[May, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *60*, *1567—1572 (1987)* 1567

The Oxidation of $PbSO_4$ to PbO_2 in Sulfuric Acid Solution

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(Received December 24, 1985)

The interface between PbO_2 and $PbSO_4$ was considered to be the reaction site of the oxidation of $PbSO_4$ to PbO_2. The area of this site depended on the changing crystal size of $PbSO_4$ with the discharge conditions. The oxidation rate of $PbSO_4$ to PbO_2 increased with a decrease in the crystal size of $PbSO_4$ since the reaction site area per unit volume increased with a decrease in the crystal size of $PbSO_4$. The oxidation of $PbSO_4$ to PbO_2 depended on the discharge current, the sulfuric acid concentration and the rest time after a discharge.

$PbSO_4$ is deposited on the electrode surface during discharging of the positive active material of a lead-acid battery. The charge reaction of the positive active material is a conversion from $PbSO_4$ by anodic oxidation at the electrode surface. This reaction has been studied by many workers.[1-8] They potentiostatically investigated the oxidation of $PbSO_4$ formed by the anodic polarization of lead in the $PbSO_4$ potential region and suggested that the formation process of PbO_2 involved the nucleation and three-dimensional crystal growth. Casson et al. used an electrodeposited PbO_2 electrode to show that there is no evidence for nucleation and crystal growth.[9] Pohl measured different current-time curves at a lead electrode in a sulfuric acid solution during anodic polarization. He used an anodic current preimpulse before potentiostatic oxidation. The current-time curves measured after an anodic current preimpulse did not have any peaks. From this result, he suggested that the charge reaction did not proceed through nucleation and crystal growth.[2]

$PbSO_4$ is a nonconducting ionic crystal that becomes depodited on an electrode surface as a thin dense film.[9] Its solubility is very small in a sulfuric acid solution.[11] Therefore, only a special site can sustain a sufficient reaction rate to oxidize $PbSO_4$ to PbO_2. In this study, the effect of the size of $PbSO_4$ on the oxidation of $PbSO_4$ to PbO_2 was investigated.

Experimental

A lead rod mounted in a teflon tube was used as the working electrode (purity:99.9%). This electrode was polished with emery paper and etched with dilute nitric acid. The lead electrode surface was oxidized to PbO_2 in 0.5 M† H_2SO_4 at 1 mA cm^{-2} for about 24 h, and then galvanostatically discharged at 1 mA cm^{-2} in 0.5 M H_2SO_4. The discharge-charge cycle was continued until the capacity of the PbO_2 electrode increased to 40 mA min.

Figure 1 shows the experimental cell used in this study. The PbO_2 electrode placed in it and discharged at a constant current. $PbSO_4$ crystals became deposited on its surface during the discharge. The surface $PbSO_4$ was oxidized to PbO_2 by utilizing the potential sweep method. Anodic sweeps from the rest potential after discharging toward the anodic direction at various sweep rates were carried out using a potentiostat (HOKUTO HA-301) and a function-generator (HOKUTO HB-104). The anodic currents were recorded with an X-Y recorder (WATANABE). A Hg/Hg_2SO_4 electrode was used as a reference electrode and a Pt wire was used as a counter electrode. All experiments were performed at 30 °C.

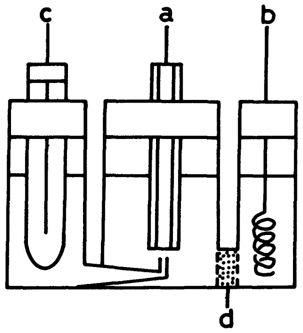

Fig. 1. Schematic representation of cell, a: working electrode (Pb; diameter=0.4 cm), b: counter electrode(Pt), c: reference electrode(Hg/Hg_2SO_4), d: fritted glass.

Results and Discussion

Figure 2 shows a potentiodynamic current-voltage curve for the oxidation of $PbSO_4$ to PbO_2 by the potential sweep method in 5.0 M H_2SO_4. $PbSO_4$ was formed by a potentiostatic discharge at 0.8 V vs. Hg/Hg_2SO_4 in 5.0 M H_2SO_4 until the cathodic current decreased to 0 mA. Two anodic peaks were observed at 1.0 and 1.43 V. The peak at 1.0 V corresponded to the oxidation of PbO to PbO_2.[12] The recovered electrode potential after the potentiostatic discharge was more cathodic than the redox potential of the $PbO_2/PbSO_4$ couple. The PbO_2/PbO redox potential was more cathodic than the $PbO_2/PbSO_4$ redox potential. The recovered redox potential may have been due to the mixed potential of the $PbO_2/PbSO_4$ and PbO_2/PbO

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† 1 M=1 mol dm^{-3}.

couples. PbO is not thermodynamically stable in an acidic media. The local pH at the interior of the film formed by the potentiostatic discharge increased, since PbO is thermodynamically stable in the film. The PbO_2/PbO electrode potential at pH=9.34 was about 0.5 V vs. Hg/Hg_2SO_4. The electrode potential of the $PbO_2/PbSO_4$ couple was about 1.0 V vs. Hg/Hg_2SO_4 at pH=0.48.[13] Therefore, the recovered electrode potential was due to a mixed potential of the $PbO_2/PbSO_4$ and PbO_2/PbO couples. The peak at 1.43 V corresponded to the oxidation of $PbSO_4$ to PbO_2. The formation of PbO depended on the discharge conditions. PbO was formed by a deep discharge at a slow rate. In order to avoid the formation of PbO at the interior of $PbSO_4$, the electrode was discharged at a high rate, but not deeply. The potential after such a discharge recovered to the redox potential of the $PbO_2/PbSO_4$ couple. This fact indicates that PbO was not formed at the interior of the film. The oxygen evolution current was observed at 1.5 V and superimposed to the anodic current for the oxidation of $PbSO_4$ to PbO_2. In order to achieve clear curves for the oxidation of $PbSO_4$ to PbO_2, the current for the oxygen evolution was subtracted from the whole anodic current. The oxygen evolution current was determined from the potentiodynamic current-voltage curve by use of a fully charged electrode. Figure 3 shows potentiodynamic current-voltage curves which were obtained after the subtraction of the oxygen evolution current from the

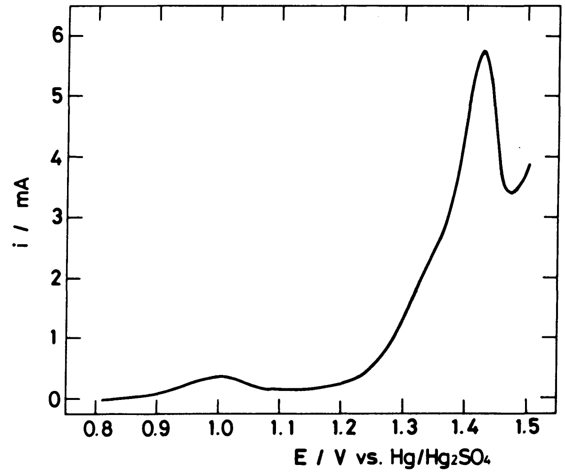

Fig. 2. Potentiodynamic current-voltage curve in 5.0 M H_2SO_4 of PbO_2 electrode discharged at 0.8 V vs. Hg/Hg_2SO_4 in 5.0 M H_2SO_4.

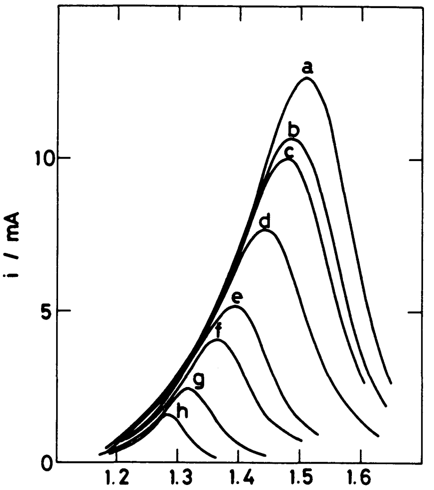

Fig. 3. Potentiodynamic current-voltage curves in 5.0 M H_2SO_4 of PbO_2 electrode discharged at 10 mA cm^{-2} in 5.0 M H_2SO_4, sweep rate a: 10, b: 8, c: 7, e: 3, f: 2, g: 1, h: 0.5 mV s^{-1}.

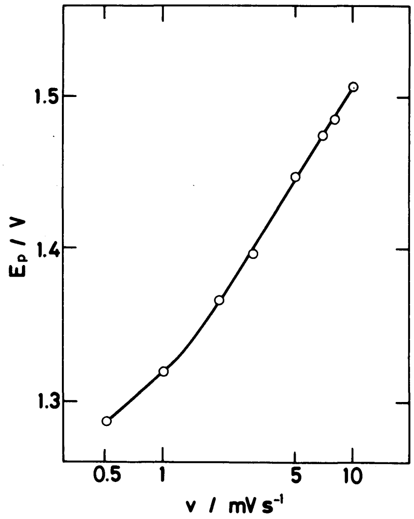

Fig. 4. Dependence of peak potential on sweep rate obtained from Fig. 3.

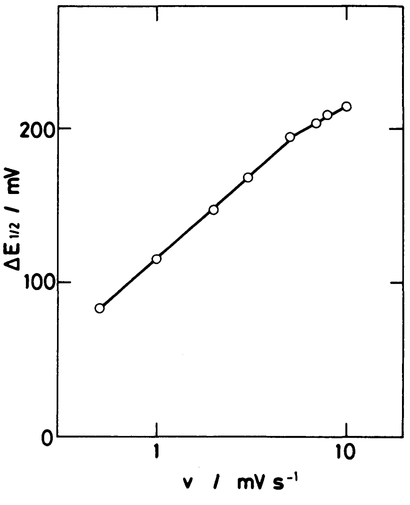

Fig. 5. Dependence of half-wave width on sweep rate obtained from Fig. 3.

whole anodic current. Symmetric current-potential curves were observed. Such curves are similar to those for a surface reaction rather than a diffusion-controlled electrode reaction.[14] Figure 4 shows the dependence of the peak potential on the sweep rate obtained from Fig. 3. The peak potential shifted to a more anodic potential upon increasing the sweep rate. Figure 5 shows the dependence of the half-wave width on the sweep rate (obtained from Fig. 3). The width became larger with increasing sweep rate. These results indicate that the charge-transfer process of the oxidation of $PbSO_4$ to PbO_2 is very slow. These dependences are very similar to those obtained for the irreversible electrode reaction of an adsorbed species on the electrode surface. Figure 6 shows the dependence of the peak current on the sweep rate (obtained from Fig. 3). The peak current was proportional to $v^{0.73}$. Such behavior regarding the oxidation of $PbSO_4$ to PbO_2 may be understood in terms of the electrochemistry of the adsorbed species on the electrode surface, if the $PbSO_4$ deposited on the electrode surface is a monolayer. $PbSO_4$ was deposited on the electrode surface as small ionic crystals. Therefore, it is very difficult to treat the oxidation of $PbSO_4$ to PbO_2 quantitatively in terms of the electrochemistry of adsorbed species, though the results shown in Figures 4, 5, and 6 were very similar to the irreversible electrode reaction of an adsorbed species on the electrode surface. In this study the electrode reaction of the conversion of $PbSO_4$ to PbO_2 was determined by an assumption regarding the reaction site (discussed below).

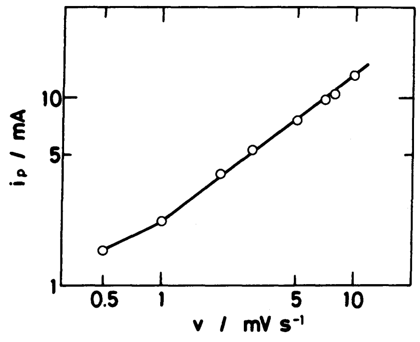

Fig. 6. Dependence of peak current on sweep rate obtained from Fig. 3.

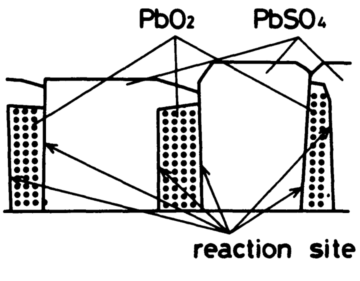

Fig. 7. Schematic representation of reaction site for charging reaction of $PbO_2/PbSO_4$ electrode.

A large ionic crystal without electronic and ionic conductivities would not be able to oxidize in the same way as soluble species. In the case of the oxidation of $PbSO_4$, the soluble species would be Pb^{2+} ions. The dissolving Pb^{2+} ions from a $PbSO_4$ crystal are oxidized to Pb^{4+} ions and react with H_2O to precipitate on the electrode surface as PbO_2:

$$Pb^{2+} + 2H_2O \longrightarrow PbO_2 + 2e^- + 4H^+. \qquad (1)$$

Conditions for the oxidation of $PbSO_4$ are not equal over the electrode surface, causing the distribution of the oxidation rate of $PbSO_4$ to PbO_2. The high oxidation rate is sustained by the high concentration of Pb^{2+} ions on the PbO_2 surface. In this study, it is assumed that the interface between PbO_2 and $PbSO_4$ is the reaction site (Fig. 7). At such an interface, Pb^{2+} ions can be adequately supplied from the $PbSO_4$ crystal; also, a charge-transfer reaction can occur on PbO_2. The peak current was larger than that estimated from the solubility of Pb^{2+} ions and the diffusion coefficient in the electrodeposition layer of PbO_2 on a planar electrode in a sulfuric acid solution. If the oxidation of $PbSO_4$ occurs at the interface between $PbSO_4$ and PbO_2, the diffusion path is so short that the mass-transport process hardly influences the oxidation of $PbSO_4$. The potentiodynamic current-voltage curve in Fig. 3 can be explained as follows. As the electrode potential becomes more positive, the charge-transfer reaction rate increases, while the reaction site area decreases. The reaction rate depends on both the charge-transfer reaction rate and the reaction site area. If the oxidation of $PbSO_4$ proceeds with an increase and a decrease of the interface area between PbO_2 and $PbSO_4$, which corresponds to the reaction site area,[15] such a simple anodic peak could not be obtained. The reaction site area seems to decrease monotonously. Therefore, the maximum rate is obtained at the peak. The reaction-site area depends on the size of the $PbSO_4$ crystal since the interface area between PbO_2 and $PbSO_4$ per unit volume of $PbSO_4$ changes with this value. If the discharge capacity is the same, the surface area of $PbSO_4$ increases upon decreasing of the crystal size. As a result, the interface area between PbO_2 and $PbSO_4$ also increases upon decreasing the crystal size of $PbSO_4$.

Figure 8 shows electronmicrographs of $PbSO_4$ precipitated by galvanostatic discharges in 5.0 M H_2SO_4 at 0.5, 1.0, 5.0 and 10.0 mA cm^{-2}. The discharge was continued until it reached 600 mC cm^{-2}. The size of $PbSO_4$ decreased with increasing discharge current. The surface concentration of Pb^{2+} ions during the galvanostatic discharge depended on the discharge current. A large discharge current resulted

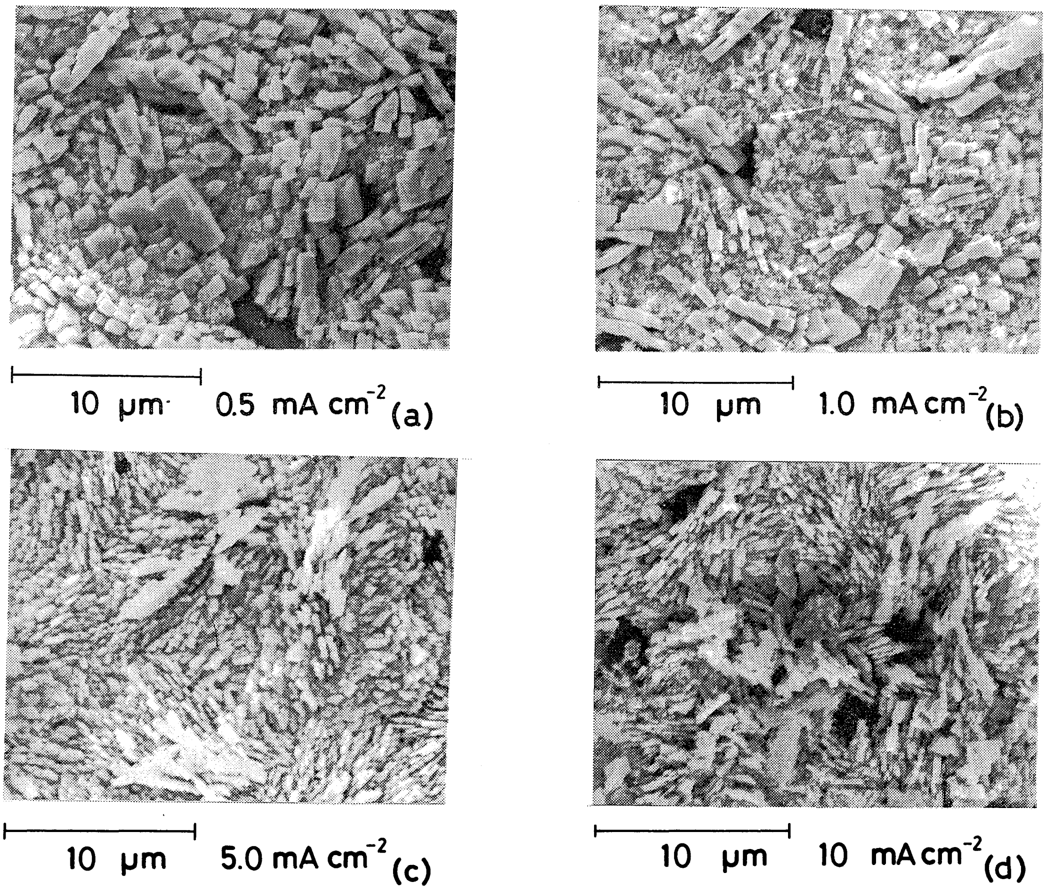

Fig. 8. Electronmicrographs of $PbSO_4$ precipitated by galvanostatic discharge at (a): 0.5 mA cm^{-2}, (b): 1.0 mA cm^{-2}, (c): 5.0 mA cm^{-2}, (d): 10.00 mA cm^{-2} in 5.0 M H_2SO_4, sweep rate 1 mV s^{-1}.

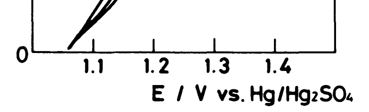

Fig. 9. Potentiodynamic current-voltage curves for the oxidation of $PbSO_4$ formed by galvanostatic discharge at 0.5, 1.0, and 10.0 mA cm^{-2} in 5.0 M H_2SO_4, sweep rate 1 mV s^{-1}.

in a large supersaturation of Pb^{2+} ions on the electrode surface and caused the formation of a lot of $PbSO_4$ nuclei. On the other hand, the large supersaturation of Pb^{2+} ions could not be caused by a small current discharge. Therefore, the crystal size of $PbSO_4$ increases with a decreasing discharge current.

Figure 9 shows potentiodynamic current-voltage curves for the oxidation of $PbSO_4$ formed by galvanostatic discharges at 0.5, 1.0 and 10.0 mA cm^{-2} in 5.0 M H_2SO_4. These discharges were continued until the current reached 1200 mC cm^{-2}. The anodic peak potential shifted to a more positive value upon decreasing the discharge current. This result indicates that the oxidation of $PbSO_4$ formed under a low discharge current is more difficult than that formed at a high discharge current. The size of $PbSO_4$ formed at a low discharge current was very large (Fig. 8). Increasing the size of $PbSO_4$ resulted in a decrease in the reaction-site area (as discussed above). Therefore, increasing the $PbSO_4$ crystal size caused difficulty regarding the oxidation of $PbSO_4$; also, the anodic peak potential shifted to more positive potentials. The shape of the anodic current peak obtained at a low current discharge was broad and nonsymmetrical. $PbSO_4$ may be oxidized with an increase and a decrease in the reaction-site area.[15] The oxidation of the very large $PbSO_4$ formed at a low discharge rate seems to be different from that of a small $PbSO_4$ crystal under high discharge rate.

Figure 10 shows electronmicrograhs of $PbSO_4$ crystals which were immersed in 5.0 M H_2SO_4 for a

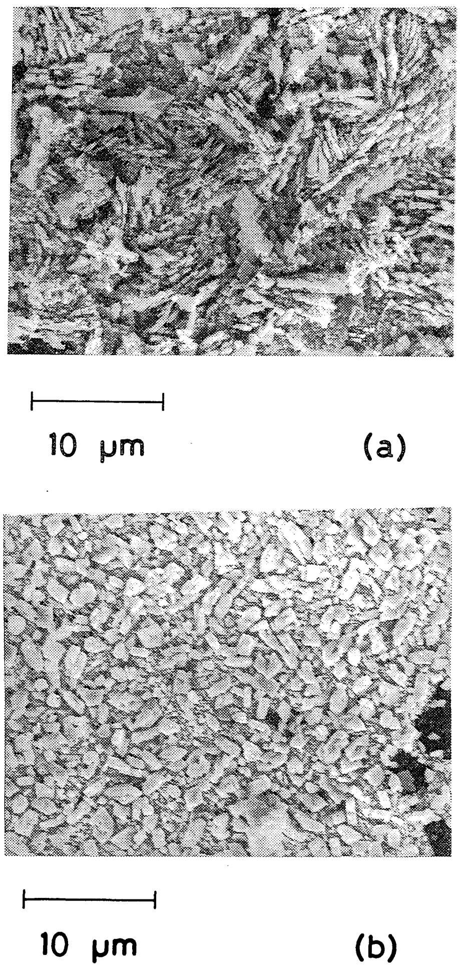

Fig. 10. Electronmicrographs of $PbSO_4$ precipitated by galvanostatic discharge at 1.0 mA cm^{-2} in 5.0 M H_2SO_4, immersion time (a): a few minutes (b): 60 min.

few minutes or one hour after a discharge at 10 mA cm^{-2} in 5.0 M H_2SO_4. The electronmicrographs show that immersion after a discharge results in an increased size of a $PbSO_4$ crystal as the result of an aging process which involves a mass transfer from small crystals to large crystals by way of the solution. A high stability and a reduction of the surface area and energy were obtained by this aging process. The difference in crystal size between (a) and (b) was smaller than that shown in Fig. 8.

Figure 11 shows potentiodynamic current-voltage curves for the oxidation of $PbSO_4$ in Fig. 10. The anodic current peak for the oxidation of $PbSO_4$ after a one-hour immersion appeared at a more positive potential than that after a few minutes. The amount of $PbSO_4$ increased as the result of immersion in a sulfuric acid solution (Fig. 10). Increasing the crystal size resulted in a shift of the current peak shown in Fig. 11, since the reaction site per unit volume of the $PbSO_4$ crystal decreased.

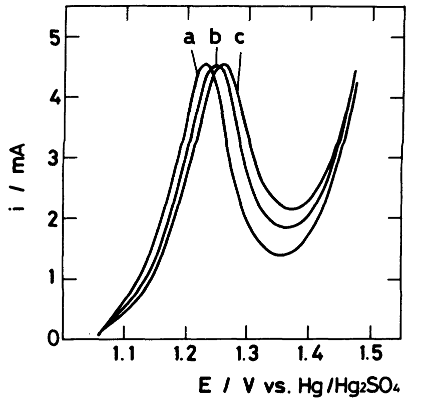

Fig. 11. Potentiodynamic current-voltage curves for the oxidation of $PbSO_4$ formed by galvanostatic discharge at 1.0 mA cm^{-2} in H_2SO_4 after immersion in 5.0 M H_2SO_4 for (a): a few minutes (b): 30 minutes (c): 60 minutes.

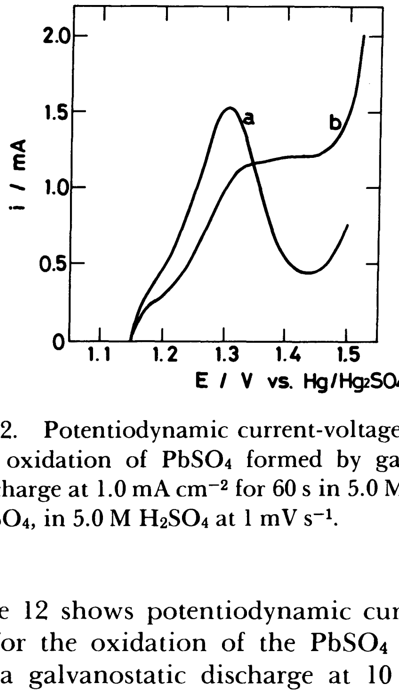

Fig. 12. Potentiodynamic current-voltage curves for the oxidation of $PbSO_4$ formed by galvanostatic discharge at 1.0 mA cm^{-2} for 60 s in 5.0 M and 0.5 M H_2SO_4, in 5.0 M H_2SO_4 at 1 mV s^{-1}.

Figure 12 shows potentiodynamic current-voltage curves for the oxidation of the $PbSO_4$ precipitated during a galvanostatic discharge at 10 mA cm^{-2} in 5.0 M and 0.5 M H_2SO_4 for 60 s. Both electrodes were oxidized in 5.0 M H_2SO_4 by a potential sweep method. The oxidation rate of $PbSO_4$ formed in 5.0 M H_2SO_4 was larger than that in 0.5 M H_2SO_4. The size of $PbSO_4$ depends on the concentration of the sulfuric acid solution (as discussed in previous paper [11]). In this case, the size of $PbSO_4$ formed in 5.0 M H_2SO_4 was less than that in 0.5 M H_2SO_4.

Thus, the reaction rate of the oxidation of $PbSO_4$ depends on the crystal size of $PbSO_4$ precipitated on the electrode surface during a discharge. The crystal size of $PbSO_4$ is very important for the oxidation of $PbSO_4$ to PbO_2. This fact indicates that the reaction site is the interface between $PbSO_4$ and PbO_2, at which a high reaction rate is sustained while allowing the oxidation of $PbSO_4$ to PbO_2.

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