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A High Energy Density of MH/Air Secondary Battery with Superlattice Hydrogen Storage Alloys

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Metal/air secondary batteries are expected as one of next-generation energy storage devices for a wide application such as electric vehicles and home electric energy storage system connected to solar or wind power generators. In principle, the air battery must have no limitation of a possible discharge capacity because the positive active mass is oxygen in air, although it is well known that the air battery using less noble metals such as lithium and magnesium suffers from the plugging of the discharge product in the positive electrode, resulting in a small discharge capacity and a difficulty of a high current operation. However, this is not the case for metal hydride/air secondary battery, because the discharge produce is water, following the total reaction below;

$$4MH + O_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 4M + 2H_2O$$

This MH/air battery has been developing by our group and has shown more than 400 Wh/L of energy density and continuous operation over 300 charge-discharge cycles [1-4]. Here, we report a further improvement of the MH/air battery with using a new type of hydrogen storage alloy, which is A_2B_7 type, superlattice structure.

The preparation procedures of the positive and negative electrodes are similar to those described previously [1,2], except that the negative electrode in this study used A_2B_7 type (superlattice structure) of hydrogen storage alloys prepared and supplied by FDK Twicell Company. The capacity of the negative electrode ranged from 1.5 to 1.6 Ah. The electrode size was *ca.* 45 mm x 45 mm, which was the same as that of the positive electrode. The electrolyte was 5 mol dm^{-3} KOH solutions and was used with a membrane separator. Two types of batteries were made using a PTFE container as shown Fig. 1; type A comprised a single negative electrode and a single positive electrode, and a separator with the solution between them, and the other, type B, consisted of a single negative electrode between two positive electrodes with the separator-solution composites placed on both sides of the negative electrode. Those cells were operated with constant current at ambient temperature without air or oxygen blow to the positive electrode.

The new negative electrode with superlattice alloys showed good polarization behaviors for charge and discharge under constant current operation up to 1.95 A (96 mA/cm^2). The polarization resistance was about 0.18 ohms and kept constant in such a wide current range, and no difference in the resistance was observed for charge and discharge. Two type of cells, types A and B, were fabricated and tested in two current modes; constant current for a continuous operation and stepwise current to examine the polarization during discharge of type A. Figure 2 shows a typical discharge curve at 100 mA, in which a stable voltage was seen and the average discharge voltage was *ca.* 0.78V. The energy density was calculated using the discharge curve and the total volume of all components (the negative and positive electrodes, the separator, and the alkaline solution), which gave an excellent energy density, 657 Wh/L. A similar calculation was also done for the result of type B and the obtained energy density was 496 Wh/L; a decrease in energy density is due to additional positive electrode and separator with the electrolyte in the type B cell. The stepwise current operation also presented a good polarization performance of both types of cells; the maximum current till reaching 0.1 V of cut-off voltage was 1.47 A (73 mA/cm^2). The batteries also demonstrated a high utilization of hydrogen storage alloy over 90% independently of discharge current. The results mentioned above indicates that the MH/air secondary battery with superlattice MH alloys is expected to be a high energy density of rechargeable battery beyond lithium ion and other type of air secondary batteries for next-generation of energy storage devices.

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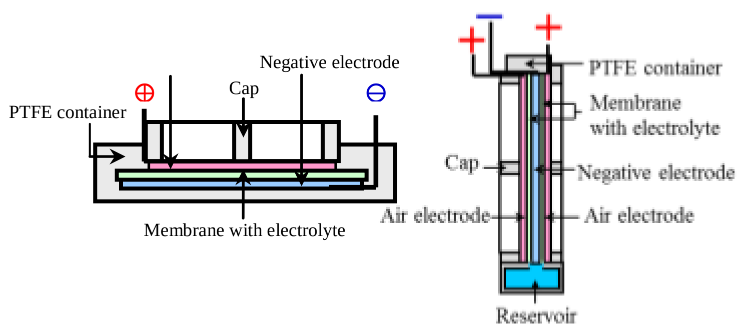

Fig. 1 Configuration of MH-air cells: type A, two-electrode cell (left) and type B, three-electrode cell (right).

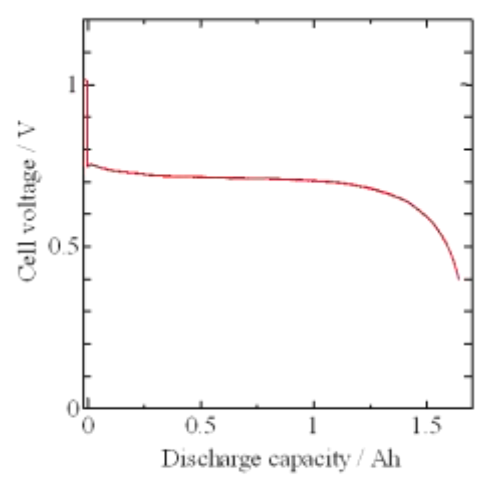

Fig. 2 Discharge curve of MH/air secondary battery (type A) at 100 mA.

References

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