Surface modification of metal hydride negative electrodes and their charge/discharge performance

Chiaki Iwakura*, Masao Matsuoka, Katsuhiko Asai and Tatsuoki Kohno

Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka 593 (Japan)

Abstract

Negative electrodes consisting of a multicomponent alloy ($MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$) in a porous nickel substrate were modified by using different kinds of electroless plating baths or alkaline solutions containing hypophosphite as a reducing agent. Electrochemical properties of the negative electrodes such as discharge capacity, electrocatalytic activity for the hydrogen electrode reaction (HER), and high-rate dischargeability were examined in a 6 M KOH solution. It was found that such simple surface modifications as described above improved the performance of negative electrodes.

1. Introduction

Nickel hydride batteries with hydrogen storage alloys as the negative electrode material have several inherent advantages over conventional rechargeable batteries, e.g. high storage capacity, cleanness for environmental protection, and superior tolerance to overcharge and overdischarge [1]. In recent years, extensive research and development of rechargeable batteries of this type directed toward practical use have been carried out [2–9]. The microencapsulation of the alloy powder with different kinds of electroless coatings such as copper and nickel has been confirmed to be effective for improving the performance of negative electrodes by preventing the poisoning of the disintegrated alloy and by giving superior electrical conductivity [10–14]. In this work, the effect of the modification of $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$ electrodes by electroless Cu, Ni–P and Ni–B coatings or reducing agent on electrocatalytic activity for HER and high-rate dischargeability was investigated in some detail.

2. Experimental

$MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$ powder with a particle size of 20–63 μm diam. was prepared by passing through sieves after mechanical pulverization. Negative electrodes were constructed by the following procedure. After mixing the alloy particles (112 mg) with a small amount of 4.4 wt.% polyvinylalcohol (PVA) solution, the mixture was poured

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*Author to whom correspondence should be addressed.

into a porous nickel substrate and then dried in vacuum before pressing it at 160 kg/cm^2. The resulting electrodes were modified by immersing them in an electroless plating solution (Cu, Ni–B, Ni–P) or a 6 M KOH solution containing hypophosphite. The chemical composition and operating conditions of the solution used for the modification are summarized in Table 1. A glass cell with three compartments which were separated from each other by sintered glass was employed for the electrochemical measurements. The modified negative electrode was placed in the central compartment, and the two positive electrodes in compartments on each side. The electrochemical capacity of the positive electrodes was designed to be sufficiently larger than that of the negative electrodes. As counter and reference electrodes, a sintered nickel hydroxide plate and a Hg/HgO/6 M KOH electrode were employed, respectively. All electrode potentials are given with respect to this reference electrode. The electrolyte was deaerated 6 M KOH solution. Galvanostatic charge/discharge cycling tests were performed at 30 °C. The negative electrode having 112 mg of active material was charged for 2.5 h and discharged to −0.5 V versus Hg/HgO, both at a constant current of 20 mA. After charging, the current was interrupted to open the circuit for 10 min. Such a cycling test was repeated by using a galvanostatic charge/discharge unit (HJ-201, Hokuto Denko).

High-rate dischargeability was determined from the ratio of high-rate capacity at 200 mA to the total capacity that was assumed to be the sum of the high-rate capacity and the additional normal-rate capacity at 20 mA. The additional capacity was measured after the high-rate discharge by resting for 10 min. Electrocatalytic activity of the modified negative electrodes for HER was evaluated by measuring the exchange current density (J_o) after 10 charge/discharge cycles. It was calculated from the slope of the polarization curve in the vicinity of the rest potential using eqn. (1).

$$J/\eta = nFJ_o/RT \tag{1}$$

The polarization curves were measured by the potential sweep method at a scan rate of 1 mV/s with the aid of a potentiostat combined with a function generator (HAB-151, Hokuto Denko). In each run, H/M molar ratio, the hydrogen content in the negative electrodes was adjusted to 0.7.

Surface morphology and composition were characterized using a scanning electron microscope (SEM:JSM-T200, JEOL/SVC) and an electron probe microanalyzer (EPMA:SEM with EDX, S-2500CX, Hitachi), respectively. The elements dissolved in a 6 M KOH solution were analyzed by using an ICP (GVM 1000P, Shimazu) and an atomic absorption spectrophotometer (Type 170-10, Hitachi).

TABLE 1

Composition and operating condition of solutions used for modification of negative electrode

Type	Solutions	Conditions
Cu	MAC-500[a]	28 °C, pH = 12.8, 10wt.%
Ni–P	MAC-600[a]	50 °C, pH = 9.0, 10wt.%
Ni–B	Top Chem Alloy B-1[a]	65 °C, pH = 6.7, 10wt.%
KOH	6 M KOH	80 °C, 8h
H$_2$PO$_2$$^-$	6 M KOH + 0.08 M H$_3$PO$_2$	80 °C, 8h

[a]Trade name of electroless plating solution produced by Okuno Chemical Industries Co., Ltd.

3. Results and discussion

3.1. Discharge capacity

Pressure-composition isotherms for hydrogen absorption and desorption in the $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$–H system, measured by Sieverts' method at various temperatures, are shown in Fig. 1. The amount of stored hydrogen (C_H) was calculated from the data shown in Fig. 1 by eqn. (2):

$$C_H(mAh/g) = 6 \times 26800 \times [(H/M)_{0.5} - (H/M)_{0.01}]/MW \qquad (2)$$

where the subscript of H/M indicates hydrogen pressure in MPa and MW is the molecular weight of the hydrogen storage alloy. The calculated reversible capacity has a maximum value of about 270 mA h/g in the temperature range of 20–40 °C. Based on this fact, all electrochemical measurements were performed at 30 °C.

Figure 2 shows the typical capacity for the modified negative electrodes as a function of the number of cycles. In a few cycles, the discharge capacity levelled off and gave rise to a saturated value depending on the kind of surface modification. The saturation capacity of the unmodified negative electrode was found to be about 180 mA h/g, which was quite small compared to the calculated one (c. 270 mA h/g). This fact indicates that a part of the hydrogen storage alloys is ineffective for charging and discharging due to insufficient microcurrent collection which is controlled mainly by an intergranular resistance and a resistance between the current collector and particles. The saturation capacity increases remarkably with surface modification upto 220–260 mA h/g, because such resistances are eliminated by electroless plating.

As the alkaline etching treatment of multicomponent alloys having a similar composition ($MmNi_{4.3-x}Mn_{0.4}Al_{0.3}Co_x$, $x = 0.5$–0.75) was reported to improve the cycle life of sealed nickel hydride batteries without the reduction of discharge capacity [3], the effect of alkaline treatment on the discharge capacity of the $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$ electrode was investigated. Surface modification with an alkaline solution under the conditions shown in Table 1 yielded no such advantage as indicated by the capacity
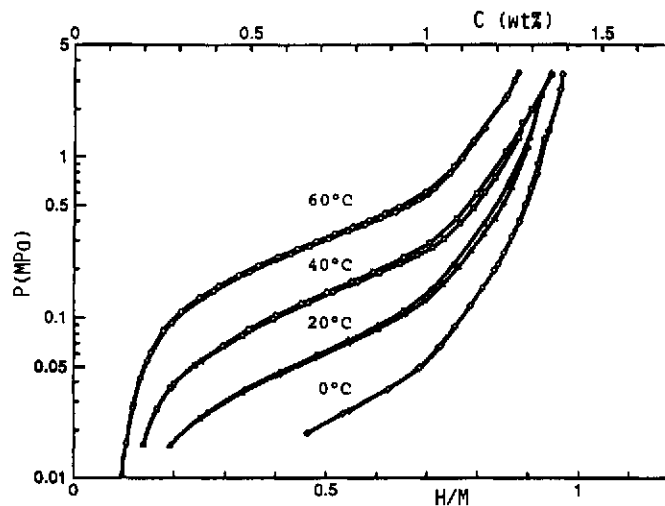

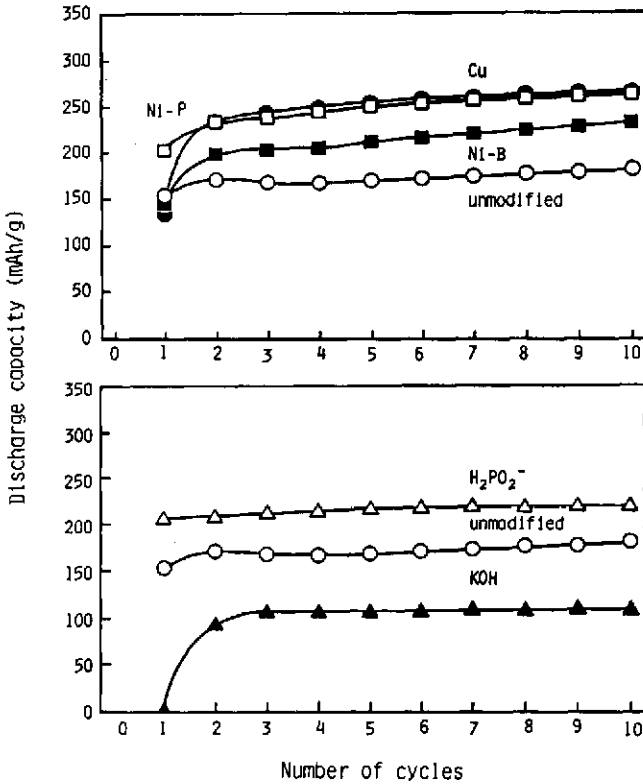Fig. 1. Pressure-composition isotherms for hydrogen absorption and desorption in $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$–H system.

Fig. 2. Discharge capacity of modified $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$ electrodes as a function of the number of cycles.

reduction (110 mA h/g). This disagreement might be attributable to the difference in etching conditions. To overcome this disadvantage a small amount of reducing agent was added in an alkaline solution. The modification of the negative electrode by the alkaline solution containing hypophosphite ions ($H_2PO_2^-$) was found to be very effective in improving the saturation capacity (220 mA h/g). The improved utilization efficiency of the active material by surface modification suggests that the chemical composition and the morphology of the interface play an important role in the charging or discharging process of the negative electrode.

3.2. Steady potential in charging and discharging

The steady potential in charging and discharging was quite different with the number of cycles. Typical results for the modified negative electrodes are shown in Fig. 3 as a function of the number of cycles. The potential difference consisting of overvoltage for charging and discharging was quite large in the early stage of charge/discharge cycles. For the case of the unmodified negative electrode, the overvoltage amounted to approximately 300 mV at the 1st cycle, but reduced to a limiting value of 50 mV with an increase in cycle number. As the internal resistance drop based on the electrolyte resistance was assumed to be 4–32 mV, most of the potential drop observed at the initial stage of cycles was due to the overvoltage for hydriding and
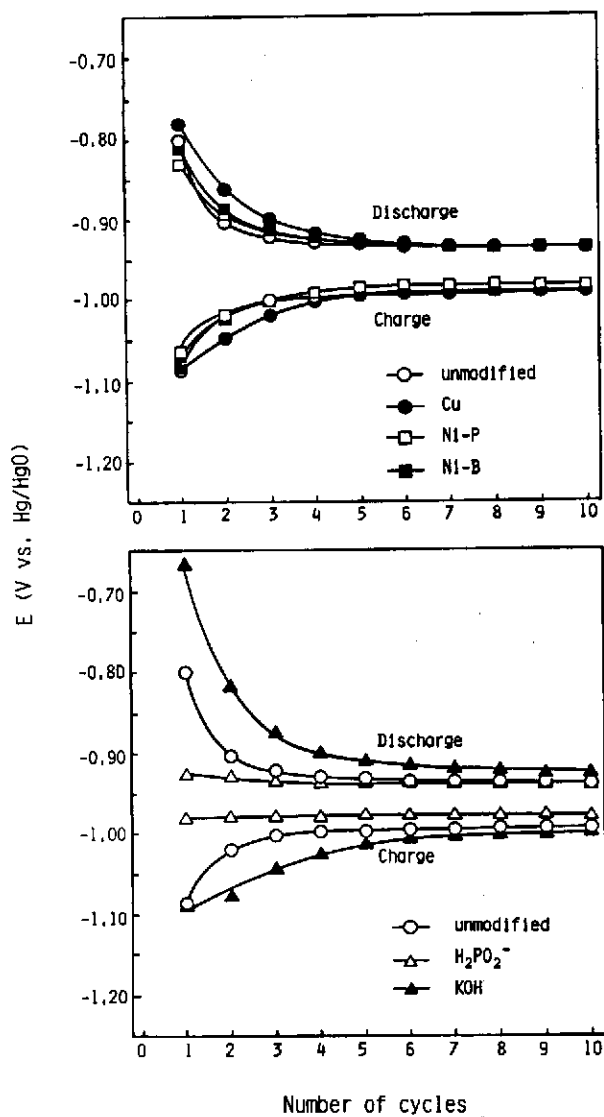
Fig. 3. Steady potentials of modified $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$ electrodes in charging and discharging as a function of the number of cycles.

dehydriding [15]. Similar results were confirmed for the modification with electroless Ni–B and Ni–P coatings. However, for the case of electroless copper coatings, the overvoltage in the initial stage of cycles was somewhat higher than that of the unmodified electrode, because the electrocatalytic activity of copper for HER is less than those of electroless nickel deposits (Ni–P and Ni–B) [16, 17]. However, the modification by Ni–P or Ni–B coating never yields such a disadvantage as observed for electroless copper coating, since the electrocatalysis of hydrogen storage alloys is not injured by the coatings of electroless nickel. On the other hand, the high overvoltage induced

by modification with an alkaline solution free from reducing agent, suggests that an inactive oxide layer will be formed on the surface of hydrogen storage alloys. In contrast, the modification by an alkaline solution containing a reducing agent reduced the overvoltage upto about 50 mV even at the 1st cycle. This fact indicates that the mode of action affecting electrocatalytic activity for HER is quite different with the different kinds of surface modification. Further discussion is given in Section 3.4.

3.3. Exchange current density and high-rate dischargeability

Since high-rate dischargeability is one of the very important characteristics in the practical use of batteries, the relationship between the rate capabilities and the values of J_o determined at the negative electrodes modified by electroless deposits or reducing agent was examined. The results are shown in Fig. 4. The high-rate dischargeability parabolically increased with an increase in J_o. In general, the high-rate capability would be determined by the electrochemical kinetics on the surface and the diffusion rate of hydrogen in the lattice. When electrochemical reaction takes place quite rapidly and discharging rate is controlled only by the diffusion of hydrogen, the high-rate dischargeability should be constant and independent of J_o. Since this is not the case, surface kinetics is very important for improving the high-rate dischargeability. On the other hand, when discharge is controlled only by the electrochemical surface reaction, a linear dependence of high-rate capability on J_o should be expected. As this is also not the case in our experimental conditions, both the surface kinetics and hydrogen diffusion contribute to the high-rate dischargeability. In particular, the delay of hydrogen diffusion in the lattice which becomes progressively greater with increasing J_o gives rise to a parabolic relationship between high-rate dischargeability and J_o. As shown in Fig. 4, the maximum rate capability was obtained for the modification by Ni–P deposits, and the maximum J_o for modification by a reducing agent.
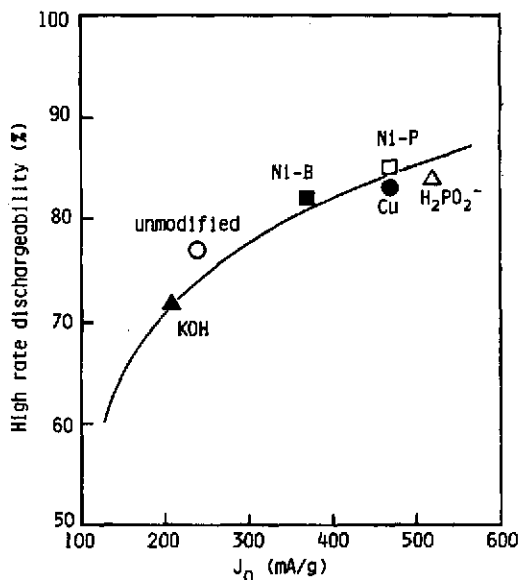

Fig. 4. Relationship between high-rate dischargeability and exchange current density (J_o) for HER.

3.4. Surface morphology and composition of hydrogen-storage alloys

As pointed out by several authors, the surface morphology and the composition of hydrogen storage alloys are very important for improving the electrocatalytic activity and the cycle life of negative electrodes [18–20]. In order to clarify the change in the electrocatalytic activity of the modified negative electrodes, surface morphology and composition were examined. Typical SEM photographs of a negative electrode modified by electroless deposition are shown in Fig. 5. The SEM observation indicated that the surface of hydrogen storage alloys was partially covered by electroless deposits with semispherical shapes. The heterogeneous regions where the hydrogen storage alloy and the electroless deposits meet each other might function as a catalytic active site. However, the electrocatalytic activity of negative electrodes in charging and discharging is not improved by the modification with electroless plating as indicated from the data shown in Fig. 3. This fact indicates that the electroless deposits on the surface of the hydrogen storage alloy mainly serve as a microcurrent collector and thus improve the utilization efficiency of the active material.

The surface composition of $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$ alloys modified by an alkali or a reducing agent was analyzed by EPMA. The results are summarized in Table 2. In both modifications, a Ni-rich surface layer was produced by the preferential dissolution of manganese as well as aluminum, which was also confirmed by the analysis of 6 M KOH solution with the aid of ICP and atomic absorption spectrometry. The tendency of preferential dissolution was confirmed to be predominant for the modification by a reducing agent. As the Ni-rich surface layer has high electrocatalytic activity for HER, the characteristics of the negative electrode modified by a reducing agent are improved as indicated by the low overvoltage for hydriding and dehydriding even at the initial stage of cycles. The other striking contrasts between the alkaline and the reducing agent treatment were found to be enrichment of cerium and slight deficiency
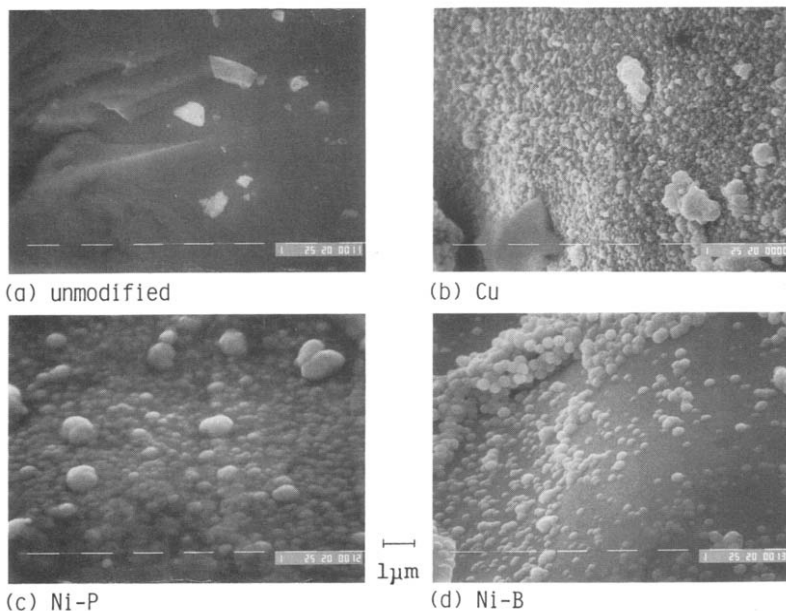

(a) unmodified   (b) Cu

(c) Ni–P   (d) Ni–B

1μm

Fig. 5. SEM photographs of the surface of modified $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$ electrodes.

TABLE 2

Atomic ratio of $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$ alloy modified by alkaline or reducing agent[a]

Sample	No.	Mm			Ni	Mn	Al	Co
		La	Ce	Pr+Nd				
Unmodified	1	4.76	8.18	1.98	59.94	5.90	6.17	11.82
	2	4.74	8.04	1.52	59.13	8.73	5.41	11.18
	3	4.95	8.22	2.10	59.83	7.65	4.48	12.43
	av.	4.82	8.15	1.87	59.63	7.43	5.35	11.81
KOH	1	4.69	8.50	2.10	59.96	6.34	5.68	11.15
	2	4.94	8.77	2.47	63.36	4.98	3.36	11.09
	3	4.85	8.36	2.62	60.99	5.16	5.25	11.08
	av.	4.83	8.54	2.40	61.44	5.49	4.76	11.11
$H_2PO_2^-$	1	4.60	7.80	2.36	61.75	4.92	5.23	11.63
	2	4.48	7.88	2.46	63.41	4.58	4.03	12.62
	3	4.78	8.55	2.72	63.14	4.21	3.60	12.02
	av.	4.62	8.08	2.51	62.77	4.57	4.29	12.09

[a]Composition analyses were carried out for each three different spots on the electrode surface by EPMA.

of cobalt in the former treatment. Such composition changes detected at the surface treated by alkaline solution might be one of the causes for poor characteristics of the negative electrode, however, the deactivation of the Ni-rich surface layer by oxidation seems to be critical. Inactivation of the Ni-rich surface results in the reduction of discharge capacity and high overvoltage for the hydrogen electrode reaction. Therefore, a key factor in modification by a reducing agent for improving the characteristics of negative electrodes is due to both the electrons and atomic hydrogen which are released by eqn. (3) [21]:

$$H_2PO_2^- + OH^- = H_2PO_3^- + H + e^- \qquad (3)$$

The oxide on the surface of the negative electrode would be reduced and eliminated. In addition, the adsorbed atomic hydrogen may penetrate into the lattice forming hydride. The activation through oxide reduction and hydride formation was demonstrated by measuring the rest potential of the modified negative electrode and the stored hydrogen capacity. The potential of the unmodified electrode in a 6 M KOH solution was more noble than -0.5 V, however, the potential of the negative electrode modified by a reducing agent shifted to a less noble potential being -0.9 V. The amount of stored hydrogen measured by discharging at 2 mA was found to be 15 mA h/g. Therefore, the oxide-free surface and the penetration of atomic hydrogen into the lattice are the main causes for high electrocatalytic activity for HER.

4. Conclusions

$MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$ electrodes modified simply by electroless deposits such as Cu, Ni–P and Ni–B or by a reducing agent gave rise to a much improved performance as negative electrodes. Both discharge capacity and high-rate capability were increased by the modification of the negative electrodes. A well-defined correlation between J_o

and high-rate dischargeability could be recognized, i.e. the rate capability increased with an increase in J_0.

Acknowledgements

References

1 C. Iwakura and M. Matsuoka, *Kidorui (Rare Earth), No. 17* (1990) 11.
2 J. J. G. Willems and K. H. J. Buschow, *J. Less-Common Met., 129* (1987) 13.
3 H. Ogawa, M. Ikoma, H. Kawano and I. Matsumoto, *16th Int. Power Sources Symp., Bournemouth, UK, 1988*, uncorrected preprint.
4 M. Nogami, S. Kameoka, I. Yonezu, K. Inoue, T. Matsumoto and N. Furukawa, *Ext. Abstr., 40th ISE Meet., Kyoto, Japan, 1989*, p. 1231.
5 Y. Moriwaki, T. Gamo, A. Shintani and T. Iwaki, *Denki Kagaku, 57* (1989) 488.
6 M. Yamamoto, K. Kanno, Y. Satoh, H. Hayashida and M. Suzuki, *Ext. Abstr., 40th ISE Meet., Kyoto, Japan,* 1989, p. 1233.
7 M. A. Fetcenko, S. R. Ovshinsky, S. Venkatesan, K. Kajita, H. Kidou and K. Jeffries, *3rd Int. Rechargeable Battery Seminar, March 5–7, 1990, Deerfield Beach, FL, USA.*
8 N. Nogami, K. Moriwaki and N. Furukawa, *3rd Int. Rechargeable Battery Seminar, May 5–7, 1990, Deerfield Beach, FL, USA.*
9 T. Sakai, A. Takagi, T. Hazama, H. Miyamura, N. Kuriyama, H. Ishikawa and C. Iwakura, *Proc. 3rd Inter. Conf. Batteries for Utility Energy Storage,* Kobe, Japan, March 18–22, 1991, p. 499.
10 C. Iwakura, T. Asaoka, T. Sakai, H. Ishikawa and K. Oguro, *Denki Kagaku, 53* (1985) 722.
11 K. Machida, M. Enyo, G. Adachi and H. Sakaguchi, *Bull. Chem. Soc. Jpn., 59* (1986) 925.
12 T. Sakai, H. Ishikawa, K. Oguro and C. Iwakura, *Prog. Batteries Solar Cells, 6* (1987) 221.
13 T. Sakai, H. Ishikawa, K. Oguro, C. Iwakura and H. Yoneyama, *J. Electrochem. Soc., 134* (1987) 558.
14 C. Iwakura, Y. Kajiya, H. Yoneyama, T. Sakai, K. Oguro and H. Ishikawa, *J. Electrochem. Soc., 136* (1989) 1351.
15 J. J. G. Willems, *Philips J. Res., 39,* Suppl. No. 1 (1984) p. 25–27.
16 H. Kita and M. Honda, *Denki Kagaku, 38* (1970) 17.
17 S. Trasatti, *J. Electroanal. Chem., 39* (1972) 163.
18 H. Tamura, C. Iwakura and T. Kitamura, *J. Less-Common Met., 89* (1983) 567.
19 T. Sakai, H. Miyamura, N. Kuriyama, A. Kato, K. Oguro and H. Ishikawa, *J. Electrochem. Soc., 137* (1990) 795.
20 P. H. L. Notten and E. Brok, *Ext. Abstr., 38th ISE Meet.,* Maastricht, Netherlands, Sept. 14–18, 1987, p. 541.
21 J. E. A. M. van den Merrakker, *J. Appl. Electrochem., 11* (1981) 395.