

Solid-state metal-hydride batteries using heteropolyacid hydrate as an electrolyte

Keisuke Hatakeyama^a, Hiroki Sakaguchi^a, Kenta Ogawa^a,
Hiroshi Inoue^b, Chiaki Iwakura^b, Takao Esaka^{a,*}

^a Department of Materials Science, Faculty of Engineering, Tottori University, Minami 4-101, Koyamacho, Tottori 680-0945, Japan

^b Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuencho, Sakai, Osaka 599-8531, Japan

Received 14 May 2003; received in revised form 6 June 2003; accepted 11 June 2003

Abstract

To develop solid-state metal-hydride batteries, heteropolyacid hydrates, such as 12-tungstophosphoric acid hydrate ($\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$) and 12-molybdophosphoric acid hydrate ($\text{H}_3\text{PMO}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$), were used as electrolytes. The Ni/MH battery using 12-tungstophosphoric acid could be charged and discharged even at a considerably high current density of 100 mA g^{-1} , but showed very poor cycle life performance due to corrosion of the electrode materials by the heteropolyacid electrolyte. The cyclability was improved by employing manganese dioxide and zirconium-based alloy as positive and negative electrodes, respectively. The best performance was obtained on the battery using 12-molybdophosphoric acid; its operation was possible up to 50 mA g^{-1} , and/or for more than 100 cycles at 5 mA g^{-1} .

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Keywords: Ni/MH battery; Solid-state battery; Heteropolyacid hydrate; Solid electrolyte; MnO_2/MH battery

1. Introduction

Ni/MH battery using nickel oxyhydroxide and metal-hydride as electrode active materials is well-known as a secondary battery with high performance. However, since a KOH aqueous solution is currently used as an electrolyte in the battery, leakage or freeze of the electrolyte solution and the dry-out phenomenon still remains as the problem to be solved. Therefore, solid-state metal-hydride battery using solid electrolyte has become a matter of interest in recent years. The battery surely has some advantages in terms of reliability, safety and cell designing compared with the battery using the conventional liquid electrolyte. For example, if a solid electrolyte is used, separator is unnecessary in a battery, since the electrolyte plays a role as a separator. Thus, the use of solid electrolyte not only simplifies the cell structure but also meets the expectation to production of a thin battery.

Mohri et al. reported the solid-state metal-hydride batteries using $\text{Sb}_2\text{O}_5\cdot n\text{H}_2\text{O}$, the ionic conductivity of which is $2.6 \times 10^{-3}\text{ S cm}^{-1}$ at 20°C [1,2]. For example, the battery shown by “hydrogenated ($\text{TiNi} + 1\text{ wt.}\% \text{Mm}$)/ $\text{Sb}_2\text{O}_5\cdot n\text{H}_2\text{O}/\text{MnO}_2$ ” exhibited a good cyclability for

500 cycles of charge–discharge. The dischargeable current density was, however, as low as $75\text{ }\mu\text{A cm}^{-2}$ because of high internal resistance resulting from the electrolyte itself and the small interface between the electrolyte and the electrode materials [1]. Kuriyama et al. made the battery using tetramethylammonium hydroxide pentahydrate, $(\text{CH}_3)_4\text{NOH}\cdot 5\text{H}_2\text{O}$, whose ionic conductivity is $4.5 \times 10^{-3}\text{ S cm}^{-1}$ at 15°C [3–5]. Although the battery could be discharged at higher current density in comparison with the battery using $\text{Sb}_2\text{O}_5\cdot n\text{H}_2\text{O}$ electrolyte and presented its life over 200 cycles, the self-discharge of the battery was undesirable.

Furthermore, the other types of electrolytes were used for Ni/MH batteries [6–8]. Vassal et al. proposed an alkaline solid polymer electrolyte based on poly(ethylene oxide) [6] and poly(epichlorohydrin-co-ethylene oxide) [7]. Iwakura et al. reported battery using polymer gel electrolytes. It is noteworthy that the performance of these batteries were comparable to that of the batteries practically used [8]. Moreover, Iwakura et al. recently demonstrated a solid-state Ni/MH battery made by using a proton-conductive H_3PO_4 -doped silica gel as an electrolyte, which operated in several 10 cycles of charge–discharge at a relatively high current density of 5 mA g^{-1} [10]. One of the problems on the battery was that preparation of the inorganic gel was too difficult.

* Corresponding author. Tel./fax: +81-857-31-5264.
E-mail address: esaka@chem.tottori-u.ac.jp (T. Esaka).

Thus, there have been only a few reports for all solid-state batteries using inorganic solid electrolyte. The performance of solid-state batteries consisting of inorganic solid electrolytes was inferior to that of polymer ones because of their lower ionic (OH^- or H_3O^+) conductivities. However, it is well-known that heteropolyacid hydrates, such as $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$, show higher proton conductivities at room temperature than the other proton conductors [9]. In the present study, we have attempted to use the electrolytes for Ni/MH and the related batteries, and investigated their charge–discharge characteristics. Since heteropolyacid hydrates exhibit strong acidity, furthermore, the suitability of the electrode materials to the hydrate electrolyte were also tested.

2. Experimental

2.1. Preparation of electrolytes and electrode materials

Heteropolyacid hydrates of $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ (Wako Pure Chemical Industries Ltd.) were used as electrolytes of the metal-hydride batteries without any pretreatment. Before setting up the battery, the hydration number of n was determined using thermobalance (Shimadzu DTG-50) heating up to 500°C and AC conductivity was measured at 30°C by an impedance meter (Hewlett-Packard 4192A) at frequencies between 5 Hz and 5 MHz. In the latter case, the heteropolyacid hydrate powders were isotropically pressed under the pressure of $1 \times 10^3 \text{ kgf cm}^{-2}$ to obtain dense pellets with a diameter of 13 mm and ca. 1 mm thickness, which were set in a gas-tight stainless steel cell (Hosen Co., HS-type cell) to prevent the loss of water content from the hydrates.

Two kinds of alloys, such as $\text{MmNi}_{3.6}\text{Al}_{0.4}\text{Mn}_{0.3}\text{Co}_{0.7}$ (Santoku Inc.) and $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}$ were used as hydrogen storage materials. The latter was prepared by mixing $\text{ZrMn}_{1.5}\text{Cr}_{0.7}$ powder (Nilaco) with Ni powder using mechanical milling. In order to get negative electrode, the hydrogen storage alloy powder (ca. 0.1 g), conductive material (acetylene black) and binder (PTFE, polytetrafluoroethylene) were mixed thoroughly in the weight ratio of 90:5:5. The alloy was activated in advance using the hydrogen gas pressurizing apparatus. On the other hand, nickel hydroxide (Hosen Co.) and manganese dioxide powders were used as positive active materials. The positive electrode was prepared in the same way as the negative electrode except for using $\text{Ni}(\text{OH})_2$ instead of an alloy.

2.2. Setup of battery

The solid-state metal-hydride batteries were constituted in the following. The negative electrode mixture was shaped into a pellet with 13 mm diameter by pressing at $1 \times 10^3 \text{ kgf cm}^{-2}$. Then, the electrolyte powder (0.2 g) was uniformly loaded on the negative electrode pellet, followed

by pressing at $1 \times 10^3 \text{ kgf cm}^{-2}$ to make a dual-layered pellet. Moreover, the positive electrode mixture was loaded on the resulted dual-layered pellet and pressed again at the same pressure. The three-layered pellet was placed in a two-electrode type cell made of stainless steel (Hosen Co., HS-type cell). Considering an increase in the interface between the electrode and electrolyte, the mixture of them should be used in all cases. Taking into account the corrosion of the electrode materials, however, the electrode mixed with the electrolyte was used only in the case using the materials ($\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}$ and MnO_2) relatively tolerant to acid. In that case, the content of electrolyte in the electrodes was 5 wt.%, while that of the active materials was reduced to 85 wt.%.

The electrochemical measurements were carried out at 30°C using the galvanostatic charge–discharge apparatus (KEISOKUKI, BS2506) controlled by a computer. The batteries “MH/ $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}/\text{Ni}(\text{OH})_2$ ” were charged at 50 or 100 mA g^{-1} up to a capacity of 10 mAh g^{-1} , and discharged at various current densities, i.e. 10–100 mA g^{-1} , to 0.8 V of the cell voltage after resting for 10 min. As to the batteries “MH/ $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}/\text{MnO}_2$ ”, charging and discharging were carried out at 1, 5, 10, 20 and 50 mA g^{-1} for 1 h. Choosing MnO_2 as a positive electrode, the cutoff voltage was set down to 0.4 V. The current densities that will be used hereafter are shown as the currents per 1 g alloy powder itself.

3. Results and discussion

The hydration numbers (n) of heteropolyacid hydrates used were determined to be 21 and 29 for $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$, respectively. These values decreased to 15 and 20, respectively, when the samples were left in the electrochemical test cell overnight at 30°C . According to the relationship between temperature and humidity investigated by Nakamura et al. [11], the humidity appears to be around 65% in the test cell. The conductivity of $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ was estimated to be ca. $3.3 \times 10^{-2} \text{ S cm}^{-1}$ at 30°C , which was nearly equal to the value of $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 18\text{H}_2\text{O}$ in the literature [11]. Thus, the hydration number estimated from thermogravimetry was almost coincided with that from conductivity. Although we have not carried out the conductivity measurement as to $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$, it is presumed to be about $1 \times 10^{-2} \text{ S cm}^{-1}$ according to the data mentioned above [11]. The difference of the conductivities between two heteropolyacids would be essentially due to the hydration numbers.

Fig. 1 shows the charge–discharge curves of the test cell consisting of “ $\text{MmNi}_{3.6}\text{Al}_{0.4}\text{Mn}_{0.3}\text{Co}_{0.7}\text{H}_x/\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}|\text{NiOOH}$ ”. In a few initial cycles, the cell was able to be discharged starting at around 1.3 V which is the theoretical voltage of Ni/MH battery, indicating that the heteropolyacid hydrate can play a role as an electrolyte

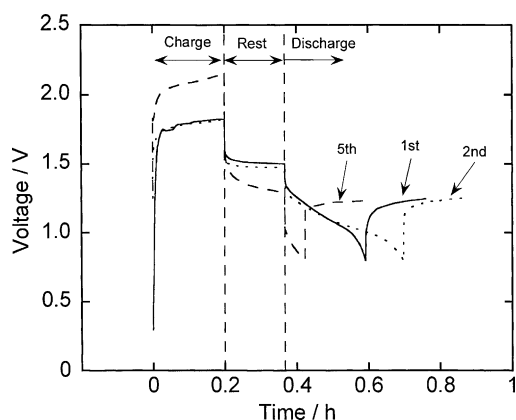
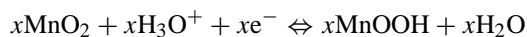


Fig. 1. Charge–discharge curves for the battery, $\text{MmNi}_{3.6}\text{Al}_{0.4}\text{Mn}_{0.3}\text{Co}_{0.7}\text{H}_x/\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}/\text{NiOOH}$. Charge and discharge current densities are 50 and 20 mA g^{-1} , respectively.

of Ni/MH battery. The charge and discharge current densities were 50 mA g^{-1} (3.8 mA cm^{-2}) and 20 mA g^{-1} (1.5 mA cm^{-2}) respectively, which were relatively high in comparison with the other batteries using inorganic solid electrolytes [1,10]. Moreover, the cell could be charged at a high current density of 100 mA g^{-1} . Considering that the cell discharging stopped after several cycles, the cyclability of charge–discharge was still poor. Here, we have to think of the electrode reactions of the present battery using an acid electrolyte. They must be different from those of the conventional Ni/MH battery using a KOH solution. The most plausible charge and discharge reactions appear to proceed based on the following reactions:

positive electrode :



negative electrode : $\text{MH}_x + x\text{H}_2\text{O} \rightleftharpoons \text{M} + x\text{H}_3\text{O}^+ + xe^-$

Generally, the hydrogen storage alloy is corroded easily under the acidic condition. Therefore, this poor cyclability would be due to the corrosion of the negative electrode material by the electrolyte with a strong acidic character. Consequently, we attempted to replace the negative electrode material with a zirconium-based alloy which is comparatively resistant to acids.

Fig. 2 shows the discharge efficiency variations with the cycle numbers for “ $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{H}_x/\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}/\text{NiOOH}$ ”. Here the discharge efficiency is defined as the ratio of measured discharge capacity to quantity of charged electricity. The cyclability (●) was somewhat improved as compared with the previous cell (○). However, the performance was still insufficient. Based on the demonstration by Mohri et al., the cycle life performance was greatly improved by using manganese dioxide for the positive electrode in the solid-state Ni/MH battery employing acidic $\text{Sb}_2\text{O}_5\cdot n\text{H}_2\text{O}$ as an electrolyte [1], we next tried to employ manganese dioxide instead of nickel hydroxide. As a result, a long life of over 200 cycles was achieved on the

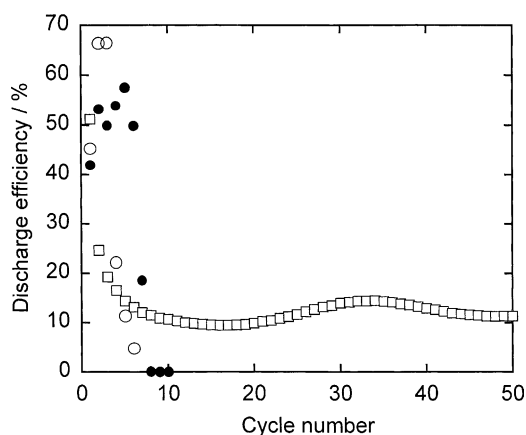


Fig. 2. Discharge efficiency variations with the cycle numbers for the metal-hydride batteries using $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$ as electrolytes: (○) $\text{MmNi}_{3.6}\text{Al}_{0.4}\text{Mn}_{0.3}\text{Co}_{0.7}\text{H}_x/\text{NiOOH}$; (●) $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{H}_x/\text{NiOOH}$; (□) $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{H}_x/\text{MnO}_2$.

cell resulted (□ in Fig. 2, charge–discharge current density was 5 mA g^{-1}). However, the discharge efficiency was low and the charge was impossible at as high as 50 mA g^{-1} . This indicated that high rate charge and discharge performance depends on the rate of reaction in positive active materials.

Next, considering the higher ionic conductivity of 12-molybdophosphoric acid hydrate under the electrochemical test condition, the battery characteristics were investigated using the hydrate as an electrolyte. Referring to the results on the battery using 12-tungstophosphoric acid hydrate, $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}$ and MnO_2 were employed as the negative and positive electrode materials. Fig. 3 illustrates the charge–discharge curves obtained in the test cell consisting of “ $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{H}_x/\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 20\text{H}_2\text{O}/\text{MnO}_2$ ” at a current density of 5 mA g^{-1} . During the initial several cycles, the cell exhibited relatively low voltage profiles owing to insufficient activation of the electrodes. Afterwards, till the 100th charge–discharge, the voltage profiles appeared to be steady. The open circuit voltages of the

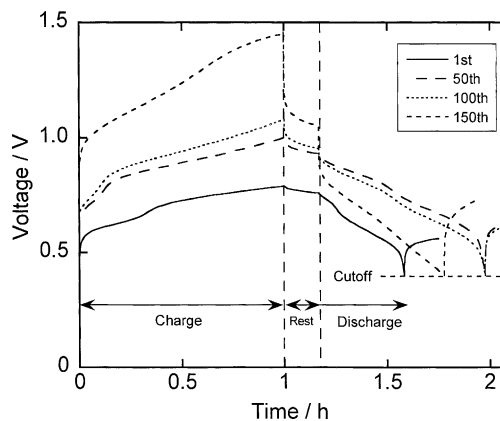


Fig. 3. Charge–discharge curves for the cell, $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{H}_x/\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 20\text{H}_2\text{O}/\text{MnO}_2$. Charge and discharge current densities are 5 mA g^{-1} .

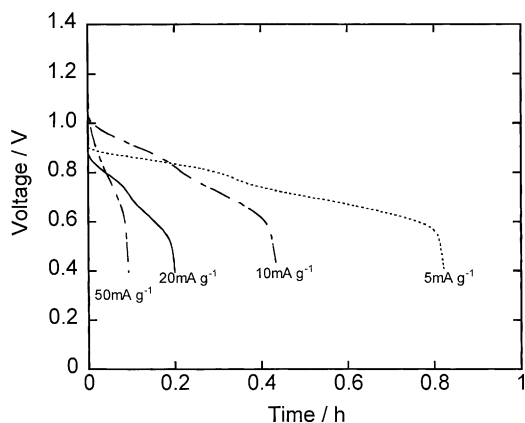


Fig. 4. Discharge curves obtained for the cell $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{H}_x/\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 20\text{H}_2\text{O}/\text{MnO}_2$.

cell after charging were lower than that of the conventional Ni/MH battery because of the lower electrode potential of MnO_2 than NiOOH . Gentle voltage drops were observed just after beginning of discharge, suggesting that $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 20\text{H}_2\text{O}$ would be a desirable electrolyte for solid-state metal-hydride batteries. However, the overpotential fairly increased after the 100th cycle. The origin of the increase in overpotential would be due to the gradual corrosion of the electrode material by electrolyte. In fact, the overpotential increased gradually with cycling as shown in Fig. 3. The corrosion of the electrode at the early step would inhibit the reaction at the electrode–electrolyte interface slightly, although the corrosion at initial cycle is useful for removal of oxidation layer on negative electrode surface. With repeating cycles, the corroded part of the electrode would expand, and then the larger overpotential would be observed.

Fig. 4 gives the discharge curves variations with time where the current density was changed from 5 to 50 mA g^{-1} . Although the discharge time decreased with increasing current density, the cell could be discharged even at a relatively high current density of 50 mA g^{-1} (i.e. 3.8 mA cm^{-2}). There have been only two reports concerning to MnO_2/MH solid-state battery, where the employed current densities were $75 \mu\text{A cm}^{-2}$ and 1.8 mA cm^{-2} for $\text{Sb}_2\text{O}_5\cdot n\text{H}_2\text{O}$ and $(\text{CH}_3)_4\text{NOH}\cdot 5\text{H}_2\text{O}$, respectively [1,5]. Thus, the cell obtained in the present investigation is found to be able to operate at higher current densities. Fig. 5 displays discharge efficiency and capacity variations with the number of charge–discharge cycle for the cells using 12-molybdophosphoric acid and 12-tungstophosphoric acid at a current density of 1 mA g^{-1} , where the discharge efficiency is defined as the ratio of measured discharge capacity (right axis in the figure) to quantity of charged electricity. The test cell using 12-molybdophosphoric acid (○) could be discharged up to 200 cycles and the discharge efficiency held at about 100%. On the other hand, the cell using 12-tungstophosphoric acid (●) did not show such a superior performance. As expected above,

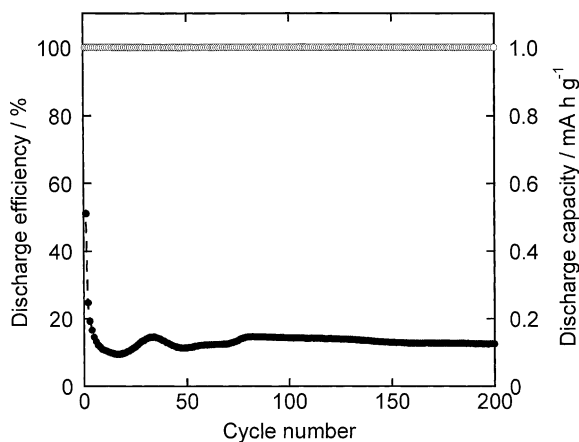


Fig. 5. Discharge efficiency and capacity variations with the number of charge–discharge cycle for the cells using 12-molybdophosphoric acid hydrate and 12-tungstophosphoric acid hydrate. Charge and discharge current densities are 1 mA g^{-1} : (○) $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{H}_x/\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 20\text{H}_2\text{O}/\text{MnO}_2$; (●) $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{H}_x/\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}/\text{MnO}_2$.

the higher conductivity of electrolyte would cause a good performance.

The cycle number dependence of the cell life at current densities of 5, 10 and 20 mA g^{-1} are shown in Fig. 6. The higher current density, the lower discharge efficiency and the shorter cycle life. However, the present cell exhibited relatively high discharge efficiency and stable reversibility over more than 100 cycles at 5 mA g^{-1} . After 100 cycles, the obvious decrease in discharge efficiency was observed. This is considered to be due to that the corrosion layer on the electrode surface inhibits the reaction at electrode–electrolyte interface. By comparing the performance with the other batteries, this battery performance was superior to the MnO_2/MH solid-state battery using $\text{Sb}_2\text{O}_5\cdot n\text{H}_2\text{O}$ or $(\text{CH}_3)_4\text{NOH}\cdot 5\text{H}_2\text{O}$ in a viewpoint of current density or self-discharge, and comparable to the Ni/MH solid-state battery using H_3PO_4 -doped silica gel.

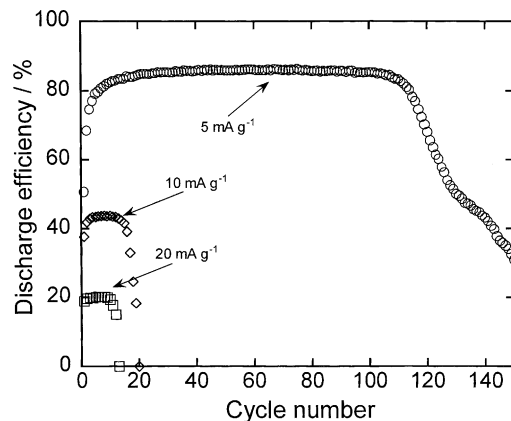


Fig. 6. Cycle number dependence of discharge efficiency for the cell, $\text{ZrMn}_{1.5}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{H}_x/\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 20\text{H}_2\text{O}/\text{MnO}_2$. Charge and discharge current densities are (○) 5 mA g^{-1} ; (◇) 10 mA g^{-1} ; (□) 20 mA g^{-1} .

4. Conclusions

Heteropolyacid hydrates, such as $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$, were applied to NiOOH/MH and MnO_2 /MH batteries. As a result, it was found that these materials work as electrolytes for the rechargeable metal-hydride batteries. The hydration numbers were determined to be $n = 15$ and 20 for $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$, respectively, under the present electrochemical test condition, and the humidity in the test cell appeared to be about 65%. The electrode materials compatible with the electrolyte were manganese dioxide and zirconium-based alloy for positive and negative electrodes, respectively. The performance of the solid-state battery using 12-molybdophosphoric acid hydrate was superior to that using 12-tungstophosphoric acid hydrate. The MnO_2 /MH battery using 12-molybdophosphoric acid hydrate was able to operate even at a current density of 50 mA g^{-1} , and exhibited the good cycle life performance, i.e. more than 100 cycles at a current density of 5 mA g^{-1} .

Acknowledgements

This work has been partially supported by a Grant-in-Aid for Scientific Research on Priority Areas of “Ionics Devices”

from the Ministry of Education, Science, Sports and Culture of Japan.

References

- [1] M. Mohri, Y. Tajima, H. Tanaka, T. Yoneda, *Sharp Technol. J.* 34 (1986) 97.
- [2] T. Yoneda, S. Satoh, M. Mohri, *Sharp Technol. J.* 38 (1987) 55.
- [3] N. Kuriyama, T. Sakai, H. Miyamura, A. Kato, H. Isikawa, *Denki Kagaku* 58 (1990) 89.
- [4] N. Kuriyama, T. Sakai, H. Miyamura, A. Kato, H. Isikawa, *J. Electrochem. Soc.* 137 (1990) 355.
- [5] N. Kuriyama, T. Sakai, H. Miyamura, A. Kato, H. Isikawa, *Solid State Ionics* 40/41 (1990) 906.
- [6] N. Vassal, E. Salmon, J.-F. Fauvarque, *J. Electrochem. Soc.* 146 (1999) 20.
- [7] N. Vassal, E. Salmon, J.-F. Fauvarque, *Electrochim. Acta* 45 (2000) 1527.
- [8] C. Iwakura, S. Nohara, N. Furukawa, H. Inoue, *Solid State Ionics* 148 (2002) 487.
- [9] O. Nakamura, T. Kodama, I. Ogino, Y. Miyake, *Chem. Lett.* (1979) 17.
- [10] C. Iwakura, K. Kumagai, K. Yoshiki, S. Nohara, N. Furukawa, H. Inoue, T. Minami, M. Tatsumisago, A. Matsuda, *Electrochim. Acta* 48 (2003) 1499.
- [11] O. Nakamura, et al., Report No. 360 of the Government Industrial Research Institute, Osaka, 1982.