

The effect of nicotinamide on the charge/discharge behavior of PbO_2 electrode in sulfuric acid solution

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(Received February 4, 1992; in revised form March 30, 1992)

Abstract

The effect of nicotinamide (NA) on the charge/discharge behavior of the positive electrode of a lead/acid battery was studied by cyclic voltammetry, charge/discharge cycling tests and scanning electron microscope observation. By adding NA into the sulfuric acid solution, the rate of capacity decrease of the PbO_2 electrode was reduced and its cycle life was prolonged. This phenomenon was considered to be due to NA adsorption on PbO_2 , which causes a morphology change in the PbO_2 and PbSO_4 crystals to enlarge the electrode surface area.

Introduction

Although many types of secondary batteries have been developed and commercialized, the lead/acid battery is the most mass-produced of these batteries because of its high reliability and relatively cheaper cost. The cycle life and the discharge capacity of a lead/acid battery is limited by the performance of the positive plate. It is interesting to study the effect of additives in the sulfuric acid solution to activate or passivate the electrode reaction of PbO_2 . The effect of inorganic additives such as SnSO_4 [1], NiSO_4 [2, 3, 5], H_3PO_4 [2, 4], MgSO_4 [3], Na_2SO_4 [3, 4], CoSO_4 [3-5], HgSO_4 [3], $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ [4], CdSO_4 [5], and ZnSO_4 [5] was studied extensively. As for organic substances, the addition of nicotinamide (NA) was reported [6] to be effective to prolong the cyclability, but its mechanism was not so clear. In the present paper, we aimed to confirm the effect of NA and to understand the role of NA, if the effect is positive.

Experimental

The lead dioxide working electrode for the charge/discharge cycling test was prepared by electrolytic oxidation of 0.3 M $\text{Pb}(\text{NO}_3)_2$ dissolved in 2 M HNO_3 solution onto a gold plate electrode of 0.785 cm^2 at 2 mA/cm^2 for 40 min. A dense lead dioxide film was obtained. The X-ray diffraction pattern of the film showed that it consisted

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mainly of β - PbO_2 . Charge/discharge cycling was carried out between 1.7 and 2.3 V versus a Pb electrode in 0.5 M H_2SO_4 at 1.27 mA/cm^2 using a charge/discharge unit (Hokuto Denko HJ-2010) and a Y-t recorder (Riken Denshi SP-65P). Nicotinamide (Wako Junyaku Co.) or isonicotinamide ((INA) (Tokyo Kasei Co.) of reagent grade was added to sulfuric acid solution, if necessary. Cyclic voltammograms of the lead (99.999%) rod electrode (surface area: 0.196 cm^2) were recorded in 0.5 M H_2SO_4 solution using a potentiostat-galvanostat (Hokuto Denko HA-301) with a function generator (Hokuto Denko HB-104) and an X-Y recorder (Riken Denshi F-3F). A rotating ring-disc electrode was also used, where the disc was β - PbO_2 made by Pb oxidation [7] and the ring was Pb. The geometry of the electrode was $r_1=5.5$ mm, $r_2=6.7$ mm and $r_3=8.5$ mm, respectively. A platinum wire as the counter electrode and $\text{Hg}/\text{Hg}_2\text{SO}_4$ as the reference electrode were used. H_2SO_4 , as the electrolyte, was deoxygenated with nitrogen gas and held at 30 ± 1 °C. A dual potentiogalvanostat (Nikko Koisoku DBGS-1) was used for ring current measurement. The surface of the PbO_2 electrode after charge or discharge was observed by a scanning electron microscope (SEM) (Riken Denshi F-3F). The solubility of PbO_2 and PbSO_4 in 0.5 M H_2SO_4 in the presence and the absence of NA or INA was measured. After having shaken the H_2SO_4 solution that contained reagent grade PbO_2 or PbSO_4 powder for 24, 48 and 72 h at 30 °C, the Pb concentration in the filtrate was determined by atomic absorption method, after adding HINO_3 to the sample solution and heating to decompose NA.

Results and discussion

Cyclic voltammograms of Pb in the absence and the presence of NA are shown in Fig. 1, where the solid line was obtained by using a conditioned electrode. Namely, Pb electrode was cycled for about 3 h with the scanning rate of 7 mV/s until peak current did not increase anymore. Peak A is the oxidation current corresponding to $\text{Pb} \rightarrow \text{PbSO}_4$ and peak B is the reverse reaction, peaks C and E correspond to $\text{PbSO}_4 \rightarrow \text{PbO}_2$,

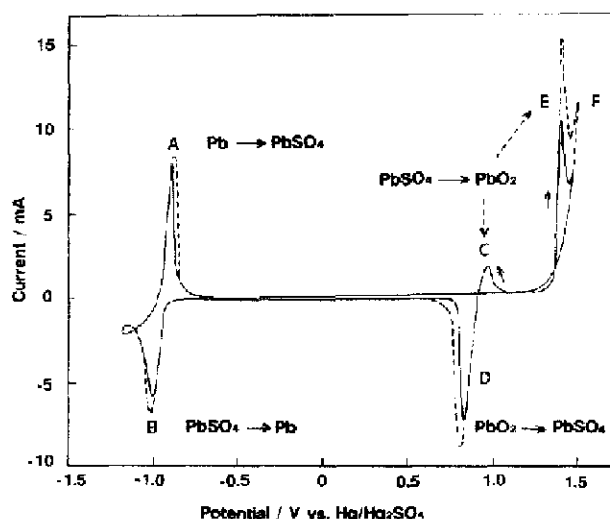


Fig. 1. Cyclic voltammograms for a Pb electrode (0.2 cm^2) in the absence (—) and the presence of 5 mM nicotinamide (---) in 0.5 M H_2SO_4 at 30 °C; $V=7$ mV/s .

peak D is its reverse reaction, and peak F is due to the oxygen evolution reaction. Peak E appeared at a less negative potential than was expected from the standard potential, caused by the retardation of the passive PbSO_4 film formed on the Pb substrate at about -0.9 V. Peak C appeared at a less noble potential than that of peak E in the cathodic scan studied by Sunderland [8]. After measuring the solid curve, NA was added into the Pb electrode inserted solution. The addition of NA enlarges the peak currents of peaks D and E, the peak potentials shift to less noble values for peak D and to less negative values for peak E, respectively. However, the NA-addition effect did not appear instantly. Peak currents increased gradually with cycling and saturated at constant values. The dotted curve in Fig. 1 was obtained 2 h later after NA addition. For this period, the potential was scanned. For peaks A and B, the NA addition also increased the peak currents. To avoid the PbSO_4 film-retardation effect, the starting potential in the cyclic voltammogram shifted to a less negative value of -0.8 V, when the normal cyclic voltammogram corresponding to the oxidation of PbSO_4 to PbO_2 and its reverse reaction was obtained (Fig. 2). The NA-concentration effect on peak current was not linear, but the peak current increased to some extent as NA concentration increased from 1 to 5 mM. The anodic peak potential became less negative and the cathodic peak potential became less noble. These potential shifts suggest that some retardation of the electrode reaction occurs, i.e., greater overpotential is needed to cause the electrode reaction to proceed though the peak currents for both peaks increased. Nicotinamide has a amide group in the β -position of a pyridine ring. The effect of NA on the cyclic voltammogram may be due to its pyridine ring, the amide group or its geometric configuration. The isomer of NA, INA, having the amide group in the γ -position of the pyridine ring, was also tested. Cyclic voltammograms are shown in Fig. 3, where the INA effect is smaller compared with the NA effect.

By using freshly prepared PbO_2 electrode, charge/discharge cycling was performed at the constant current of 1.27 mA/cm^2 between 1.7 and 2.3 V versus Pb electrode. At first discharge, the electrode showed the capacity of about 7 mA min. The capacity increased with the cycle number and showed a maximum value of about 30 mA min around 10 cycles, then gradually decreased. The charge/discharge current efficiency

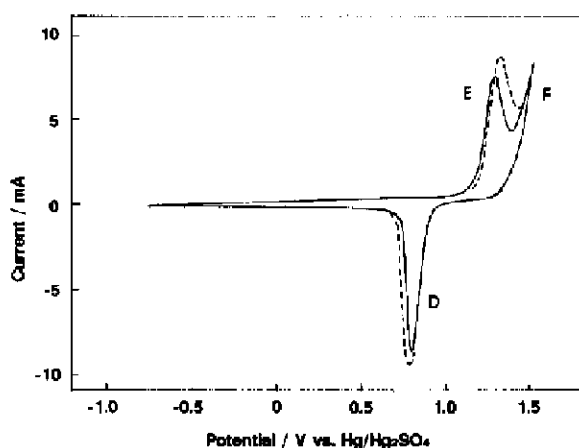


Fig. 2. Cyclic voltammograms for a Pb electrode. Experimental conditions are the same as Fig. 1.

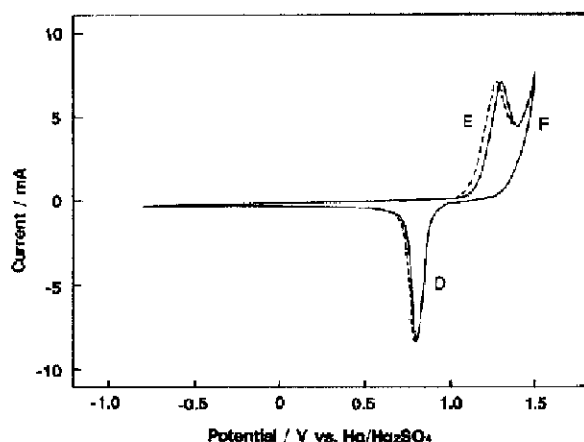


Fig. 3. Cyclic voltammograms for a Pb electrode (0.2 cm^2) in the absence (—) and the presence (---) of 5 mM isonicotinamide in $0.5 \text{ M H}_2\text{SO}_4$ at 30°C ; $V=7 \text{ mV/s}$.

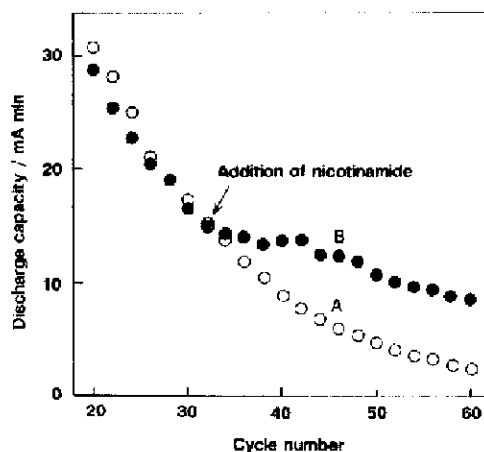


Fig. 4. Cycle life performance of a PbO_2 electrode (A) in the absence and (B) the presence of 5 mM nicotinamide in $0.5 \text{ M H}_2\text{SO}_4$ at 1.27 mA/cm^2 and voltage-limited charging and discharging at $1.70\text{--}2.30 \text{ V}$ at 30°C .

was about 75% at the initial cycles. When 5 mM of NA was added to the solution, the rate of capacity loss was reduced and the charge/discharge cycle life was prolonged (Fig. 4). When NA was present from the initial stage of the cycling test, it also showed a good effect as seen in Fig. 5. If the capacity decrease did not progress so much, the effect of NA appeared at any cycle number when it was added. However, the addition of INA in the H_2SO_4 solution did not result in as clear an effect compared to NA. The long-term stability of NA under strongly oxidizing conditions is unclear at present, but the effect of NA was kept at least for 10 cycles. This was proved by the SEM photographs of the Pb electrode surface (see later).

It is said that $\beta\text{-PbO}_2$ is discharged in H_2SO_4 solution through the following dissolution-precipitation mechanism [7]:

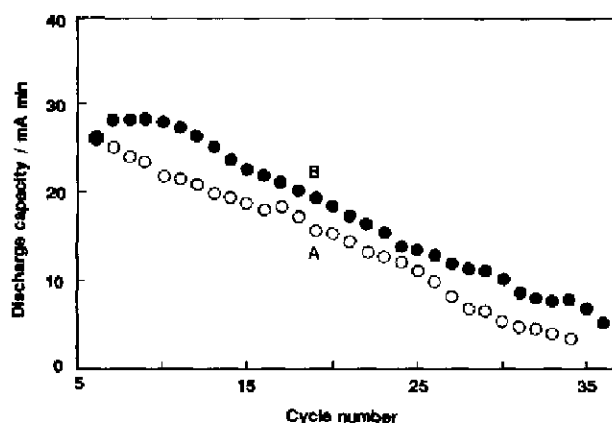


Fig. 5. Cycle life performance of a PbO_2 electrode (A) in the absence and (B) the presence of 5 mM nicotinamide in 0.5 $\text{M H}_2\text{SO}_4$ at 1.27 mA/cm^2 and voltage-limited charging and discharging at 1.70–2.30 V at 30°C .



Since the solubility of Pb^{2+} ions in H_2SO_4 solution is very small, Pb^{2+} ions formed by the disproportionation reaction accumulate on PbO_2 surface as a colloidal film and this accumulation causes a high overpotential at high-current discharge. If NA coordinates to Pb^{2+} ions to form complex ions and the solubility of total Pb(II) ions increases, the increased peak current on cyclic voltammograms and the good effect on charge/discharge cyclability of the PbO_2 electrode in the presence of NA will be understandable. To confirm this speculation, the discharge reaction of PbO_2 was studied using a rotating ring-disc electrode. Figure 6 shows a cyclic voltammogram of a $\beta\text{-PbO}_2$ disc in 0.5 M (A) and the ring current (B) corresponding to the reaction of the disc. The peak of cathodic disc current is due to the formation of PbSO_4 during the discharge of PbO_2 and the broad anodic peak is due to the formation of PbO_2 during the charging of PbSO_4 . Both peak currents were increased by the addition of 5 mM NA as has been seen in Figs. 1 and 2. A peak of ring current corresponding to a cathodic peak on the disc was observed during discharge. However, the expected ring current increase was not observed by the addition of NA, which suggests that the total Pb ion concentration did not increase in the presence of NA. In this case, it was assumed that Pb complex ions, if present, were also reducible at the nearly equal potential of Pb^{2+} reduction.

The solubilities of PbSO_4 and PbO_2 in H_2SO_4 in the absence and the presence of NA or INA were measured (Table 1), and they did not change by adding NA or INA. The UV-absorption spectra of the solution after filtration of PbSO_4 or PbO_2 powder were measured. There were no differences for the spectra of the solution containing NA or not, i.e., Pb–NA complex formation may not occur in acidic solution of 0.5 M H_2SO_4 .

After 10 charge/discharge cycles of PbO_2 in the H_2SO_4 solution with or without 5 mM NA or INA were carried out at the same condition given in Fig. 4; the surface morphology of PbO_2 was observed with a SEM. Figure 7 shows the electrode surface

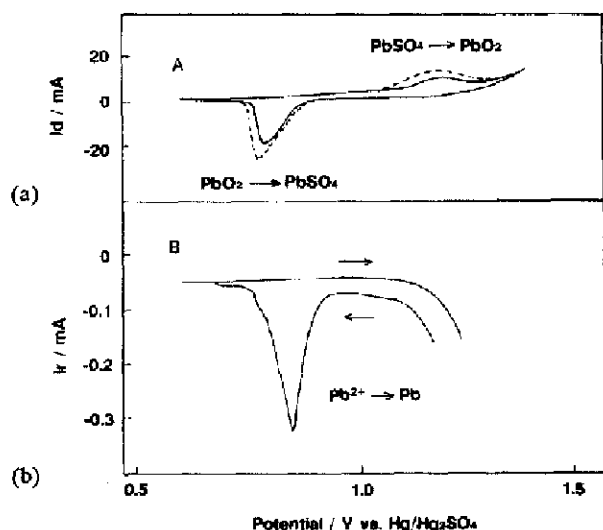


Fig. 6. Cyclic voltammograms of a PbO_2 (a) in the absence (—) and the presence of 5 mM nicotinamide (---) in 0.5 M H_2SO_4 at a scan rate of 10 mV/s and a rotation speed of 2000 rpm and (b) ring current in the absence and the presence of 5 mM nicotinamide. Almost the same ring currents were obtained. The ring potential was set at -1.02 V. (I_r , ring current; I_d , disc current.)

TABLE 1

Solubilities of PbSO_4 and PbO_2 in 0.5 M H_2SO_4 in the absence and the presence of nicotinamide or isonicotinamide at 30°C

	Solubility (10^{-5} M)	
	PbSO_4	PbO_2
No additive	2.64	2.76
5 mM nicotinamide	2.66	2.82
5 mM isonicotinamide	2.62	2.70

of discharged state. The crystals seen in the SEM photographs are PbSO_4 , and the morphology is changed by adding NA. The crystal size become smaller in the presence of NA, whereas it did not change much in the presence of INA. Figure 8 also shows the charged surface of the electrode. The surface of the crystals was covered by PbO_2 , though the shape of PbSO_4 was maintained. From both SEM photographs, it is found that the addition of NA in H_2SO_4 solution makes the crystal size become smaller compared to that obtained without NA, and this NA effect was at least kept for 10 cycles. On the contrary, the effect of INA is smaller than that of NA. This NA effect suggests the enlargement of the electrode surface area, which causes the peak current enlargement of the cyclic voltammograms (Figs. 1 and 2) and the prolonged cycle life in the charge/discharge cycling tests (Figs. 4 and 5). Comparing dotted curves in Figs. 1 and 2, there appears to have been less of NA effect on peak E when scanning was stopped before the $\text{Pb}-\text{PbSO}_4$ transition (Fig. 2). The NA affects this reaction as well.

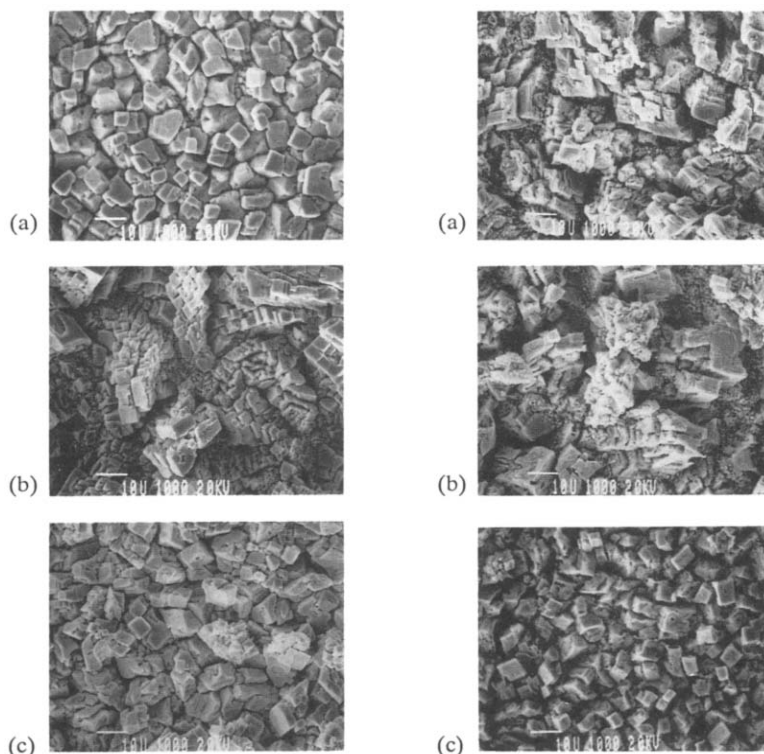


Fig. 7. Surface morphology of the discharged state of PbO_2 obtained (a) in the absence of additives, (b) in the presence of 5 mM nicotinamide, and (c) 5 mM isonicotinamide.

Fig. 8. Surface morphology of the charged state of PbO_2 obtained (a) in the absence of additives, (b) in the presence of 5 mM nicotinamide, and (c) 5 mM isonicotinamide.

Maybe an increase in surface area in this region contributed to the increase in peak current in the more positive region (peak E). The fact that the peak potential in the cyclic voltammogram, obtained in the presence of NA, shifted to a less noble potential on the cathodic scan and the reverse direction on the anodic scan (Fig. 2) is reasonable due to NA adsorption on the Pb electrode. It was understandable that the shape of the charge and discharge curves was affected and overpotentials were somewhat reduced compared to those in the absence of NA. If we assume that NA is adsorbed on the PbO_2 electrode more strongly than INA, NA will change the morphology of PbO_2 and PbSO_4 crystal more remarkably.

Conclusion

The addition of NA in the H_2SO_4 solution increased both the anodic peak current due to PbSO_4 to PbO_2 and the cathodic peak current due to the reverse reaction in the cyclic voltammograms. The anodic peak potential shifted to a less negative direction and the cathodic potential shifted to a less noble potential in the presence of NA. In the case of charge/discharge cycling of the PbO_2 electrode, the addition of NA

also reduced the rate of capacity decrease and prolonged the cycle life. On the contrary, INA, the isomer of NA, scarcely affected the cyclic voltammograms and the discharge capacity of PbO_2 compared to NA. These effects may be due to the NA adsorption on the Pb electrode, which causes a morphology change of the PbO_2 and PbSO_4 crystals to enlarge the electrode surface area. The SEM pictures revealed that the NA addition in the solution reduced the crystal size of PbSO_4 and caused a PbO_2 -spongy morphology, while the addition of INA hardly affected the morphology of PbO_2 and PbSO_4 .

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