

Suppression of the Side Reaction of Nickel-based Air Electrodes for Secondary Cells

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Nickel-based air electrodes for use as the positive electrode of a secondary cell have been recently developed, and a high durability for oxygen evolution and reduction in alkaline solutions has been demonstrated in our laboratory [1,2]. A novel secondary cell consisting of the nickel-based air electrode and a hydrogen storing alloy as the negative electrode has been also introduced [3]. The components of the air electrode are PTFE and nickel powders, in which the latter are the mixture of nickel powders with and without catalysts for oxygen evolution and reduction. The durability of the air electrode essentially depends on the stability of nickel and the activity of catalysts in alkaline solutions. The stability of nickel is based on the formation of Ni(OH)₂ on the surface, which is well known to be the active mass of nickel-hydrogen secondary cells. However, the reaction between Ni(OH)₂ and NiOOH, which is the positive electrode reaction of the nickel-hydrogen cell, is unfavorable for the nickel-based air electrode, since the electrode's reactions should be oxygen evolution and reduction. This means that the reactions of NiOOH/Ni(OH)₂ couple are the undesirable side reaction in the air electrode, and the side reaction has to be inhibited. In this study, a new preparation method of nickel-based air electrodes was developed so as to suppress the side reaction.

Our previous method to prepare an air electrode is described below. Nickel powders were dispersed in the aqueous solution containing H₂PtCl₆ and H₂IrCl₆, dried at 393 K for 15min, and heated at 743 K under air atmosphere to produce platinum and iridium oxide on the nickel surface. The nickel powders with and without catalysts were mixed with PTFE powders, and then the mixture was molded on a nickel mesh sheet to form a disk. The disk was heated at 643 K for 12.5 min. under nitrogen atmosphere (Method A). On the other hand, another way of the electrode preparation was proceeded by calcinating of the aqueous solutions separately containing H₂PtCl₆ or H₂IrCl₆ at 743 K for 30 minutes under air atmosphere so that platinum and iridium oxide particles were obtained. Then these particles were mixed with nickel and PTFE powders followed by the same procedure of molding and heating in the previous method. The new preparation method is assigned as B.

Two types of air electrodes obtained in the above procedures were used in electrochemical measurements and charge-discharge cycle test. Each electrode was mounted in a self-made PTFE holder, which allows the

electrode to contact to an electrolyte on one side and to open to air on the other side. The electrolyte was a 7 mol dm⁻³ KOH solution. A platinum counter electrode and an HgO/Hg reference electrode were used. Cyclic voltammetry and charge-discharge test of the air electrode were carried out at 333K. In the latter case, oxygen gas was supplied to the electrode at 140 cm³ min⁻¹.

The cyclic voltammograms obtained with two types of air electrodes (A and B) each showed a pair of redox waves corresponding to the oxidation of Ni(OH)₂ to NiOOH and the reverse reaction. However, the peak current densities for the oxidation and reduction waves on the electrode B were much lower than those on the electrode A, implying that the side reactions are effectively suppressed on the electrode B compared to the electrode A. The charge-discharge curves were measured for each electrode with constant current being periodically reversed. The discharge curve of the electrode A presented two potential plateaus, of which the higher potential plateau is the reduction of NiOOH while the lower one is that of oxygen. However, the discharge curve of the electrode B had only one plateau for oxygen reduction at the first cycle. The time for NiOOH reduction in the discharge curve was determined, and its dependence on the number of cycles was summarized in Fig. 1. It can be clearly seen that the discharge time of NiOOH on the electrode B is shorter than that of the electrode A. Moreover, the increase in the discharge time with the number of cycles is suppressed for the electrode B compared to the electrode A. From the results, the preparation method B is more favorable than the method A to restrain the side reaction in the nickel-based air electrode.

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References

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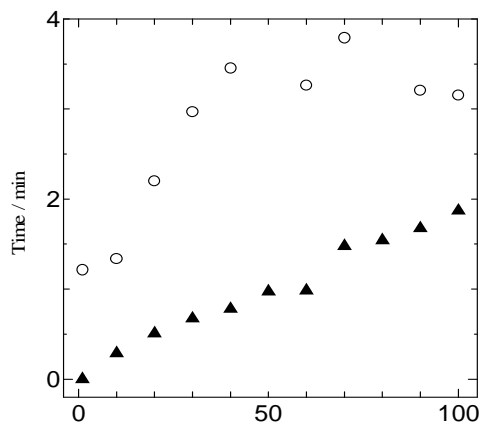


Fig. 1 Dependence of the discharge time of NiOOH with the number of cycles. Electrodes: A (circle) and B (triangle).