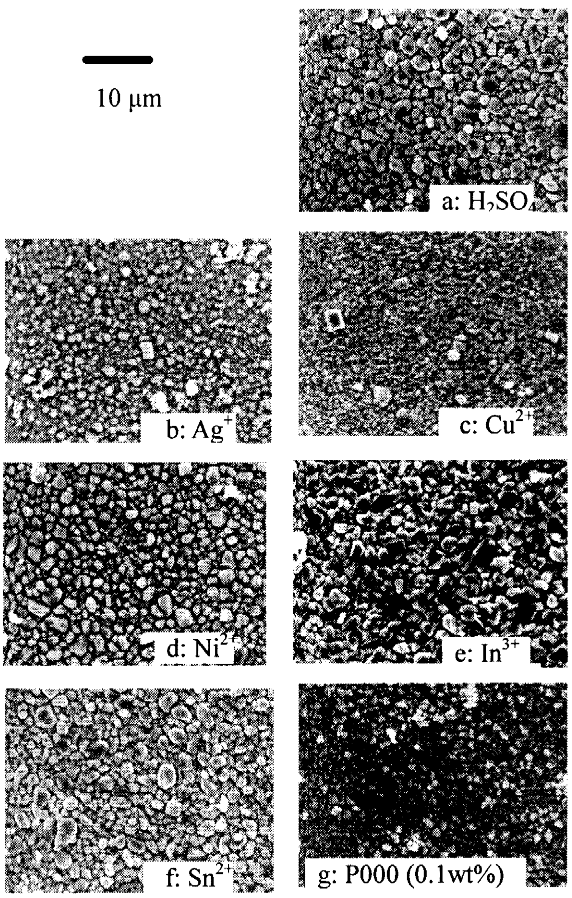


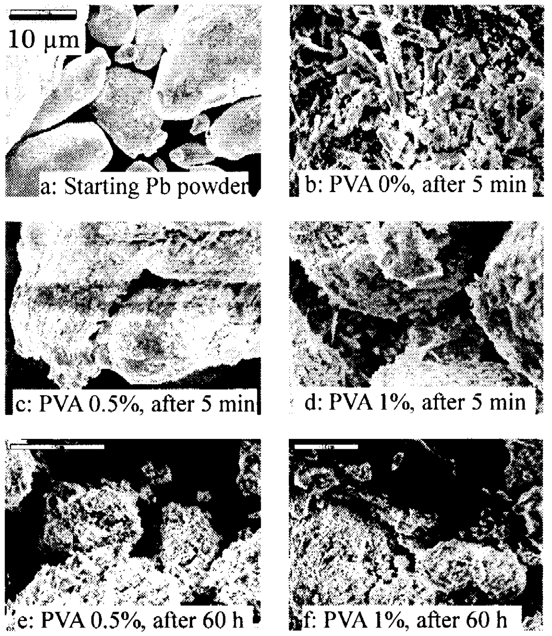
Fig. 7 Effect of metal ions on morphology of Pb negative electrode after charge-discharge cycles

The effect of Ag^+ and Cu^{2+} is assumed as follows. In the potential region of the $Pb/PbSO_4$ redox reaction, the added ions are reduced to Ag and Cu metal to form adatoms on the Pb electrode. These ad-atoms act as adsorption centers of H_2SO_4, and hence the formation of $PbSO_4$ rapidly proceeds resulting in the fine particles [7]. Further study is required to confirm this speculation.

3.3 Surface morphology of $PbSO_4$ on Pb and PbO_2 powders by chemical redox reaction

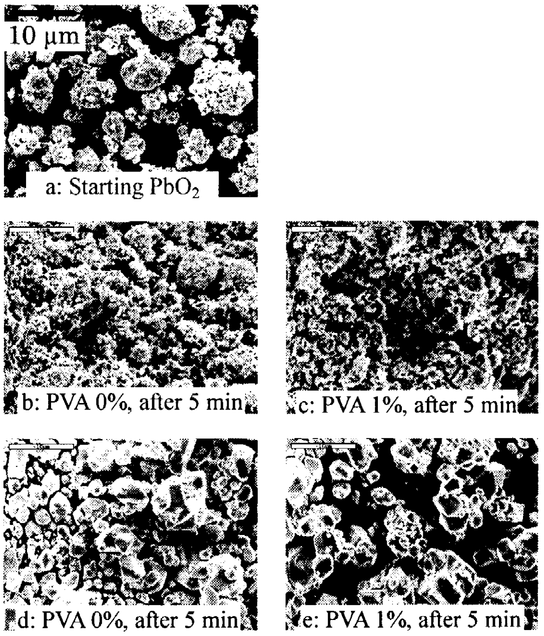
The XRD profiles of Pb and PbO_2 powders after the reaction with H_2O_2, indicated the formation of $PbSO_4$ on the starting powders. There was no difference between the two solutions with and without PVA. These reactions for Pb and PbO_2 with H_2O_2 is resemble in the formation of $PbSO_4$ to the discharge reaction of lead-acid battery. It is expected that the useful information may be obtained for the mechanisms of the battery reactions.

Figure 8 shows the morphology of Pb after the reaction with H_2O_2 in 5 M H_2SO_4 with and without PVA. The



a: Starting Pb powder
b: PVA 0%, after 5 min
c: PVA 0.5%, after 5 min
d: PVA 1%, after 5 min
e: PVA 0.5%, after 60 h
f: PVA 1%, after 60 h

Fig. 8 SEM pictures of the Pb powders obtained by the reaction with H_2O_2 in 5 M H_2SO_4 with and without PVA



a: Starting PbO_2
b: PVA 0%, after 5 min
c: PVA 1%, after 5 min
d: PVA 0%, after 5 min
e: PVA 1%, after 5 min

Fig. 9 SEM pictures of the PbO_2 powders obtained by the reaction with H_2O_2 (b and c) and Na_2SO_3 (d and e) in 5 M

deposition of $PbSO_4$ on Pb is observed in every case, and hence indicates the reaction on Pb surface in the same results as that in the Pb electrode [2]. When PVA (0.5%) was added to H_2SO_4 solution (Figure 8c), the particle size became fine compared with that formed in H_2SO_4 without PVA (Figure 8b). This result agrees with that reported in the charge and discharge of Pb anode. There was no significant difference between PVA concentration (Figure 8c and Figure 8d).

It is considered that PVA is predominantly adsorbed on Pb surface, and the higher concentration of Pb^{2+} in adsorbed layer to produce the fine particles of $PbSO_4$. The morphology after 60 h (Figure 8e and Figure 8f indicated larger particle sizes than that obtained at 5 min. The formation of $PbSO_4$ is fast, and the subsequent reaction time (60 h) results in the crystal growth by dissolution and redeposition. This corresponds to the rest period without charge and discharge in the battery use.

Figure 9 shows the morphological observation of PbO_2 powders after the reduction with H_2O_2 and Na_2SO_3. There was no difference on the morphology with and without PVA (Figure 9a, Figure 9b, and Figure 9c). On the other hand, the larger particle sizes of $PbSO_4$ were deposited by the reduction with Na_2SO_3.

Since the reduction of PbO_2 with H_2O_2 is fast, it is considered that the significant effect of PVA on the morphology is small for the $PbSO_4$ particle on PbO_2. This result corresponds to that previously reported in the charge-discharge of PbO_2 electrode. It seems reasonable that the deterioration of battery is attributable to the sulfation on Pb anode. The present method is considered to be useful for the consideration of battery reaction.

4. CONCLUSION

The morphological observation of $PbSO_4$ formed on Pb and PbO_2 electrodes was carried out in the sulfuric acid electrolyte containing some additives. The obtained results are as follows.

1. The fine particle sizes of $PbSO_4$ on the negative electrode deposited after the charge-discharge cycles in the electrolyte with organic polymers. The $PbSO_4$ formed in the electrolyte with the organic polymers on the positive electrode became larger in the size than that in the electrolyte of H_2SO_4.
2. The addition of Ag^+ and Cu^{2+} with higher redox potential for Ag and Cu resulted in the formation of smaller particles of $PbSO_4$ compared with those formed in H_2SO_4. On the other hand, there was no effect by In^{3+}, Ni^{2+}, and Sn^{2+} with a lower redox potential on the particle sizes of $PbSO_4$. The deposition of Ag and Cu during the redox cycles of Pb and $PbSO_4$ occurs, resulting in the $PbSO_4$ formation on the undeposited areas. Accordingly, it is considered that the addition of Ag^+ and Cu^{2+} causes the formation of $PbSO_4$ with smaller particle sizes.
3. The $PbSO_4$ on the particles of Pb and PbO_2 was formed by the redox reaction with H_2O_2 or Na_2SO_3 in 5 M H_2SO_4 containing PVA, and characterized by SEM observation. The fine particle sizes of $PbSO_4$ were deposited on the Pb after the reaction with H_2O_2

in the H_2SO_4 containing PVA. On the other hand, there was a significant difference of the particle sizes of the $PbSO_4$ formed on PbO_2 between the H_2SO_4 with and without PVA. It is considered that these reactions give useful information for the electrode processes of lead-acid batteries.

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(Received September 8, 2007; accepted November 21, 2007)