Influence of MH electrode thickness and packing density on the electrochemical performance of air–MH batteries

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Abstract

Thin and thick metal hydride (MH) electrodes used in air–MH batteries were evaluated with respect to electrochemical performances. The influence of electrode thickness on the discharge capacity, rate capability, charge and discharge voltages was investigated as well as the effect of MH packing density within electrodes on the electrode performances was also examined. The mass transport within the porous electrode was found to be the rate limiting step with increasing electrode thickness. The power output could be increased by either using thin electrodes or decreasing electrode density. This was, however, done at the expense of the energy density of the cell. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen storage alloy; Metal hydride electrode; Electrode thickness; Particle packing density; Air–metal hydride battery

1. Introduction

During the past years, several air–metal hydride (MH) cell systems have attracted substantial attention [1–9]. A significant increase in energy density per unit weight can be possible by replacing the heavy Ni oxide cathode in Ni/MH cells with a light-weight air gas-diffusion electrode. However, two key technological problems need to be solved before the air–MH cell can be used in practical applications. Firstly, the air electrodes are seriously damaged when used as charging electrodes. This can be overcome by installing a third charging electrode in the air–MH cell system [4]. However, such a three-electrode cell system looses the advantage of a high energy density. Recently, a bifunctional air gas-diffusion electrode for both oxygen reduction and oxygen evolution was developed which may open up for a further improvement of the energy density [6,7]. The second problem is usually a poor electrochemical performance of the MH electrode when the thickness is increased (say, more than 2 mm). When designing an air–MH cell, it is tempting to use a thicker MH electrode as it increases the energy capacity. This is, however, done at the expense of power output. For a thin MH electrode used in already commercial Ni/MH cells, the MH electrode performance is generally

determined by the rate of hydrogen diffusion from the bulk to the active surface of the MH particles. The mass diffusion and migration within the electrode have a marginal effect on the electrochemical properties. For a thick MH electrode, however, these effects can not be neglected and the electrochemical performance becomes governed by the rate of mass transport within the electrode. This is because the diffusion and migration path for OH^- and water become long from surface to the interior of the electrode. A gradient of electrolyte concentration is formed during the charge or discharge process, especially at higher rates. Thus, the total performance of air–MH cell system such as capacity, rate capability, cycle life, etc. is very dependent on the thickness of a MH electrode. Vidts et al. [11] and Heikonen et al. [12] made a theoretical analysis about the effect of MH electrode thickness on the electrochemical properties. According to their models, the electrode potential will rapidly decrease and capacity will be lost when the thickness increases to more than 4 mm. The combined influence of all the parameters involved such as electrode design with substrate, binder, active mass, porosity is, however, difficult to evaluate theoretically. In this work, we want to empirically evaluate how electrode thickness and electrode porosity influence the electrochemical performance. One advanced La-rich AB_5-type alloy with a capacity of more than 300 mAh/g was chosen as an active material of MH electrodes. The alloy composition is expressed as $MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$. The charge–discharge voltages, capacity and rate capability were

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investigated and compared for different electrode thickness. In addition to the thickness, the packing density of metal hydride particles inside an electrode was varied to investigate the mass transport rate dependence of the MH electrode porosity. The aim was to optimise electrode thickness and porosity to construct a practical air–MH battery with acceptable capacity as well as good high power performance.

2. Experimental details

MH electrodes with different thicknesses were fabricated at our laboratory. Each electrode consists of 74 wt.% active MH alloy, 19 wt.% Ni powder, 4 wt.% carbon powder and 3 wt.% binder. The active MH alloy density in the electrode was about 3.63 g/cm^3 and the electrode thickness was varied between 0.36 and 4.05 mm. Electrochemical properties of these MH electrodes were tested in a half-cell with 6 M KOH solution at 22°C. A sintered nickel electrode with a larger capacity and a Hg/HgO (6 M KOH) electrode were used as the counter-electrode and reference electrode, respectively. The MH electrodes were achieved in 2 cycles charging at 31 mA/g (about 0.11C rate) for 12 h and discharging at the same rate down to 0.74 V. The cycling stability examination was conducted through charging at 0.22C rate for 6 h and discharging at the same rate to end potential of −0.74 V versus a Hg/HgO electrode using a computer controlled current source in 6 M KOH at 22°C.

In order to examine the effect of MH packing density on the electrode performance, three cylindrical MH electrodes with a thickness of about 3.2 mm and different levels of MH packing density were constructed. The density of the electrode was varied by spirally winding their band MH electrodes (0.4 mm thick) with different amounts of separator. The MH packing density of the electrode was calculated by dividing the weight of MH powder alloy used with the electrode volume (g/cm^3).

3. Results and discussion

3.1. Electrochemical behaviour of thin MH electrodes

Fig. 1a shows the discharge curves of a thin electrode (0.36 mm) with discharge currents between 31 and 125 mA/g. It can be seen that the thin MH electrode has a flat discharge plateau with no marked potential and capacity drops. The influence of mass transport on the electrochemical behaviours can be neglected because the diffusion or migration path of the mass (OH$^-$ and water molecular) from the electrode/electrolyte interface to the interior of the electrode is short. Thus, the electrochemical behaviour for the thin electrode is usually controlled by the charge-transfer reaction occurring on the surface of the MH particles and hydrogen diffusion from the inside to the surface of the MH particles. As the discharge rate increases to 314 mA/g
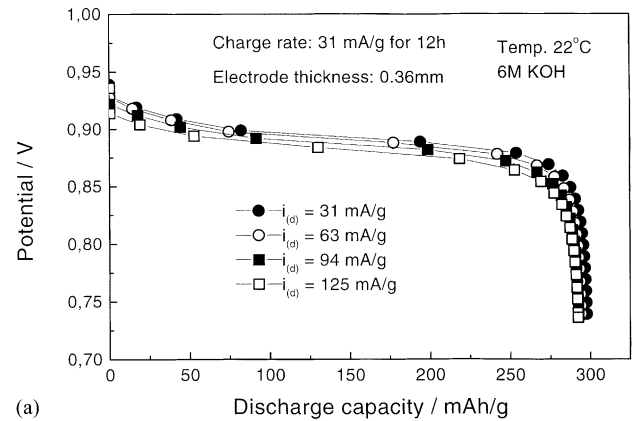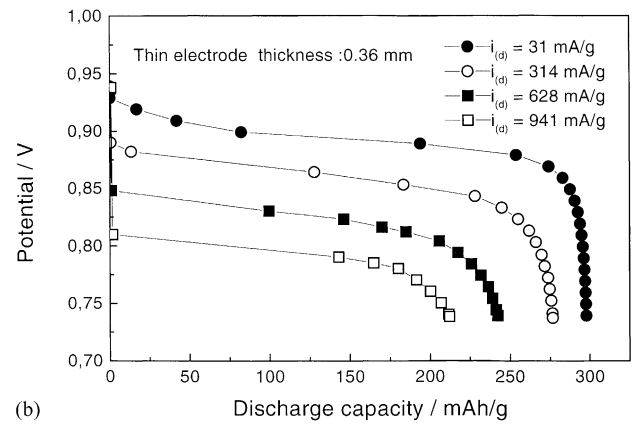
Fig. 1. (a) Discharge curves of thin electrodes in the range of discharge current density between 31 and 125 mA/g; (b) discharge curves of thin electrodes at high discharge rates and compared with that of 31 mA/g.

(about 1.0C) or higher, however, the potential and capacity drops were seen as shown in Fig. 1b. A similar discharge curves of AB5-type MH electrode has also been observed by other authors [10]. An explanation can be suggested as follows. The rate of the charge-transfer reaction increases with discharge rate. Thus, the atomic hydrogen on the surface of the MH particle is rapidly consumed by the charge-transfer reaction, which results in a sudden drop of discharge potential at the beginning of discharge stage. Compared to the rate of charge-transfer reaction, the rate of hydrogen diffusion reaction from the bulk to the surface of MH particles becomes slow. As a result, the potential and capacity drops were observed at a high discharge rate. In this case, the electrode reaction was fast and the rate determining step was the hydrogen diffusion process from the bulk to the surface of MH particles.

3.2. Effect of electrode thickness on the electrochemical properties

Fig. 2 shows the charge and discharge curves of the MH electrodes as a function of thickness. As seen from Fig. 2, the charge potential rapidly increases as the electrode thickness
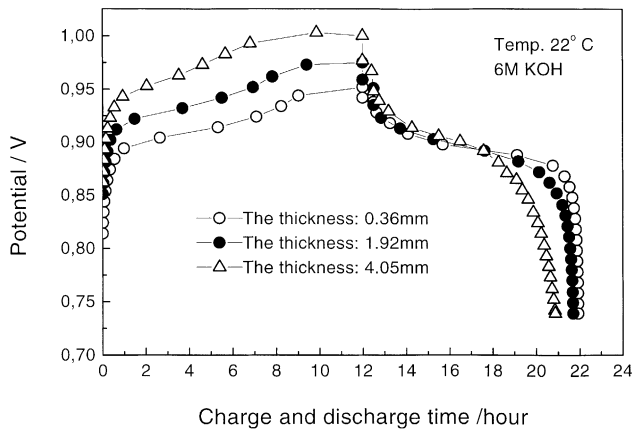
Fig. 2. Charge and discharge curves of MH electrodes with different thicknesses. Charge rate: 31 mA/g for 12 h; discharge rate: 31 mA/g; rest time: 30 min.

Fig. 3. Comparison of discharge curves for three electrodes at 31 mA/g discharge rate.

increases. This behaviour is supposed to be related to the rate of mass transport (H_2O, OH^-) to/from the electrode/electrolyte interface to the interior of the electrode, as the diffusion and migration path becomes longer with increasing electrode thickness. During the charge process, the H_2O molecule on the surface of MH alloy particle is consumed by the charge-transfer reaction (Volmer reaction), i.e. $M + H_2O + e^- = MH + OH^-$, and needs to be replenished through diffusion from the electrode/electrolyte interface. Due to longer diffusion paths in a thicker electrode, a slower diffusion is expected. Thus, the rate of H_2O consumption by the Volmer reaction overcome the diffusion of H_2O molecules. The concentration of H_2O inside the interior of electrode is substantially decreased. This leads to a concentration gradient within the electrode, resulting in a higher electrode polarisation for the thicker electrode and leading to a rapid increase of the necessary charge potential.

During the discharge process, OH^- ions are consumed by the electrochemical reaction, i.e. $MH + OH^- = M + H_2O + e^-$. The concentration of OH^- inside the electrode can be made up by diffusion as well as charge migration from the electrode/electrolyte interface toward the electrode interior. Thus, the replenishment of OH^- ions inside the electrode is supposed to be faster since it is driven by both diffusion and migration. Therefore, the potential drop during discharging is not so large as during the charging process, as shown in Fig. 2.

A gradual decrease of discharge capacity with increasing the electrode thickness was also observed, as shown in Fig. 3. The reason is related to the lower charging efficiency for a thicker electrode due to the higher charging potential. Fig. 4a and b give the discharge curves of two electrodes with different thicknesses for discharge currents of 31–125 mA/g. As seen from the two figures, the discharge curves of the thicker electrodes become a steep slope without a typical discharge plateau compared to the thin electrode in Fig. 1a. The phenomenon was interpreted to be a mass transport effect. The potential drop increases as the electrode
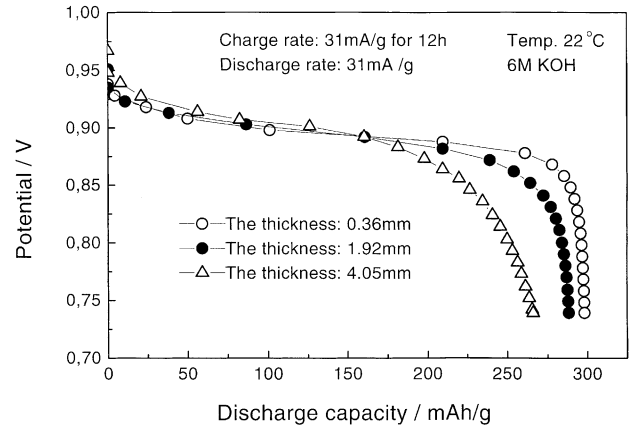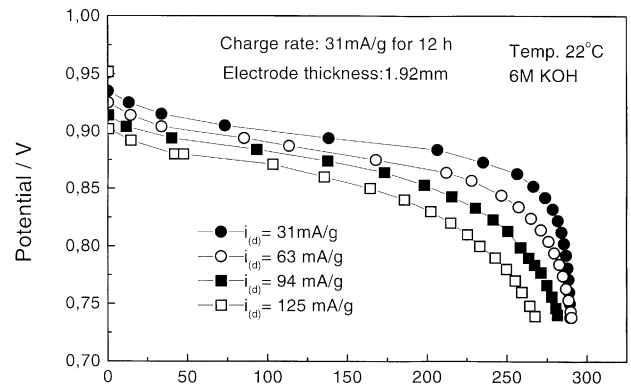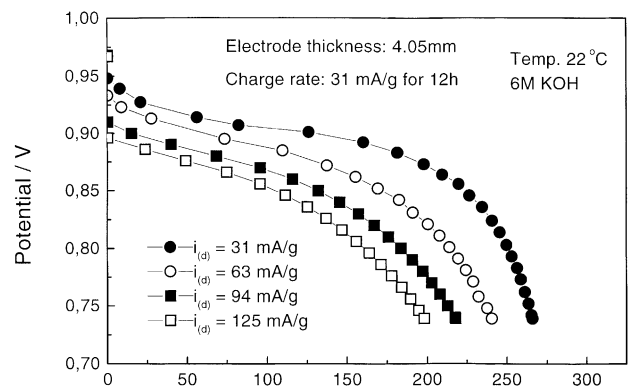
thickness increases. The three electrodes are compared at a discharge rate of 125 mA/g in Fig. 5. This implies that the difference in the potential drop becomes larger at a relatively higher discharge rate. This behaviour could be explained by considering the following two factors: (1) the rate of OH^- ions consumption and (2) the rate of OH^- ions transport.

(a)

(b)

Fig. 4. Discharge curves of two electrodes at the different discharge rates: (a) the electrode thickness, 1.92 mm; (b) the electrode thickness, 4.05 mm.
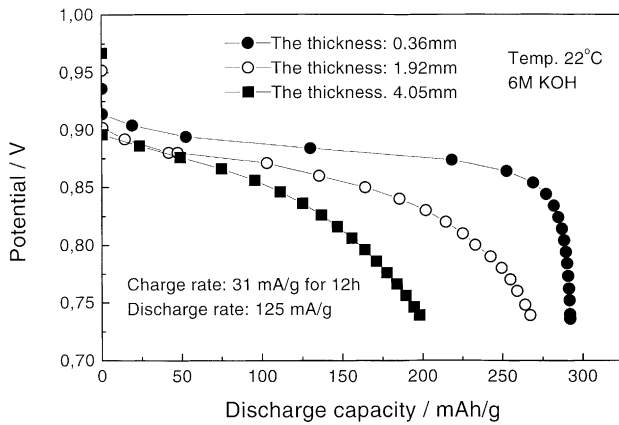
Fig. 5. Comparison of discharge curves for three electrodes at 125 mA/g discharge rate.

Fig. 7. Charge and discharge curves of MH electrodes with different MH packing densities. Charge rate: 30 mA/g for 12 h; discharge rate: 30 mA/g; rest time: 30 min.

In the case of a low discharge rate, it is supposed that the rate of OH^- ions consumption by the electrochemical reaction $(MH + OH^- = M + H_2O + e^-)$ and the rate of OH^- ions transport from the electrode/electrolyte interface to the interior of electrode are almost balanced. As a result, no obvious effect of electrode thickness on the electrochemical behaviours was observed. In the case of a relatively high discharge rate, the rate of OH^- ions consumption is considered to be larger than the rate of OH^- ions transport. Consequently, a great effect of electrode thickness on the electrochemical behaviours was observed. From Figs. 1a and 4a and b, it is clear that the thin electrode exhibits very good rate capability, whereas the electrode with the thickness of 4.05 mm appears to have a poor rate capability. These electrochemical performances observed in this work are basically consistent with the prediction from models for thick MH electrodes [11,12].

The cycling stability of the electrode with the thickness of 1.92 mm was examined and the result is shown in Fig. 6. The capacity decay after 150 cycles was about 9%, which basically satisfies the requirements of an air–MH cell system.
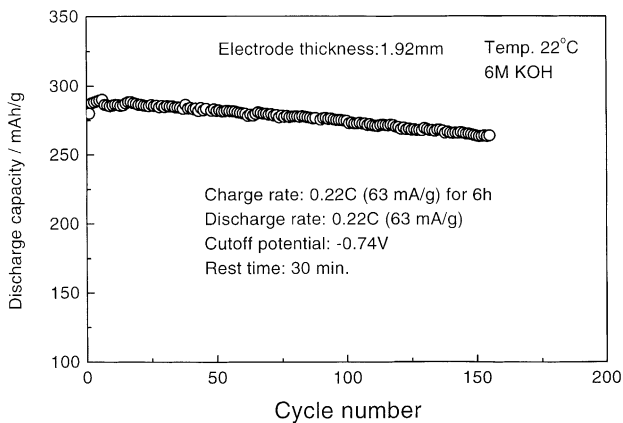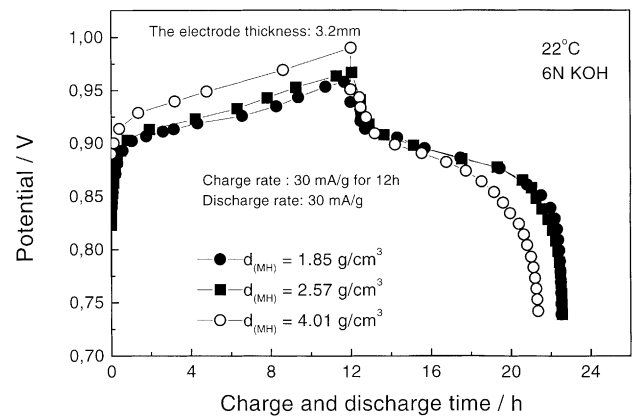
3.3. Effect of MH packing density on electrode performance

For a thick MH electrode, the packing density of the metal hydride particles inside the electrode also plays an important role for the electrochemical performance. Fig. 7 shows the charge and discharge potentials of three different MH density electrodes at the same electrode thickness of 3.2 mm. As seen from the Fig. 7, the charge potential increases as the MH density increases, especially when the MH packing density increases to about 4 g/cm^3. This is because the electrode porosity available for the mass transport decreases with increasing MH packing density. A low electrode porosity limits the mass transport from the electrode/electrolyte interface to the interior of electrode, making the concentration gradient steeper within the electrode. As a result, a larger charging polarisation potential is observed for an electrode with a higher MH packing density.

Fig. 8 presents the discharge curves of the three different MH electrode densities at a discharge rate of 60 mA/g (about 0.2C). A lower MH packing density electrode (or higher

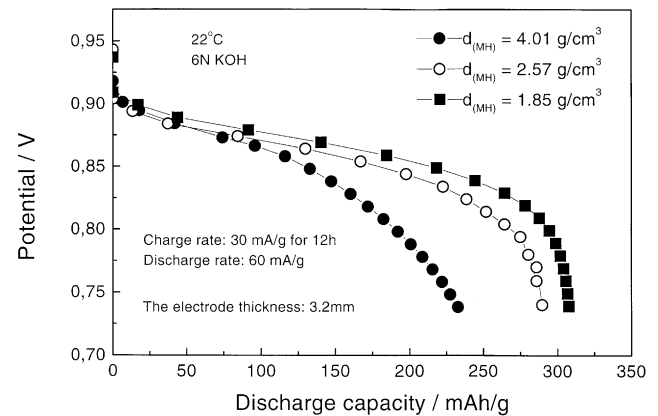Fig. 6. Discharge capacity vs. cycle number for the electrode with the thickness of 1.92 mm.

Fig. 8. Comparison of discharge curves for three electrodes with different MH packing densities at 60 mA/g discharge rate.
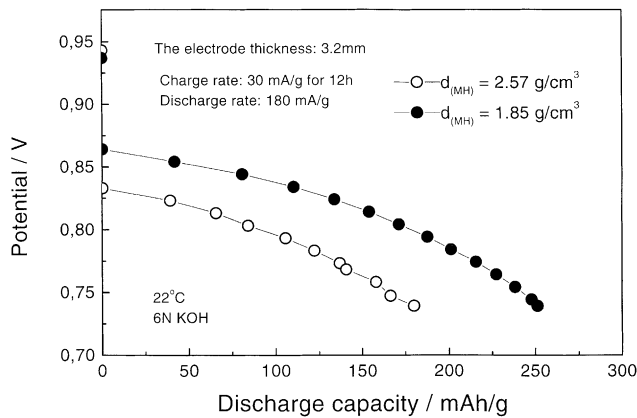
Fig. 9. Comparison of discharge curves between two electrodes with different MH packing densities at 180 mA/g discharge rate.

porosity) leads to a higher discharge potential, a higher capacity and a higher utilisation of active material. The electrode with the higher MH packing density of about 4 g/cm^3 exhibits a rather poor electrochemical behaviour even at the lowest discharge rate. If the discharge rate reaches 180 mA/g (about 0.6C), the electrode with the MH packing density of 2.57 g/cm^3 has also a poor performance, as shown in Fig. 9. Only the electrode with the MH packing density of 1.85 g/cm^3 still exhibits a satisfactory performance at this relatively high discharge rate. Besides considering mass transport, the amount of electrolyte available inside the MH electrode before charging should also be considered. The amount of available electrolyte increases as the electrode porosity increases. Thus, the mass flow for the low MH packing density electrode does not immediately become critical for the diffusion or migration in the electrode. Therefore, a good electrochemical performance was observed for the MH electrode with a low MH packing density. This implies that a high power output could be obtained by increasing the MH electrode porosity. However, this is done at the expense of the energy density of the MH electrode. The energy density of MH electrode is also an
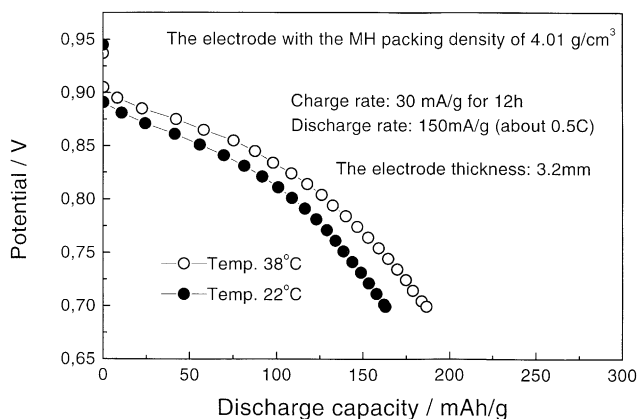
important parameter in practical applications of air–MH batteries. Thus, the electrode thickness, the MH packing density and the energy density of MH electrode must be optimised for the best overall performance.

Also, the operating temperature also has a great effect on the electrode performance. Generally, the mass transport and electrode reaction kinetics will be improved when the operating temperature rises. Fig. 10 presents the results of an electrode with the MH packing density of 4.01 g/cm^3 at 0.5C discharge rate after increasing the operating temperature by 16°C. Obviously, the discharge potential and capacity were improved.

4. Conclusions

Thin MH electrodes show good electrochemical charge and discharge performances. However, thick MH electrodes with a thickness of about 4 mm will be severely limited leading to lower capacities and poor rate capabilities. The potential drop during discharging increases substantially with electrode thickness. This drop increases further with increasing discharge current. Also, the charge potential was observed to increase with electrode thickness even at low charge rates. These phenomena were explained by limitation in the mass transport from the electrode/electrolyte interface to the interior of the electrode. For a thick MH electrode, the electrode performance was mainly governed by the rate of mass transport, especially at higher rates. However, the electrode performance can be improved by reducing the MH packing density within the electrode. It is possible to increase the power output from a thick MH electrode to reach the requirement of air–MH batteries if the MH packing density is reduced to about 2 g/cm^3. Unfortunately, the energy density of the MH electrode will decrease as the MH packing density decreases. In order to keep a high energy density, thus, the thickness of MH electrode used in air–MH batteries is suggested to be not more than 2 mm. For optimal energy densities and power performance of air–MH cells, the MH electrode thickness should be designed to be between 2 and 4 mm with a density in the range of 4–2 g/cm^3.

References

[1] C. Folonari, G. Iemmi, F. Manfredi, A. Rolle, J. Less-Common Met. 74 (1980) 371.
[2] K. Nishio, M. Kimoto, F. Mizutaki, M. Takee, S. Furukawa, Sanyo Electric Co., Japan Patent 05,242,906 (1993).
[3] M. Tadokoro, M. Kimoto, K. Nishio, T. Saito, Sanyo Electric Co., Japan Patent 06,223,887 (1994).
[4] T. Sakai, T. Iwaki, Z. Ye, D. Noreus, O. Lindström, J. Electrochem. Soc. 142 (12) (1995) 4040.
[5] N. Vassal, E. Salmon, J.-F. Fauvarque, J.-F. Penneau, Batteries for portable applications and electric vehicles, Proc. Electrochem. Soc. 97 (18) (1997) 869–880.
[6] S. Gamburzev, W. Zhang, O.A. Velev, S. Srinivasan, A.J. Appleby, J. Appl. Electrochem. 28 (1998) 545.

Fig. 10. The effect of temperature on the discharge curves for the electrode with the MH packing density of 4.01 g/cm^3.

[7] S. Gamburzev, O.A. Velev, R. danin, S. Srinivasan, A.J. Appleby, A. Visintin, Batteries for portable applications and electric vehicles, Proc. Electrochem. Soc. 97 (18) (1997) 726–733.

[8] M. Lampinen, M. Famino, J. Electrochem. Soc. 140 (12) (1993) 3537.

[9] J. Heikonen, T. Noponen, M. Lampinen, J. Power Sources 62 (1996) 27.

[10] B.S. Haran, B.N. Popov, R.E. White, J. Electrochem. Soc. 145 (1998) 4082.

[11] P. De Vidts, J. Delgado, R.E. White, J. Electrochem. Soc. 142 (12) (1995) 4006.

[12] J. Heikonen, K. Vuorilehto, T. Noponen, J. Electrochem. Soc. 143 (12) (1996) 3972.