## Charge-discharge Behaviors of a MH-Air Secondary Cell

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Metal-air cells have attractive properties such as a high theoretical energy density and a possible high power density. In general, commercialized metal-air cells are limited to be a primary one, because of low rechargeability of the metal and air electrodes. Especially, the difficulty to develop a bi-functional air electrode has discouraged from the rechargeable use of the metal-air cell. The bi-functional air electrode has to possess a high durability for oxygen evolution, which is impossible for carbon-based air electrodes, since carbon is easily consumed by the oxidation to CO<sub>2</sub> during oxygen evolution. On the other hand, our laboratory has recently developed a new air electrode consisting of nickel and PTFE powders for a secondary cell [1]. The electrode has demonstrated an excellent stability in charge-discharge test, and a long lifetime over 500 charge-discharge cycles has been accomplished with no serious degradation [2].

In this study, we attempted to preliminarily evaluate the air secondary cell using the developed bi-functional air electrode. A hydrogen storing alloy was chosen as the material of the negative electrode, because of its high rechargeability in alkaline solutions. The charge-discharge behaviors of a novel MH-air secondary cell are presented in this paper.

Nickel powders were used as a conductive and catalyst-supporting material for an air electrode. The nickel powder was mixed with the solution containing  $H_2IrCl_6$  and  $H_2PtCl_6$ , dried at 393 K, and heated at 743 K for 2 minutes to generate platinum and iridium oxide on nickel powders as catalysts. The catalyst-loaded nickel powder, PTFE, and catalyst-free nickel powder were mixed with 30:10:60 mass ratio, dried, and pressed on nickel mesh sheet to make a disk. Then, the disk was calcinated at 643 K for 12.5 minutes under nitrogen atmosphere.

A hydrogen storing alloy ( $MmNi_{3.55}Co_{0.4}Mn_{0.4}Al_{0.3}$ ) was used to prepare the negative electrode. The alloy powders, nickel powders, and polyethylene powders were mixed, pressed to form a disk, and heated at 423 K for 60 min. under vacuum. The theoretical capacity of the negative electrode was 93 mAh.

The air 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<sup>-3</sup> KOH solution, and the negative electrode was completely immersed in the solution. The MH-air secondary cell was operated at 333 K with constant current method, in which oxygen or air was supplied to the air electrode at 140 cm<sup>3</sup> min<sup>-1</sup>.

The cell voltages during charge and discharge were recorded at various rates from 0.05 C to 0.75 C, in which the charge and discharge rates were the same. From the results obtained in the condition that oxygen gas was supplied, the dependence of the cell voltage on the charge-discharge rate was obtained as shown in Fig. 1. At higher rates, the cell voltage at the end of discharge for 5 min. became lower, and that at the end of charge for 5 min. became higher. The difference in CCV (closed circuit voltage) and OCV (open circuit voltage, 1.23 V) for discharge was larger than that for charge at each rate, which is mainly caused by a high overpotential for oxygen reduction on the air electrode. The voltage efficiency calculated from the data shown in Fig. 1 ranged from 65 % at 0.05 C to 30 % at 0.75 C. The output power increased with the discharge rate, suggesting a maximum power being expected at higher rate above 0.75 C. Substituting air for oxygen gas resulted in the decrease in cell voltage during discharge, while the substitution caused no apparent change in charge voltage.

This study was supported by Industrial Technology Research Grant Program in '03 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

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- 2. T. Ogawa, M. Morimitsu, S. Taniguchi, M. Takahashi, M. Matsunaga, in the paper presented in this meeting.



Fig. 1 Dependence of the cell voltage on the chargedischarge rate.