

## Solid-state Metal Hydride Secondary Batteries Using Heteropolyacid Hydrate as an Electrolyte

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### INTRODUCTION

Solid-state metal-hydride (MH) batteries using solid electrolytes have become of interest in recent years, because the batteries have some advantages in terms of reliability, safety and cell designing compared with batteries using conventional liquid electrolytes (1).

Recently, a few papers were reported for the solid-state MH batteries using inorganic solid electrolyte (2,3). However, the performance of the batteries consisting of inorganic solid electrolytes was inferior to that of polymer ones because of their lower ionic conductivities. It is well-known that heteropolyacid hydrates, such as  $H_3PMo_{12}O_{40} \cdot nH_2O$ , show very high proton conductivities at room temperature among the proton conductors (4). We reported a manganese dioxide-metal hydride ( $MnO_2/MH$ ) battery using the electrolyte (2). The battery was able to operate in more than 100 cycles at a current density of  $5 \text{ mA g}^{-1}$ . The battery performance was, however, not so sufficient as the batteries practically used. In the present study, we have attempted to improve the electrochemical properties.

### EXPERIMENTAL

A heteropolyacid hydrate of commercial  $H_3PMo_{12}O_{40} \cdot 20H_2O$  was employed as an electrolyte and a hydrogen storage alloy,  $ZrMn_{1.5}Cr_{0.7}Ni_{0.3}$ , as an anode active material. To get a negative electrode, the hydrogenated alloy powder (*ca.* 0.1g), acetylene black, polytetrafluoro-ethylene (PTFE), and the solid electrolyte were mixed in a weight ratio of 85:5:5:5. Two kinds of manganese dioxide powders, *i.e.* reagent grade manganese dioxide and electrolytic manganese dioxide for the battery use, were employed as cathode active materials. As to the positive electrode, the solid electrolyte was mixed in the same way as the negative electrode; the contents of electrolyte were varied to 5, 10, 20, and 40 wt%.

In order to construct the solid-state MH battery, the piled powders (anode/ electrode/cathode) were pressed by  $1 \times 10^3 \text{ kgf cm}^{-2}$  at a time to obtain a pellet with 13 mm in diameter. This process was completely different from the previous way to repeat loading and pressing each component three times in turn (2). The pellet was mounted in an airtight two-electrode-type cell. The electrochemical tests were carried out at  $30^\circ \text{C}$  using the galvanostatic charge-discharge apparatus controlled by a computer. The cell was charged at 5 or  $10 \text{ mA g}^{-1}$  for 1 h, and discharged in the same manner down to 0.4 V. A ten-minute break was set after every charging and discharging.

### RESULTS AND DISCUSSION

To enhance the electrochemical performance of our

$MnO_2/MH$  battery using the heteropolyacid hydrate, we tried to improve the total battery construction; the interface between electrode and electrolyte was increased by changing the cell construction process and the electrolytic manganese dioxide was adapted as a positive electrode material instead of reagent grade manganese dioxide previously used. Figure 1 shows the variations of the discharge efficiency with charge-discharge cycling. It is noteworthy that the discharge efficiency comes up to about 90 % and the cell cycle life extends to about 450 cycles. Thus, the resultant battery exhibited higher discharge efficiency, remarkably longer cycle life performance, and smaller polarization than the previous one.

As shown in Fig. 2, the high rate characteristics of the battery were improved significantly by optimizing the electrolyte content in the positive electrode; the battery was able to operate over 200 cycles at a larger current density,  $10 \text{ mA g}^{-1}$ , and keep the relatively high discharge efficiency about 95 %. In addition, the battery performance varied scarcely after exposure to the atmosphere for a long time.

### REFERENCES

1. C. Iwakura, S. Nohara, N. Furukawa, H. Inoue, *Solid State Ionics*, **148**, 487 (2002).
2. K. Hatakeyama, H. Sakaguchi, K. Ogawa, H. Inoue, C. Iwakura and T. Esaka, *J. Power Sources*, **124**, 599 (2003).
3. C. Iwakura, K. Kumagae, K. Yoshiki, S. Nohara, N. Furukawa, H. Inoue, T. Minami, M. Tatsumisago and A. Matsuda, *Electrochim. Acta*, **48**, 1499 (2003).
4. O. Nakamura, T. Kodama, I. Ogino, Y. Miyake, *Chem. Lett.*, 17 (1979).

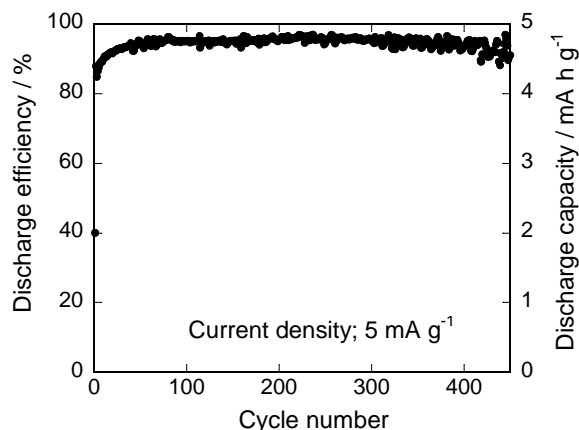


Figure 1 Discharge efficiency variation with the cycle numbers.

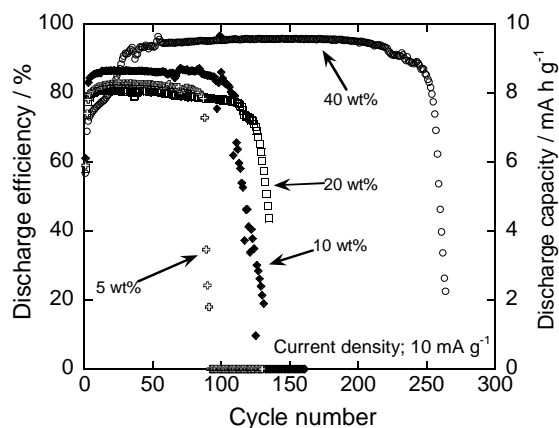


Figure 2 Discharge efficiency variations with the cycle numbers for the battery with different electrolyte contents in the positive electrode.