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Performance improvement of a MH/MnO$_2$ rechargeable battery

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Abstract

Several important features have been introduced to make the MH/MnO$_2$ system competitive with other rechargeable batteries. These include improvement in cell construction, the adoption of a good hydrophilic separator, the adoption of a new charging regime and the substitution of the multicycle step formation procedure for the single-cycle step formation procedure. Test results show that the performance of the MH/MnO$_2$ cell is significantly improved. 400 cycles can be expected at 100% DOD and 1100 cycles can be obtained at 60% DOD. The high rate capability of the MH/MnO$_2$ cell is also improved.

1. Introduction

The MH/MnO$_2$ rechargeable battery is attractive because of its nontoxicity, low self-discharge rate, high performance/cost ratio and nonmemory effect [1]. However, the disadvantages of the battery are its relatively low cycle life and poor high rate capability, which thus make it unsuitable for certain applications. Based on test results, a volume expansion of the MH/MnO$_2$ cell has been found after hundreds of charging/discharging cycles. The discharge capacity also decreases rapidly. Possible reasons for these phenomena may be: (i) The internal pressure of the cell is increased due to the evolution of oxygen and hydrogen during charge/discharge cycling; (ii) Plates expand and become out of shape during cycling; and (iii) The construction of the cell is damaged because of the unsuitable charge/discharge regime.

To overcome these problems, different methods have been used in this study. These include improvement of cell construction, adoption of a good hydrophilic separator, choice of a suitable binder, adoption of a new charging regime to prevent overcharging and substitution of a multicycle formation procedure for the single-cycle formation procedure. Significant improvements in MH/MnO$_2$ cell performance have been achieved, which make the MH/MnO$_2$ system competitive with other rechargeable batteries.

Continuous testing verified that the cycle life of the improved MH/MnO$_2$ cell exceeded 1100 cycles (the test is still running) at 60% DOD, which is far superior to that of the MH/MnO$_2$ cell before improvement. At 100% DOD, 400 cycles can be expected. In addition, the high rate capability of the MH/MnO$_2$ cell is also improved. The energy density has reached 45 W h kg^{-1}, which approaches that of commercial Ni/Cd cells. Typical discharge curves for the 3.5 A h prismatic MH/MnO$_2$ cell at 0.2 *C*, 0.5 *C* and 1 *C* charge/discharge rates are illustrated in Figure 1. The cell was cycled at a temperature of 25 °C.

2. Experimental details

2.1. *Improvement in cell construction*

Improvement in cell construction is confined to a 3.5 A h prismatic MH/MnO$_2$ cell with a size of 75 mm × 120 mm × 8 mm and a weight of 85 g. In the previous design, the active material was coated on four or five 60 mm × 80 mm plates, then dried, pressed and assembled. Cells produced in this way have a low specific capacity (volume basis) because the nickel foam substrate occupies a large space in the cell. For this reason, the same amount of active material was spread on three or four plates of a larger area (70 mm × 90 mm) than that of the previous ones, to decrease the thickness of the plate assemblies. Cells assembled with or without the improvement were initially charged at 0.7 A for 2 h, and were then charged at 1.55 V to 80% of the theoretical capacity and discharged at 0.7 A to 60% of the theoretical capacity. Curves showing the cut-off voltage against cycle number are shown in Figure 2.

2.2. *Improvement in formation procedure*

The behaviour of the MH/MnO$_2$ cell during its initial charge/discharge cycle is different from those of the Ni/

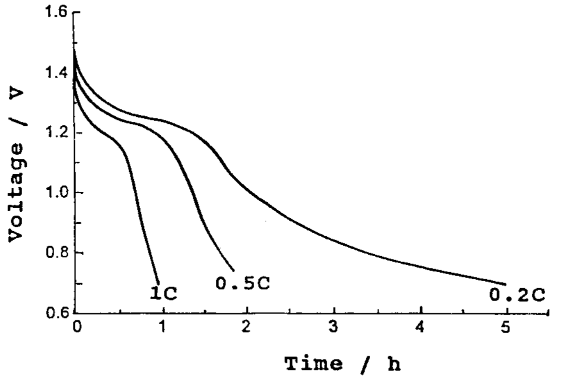

Fig. 1. Typical discharge curves for 3.5 A h prismatic MH/MnO_2 rechargeable battery at 0.2 *C*, 0.5 *C* and 1 *C* respectively. Curves show the first discharge cycle.

MH and Ni/Cd cells because the initial electrode states are mismatched. We found that mixing MnO_2 with an appropriate amount of $Ni(OH)_2$ provided the best formation result. The optimum weight ratio of MnO_2/$Ni(OH)_2$ was from 5:1 to 7:1. The theoretical capacity ratio of the positive to the negative electrode is 1:1.2 [1]. To avoid overcharging the MnO_2 electrode and generating oxygen, the cell was initially charged to 120% of the theoretical capacity of $Ni(OH)_2$, and then the charge capacity was progressively increased. During this study, several formation procedures were tested; only the typical ones are presented here.

2.2.1. *One-step formation*

The cell was charged to 120% of the theoretical capacity of MH (AB_5-based alloy provided by the Institute of Metallurgy of ShangHai, China) and then discharged at a constant current of 0.7 A to a cut-off voltage of 0.7 V. The same procedure was repeated three times.

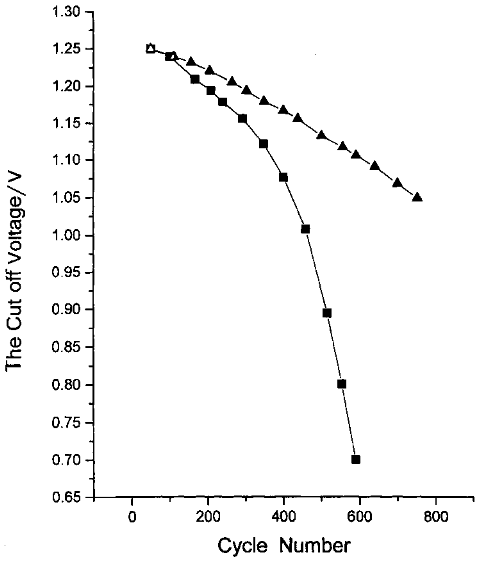

Fig. 2. Variation of the cut-off voltage with the cycle number for the MH/MnO_2 rechargeable cell. Cells were charged at 1.55 V to 80% of its theoretical capacity and discharged at 0.7 A to 60% of its theoretical capacity. Key: (■) before improvement; (▲) after improvement.

2.2.2. *Seven-step formation*

Step one: The cell was first charged at 0.7 A to 120% of theoretical capacity of $Ni(OH)_2$ in the cathode and then discharged at 0.7 A to a cut off voltage of 0.7 V.
Step two: After the first step, the cell was charged at 1.55 V to 180% of theoretical capacity of $Ni(OH)_2$ and then discharged to 0.7 V.
Step three: Charge at 1.55 V to 270% of theoretical capacity of $Ni(OH)_2$, then discharge to 0.7 V.
Step four: Charge at 1.55 V to 346% of theoretical capacity of $Ni(OH)_2$, then discharge to 0.7 V.
Step five: Charge at 1.55 V to 400% of theoretical capacity of $Ni(OH)_2$, then discharge to 0.7 V.
Step six: Charge at 1.55 V to 450% of theoretical capacity of $Ni(OH)_2$, then discharge to 0.7 V.
Step seven: Finally, the cell was charged to 120% of the MH theoretical capacity and then discharged (at 0.7 A) to a cut off voltage of 0.7 V.

2.2.3. *Seven steps with multicycle formation*

This procedure was similar to the seven-step procedure, but cells formatted by this procedure were charged/discharged for several cycles in every step to activate the MH electrode more efficiently.

Cells formatted by different procedures were then cycled using the full charging/discharging regime. Curves of discharge capacity against cycle number are shown in Figure 3. The cathode materials in the cells were tested by X-ray diffraction after partial formation; the test results are shown in Figure 4.

2.3. *Charging regime*

The previous charging regime for the MH/MnO_2 cell involved charging at a constant voltage of 1.55 V for 12 h, which would unavoidably lead to overcharge. This

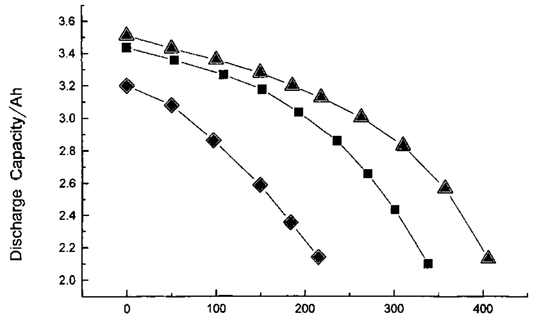

Fig. 3. Curves of discharge capacity against cycle number for the MH/MnO_2 rechargeable cell formatted by different procedures. Key: (◆) formatted by one-step procedure; (■) formatted by seven-step procedure; (▲) formatted by seven steps with multicycle procedure.

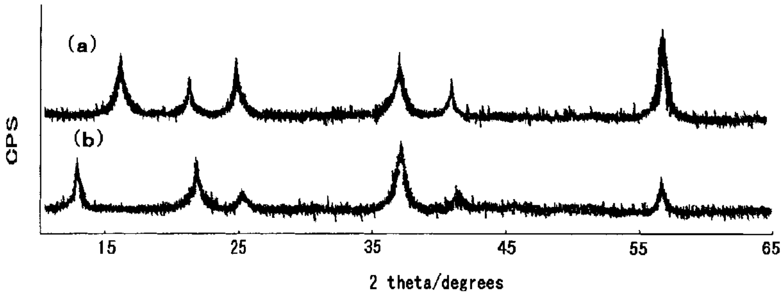

Fig. 4. X-ray diffraction patterns of the cathode material (MnO_2) + $Ni(OH)_2$ (a) without formation, (b) formatted by seven step with multicycle procedure.

overcharging condition may be alleviated by changing the charging regime, that is, by first charging the cell at a constant current of 0.7 A for 2 h, and then charging at 1.55 V to 120% of theoretical capacity. The discharge curves before and after the change in charging regime are shown in Figure 5.

2.4. *Improvement in separator*

Previously, polypropylene was used as the separator in MH/MnO_2 cells. To improve the hygroscopicity, separator consisting of a compound of polypropylene and hydrophilic separator (such as vinylon) was chosen instead of polypropylene. The discharge curves before and after the separator improvement are shown in Figure 6.

3. Results and discussion

3.1. *Development of cell construction*

In order to improve the performance of the MH/MnO_2 cell and to obtain high reliability, it is important to optimize the cell construction and to develop materials which are suitable for the optimization of cell structure. Figure 2 shows curves of the cut-off voltage vs the cycle number before and after the improvement in cell construction. Before improvement, the cut-off voltage began to decrease quickly after 300 cycles and fell to 0.7 V after 590 cycles. However, improved cells showed only a slight decline in cut-off voltage with cycling. The cut-off voltage was about 1.03 V after 800 cycles, which demonstrated that improved cells had better capacity maintenance.

The difference between cells with and without improvement is the number of plates and the interelectrode space. Kordesch et al. proposed a ‘thin design’ [2] and expected that the thin design would increase the utilization of active material. In a MH/MnO_2 rechargeable cell, the utilization of active material has been improved by the ‘thin design’, which can be demonstrated by the cell performance during the first 50 cycles. However, after 150 cycles, the discharge capacity of the cell with ‘thin design’ obviously decreased. This capacity decline may be attributed to the fact that a cell of ‘thin design’ has a larger reactive area and less interelectrode space, which results in high utilization of active material, lower internal resistance and better efficiency during the first 50 cycles. However, the electrode expands and produces microcracks with prolonged cycling. This leads to deterioration of the electronic-conductive network formed by the electrode active material and disintegration of the electrode with consequent capacity decline. Thus electrode shorts may occur and eventually cause cell failure.

Electrode shorting happened earlier in cells without improvement compared with improved cells. Electrode

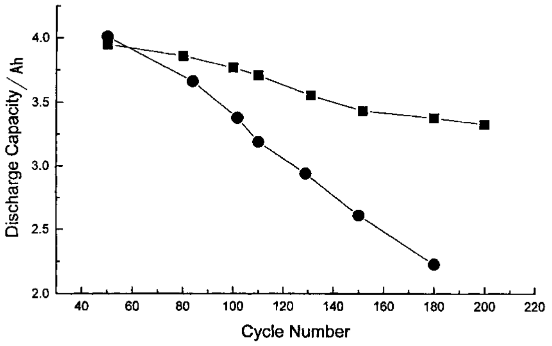

Fig. 5. Discharge curves for the MH/MnO_2 rechargeable cell before and after the charging regime improvement. Key: (●) before improvement; (■) after improvement.

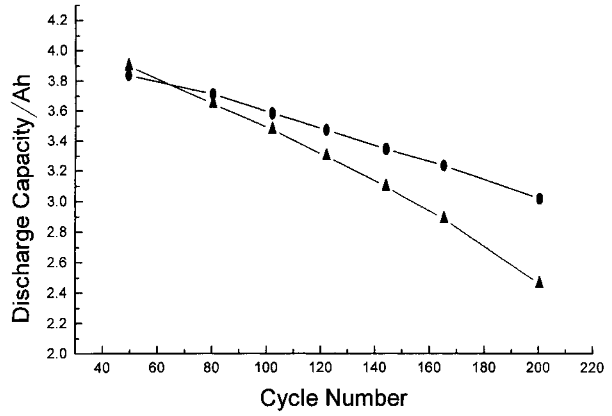

Fig. 6. The discharge curves for the MH/MnO_2 rechargeable cell before and after separator improvement, Cycling was carried out in the full charge/discharge regime. Key: (▲) before improvement; (●) after improvement.

shorting was observed in 3.5 A h prismatic MH/MnO_2 test cells. All of those cells have a definite volume because the same battery case was used; therefore, the 'thin design' improves the utilization of active material. However, the ratio of inactive nickel foam as current collector to the active material is higher for a 'thin design' cell because the nickel foam occupies more free space. The $Ni(OH)_2$ in the cathode is converted to γ-NiOOH: this leads to a 44% volume expansion during charging. The MnO_2 in the cathode also expands during cycling [3]. The expansion of the cathode unavoidably absorbs some of the electrolyte in the separator and the anode surface leading to electrolyte starvation in the separator and at the anode surface. Therefore, 'drying-out' may cause electrode oxidization and promote cell deterioration [4]. This disadvantage can be remedied if more free space is provided in the cell. The larger the free space, the higher the tolerable electrode volume expansion. As long as adequate free space is provided, the possibility of electrode shorting can be reduced.

It can thus be concluded that free space in the cell is a key factor in cell performance. The performance of the MH/MnO_2 rechargeable cell can be improved by reducing plate thickness.

3.2. *Development of the separator*

The separator influences virtually all cell characteristics, including the cycle life [5]. It is common knowledge that to retain electrolyte and to resist oxidation are two key requirements of a separator. Polypropylene (PPP) separators previously used in the MH/MnO_2 rechargeable cell have high oxidization resistance and good stability. Unfortunately, polypropylenes are naturally hydrophobic and their poor electrolyte holding capability leads to electrode polarization and cell deterioration. However, a hydrophilic separator, such as a Vinylon, also deteriorates with time due to oxidization. It was found that a cell using a hydrophilic separator showed a rapid drop in capacity after 100 cycles, although it performed well and maintained excellent capacity during the first 70 cycles. For these reasons, a laminated separator was made by combining a hydrophilic material with a polypropylene layer. Figure 5 shows the discharge curves of cells with and without the laminated separator. Cells using the laminated separator display better performance.

3.3. *Formation methods*

Figure 3 shows the charge/discharge cycling behavior of 3.5 A h MH/MnO_2 cells which had undergone the seven-step, the one-step and the seven step with multicycle formation procedures. The cell with the seven step with multicycle formation procedure delivered 88% of its theoretical capacity after 215 cycles, while cells with the one-step and the seven-step formation procedure delivered only 61% and 81% of theoretical capacity, respectively.

Cells formatted by different methods also have different initial discharge capacities. A low initial capacity of 91.5% of theoretical capacity was observed in a cell with the one-step formation procedure. The low initial capacity may be explained by the following. The cell formatted by one-step formation was initially fully charged, which led to serious overcharge and produced MnO_4^{2-} [6]. MnO_4^{2-} was reduced to Mn^{2+} and then changed to Mn_3O_4 during cycling. Mn_3O_4 has poor electrochemical activity in aqueous media, and reoxidation is difficult [7]. Accumulation of Mn_3O_4 may also result in an inactive layer which would prevent protons diffusing into the MnO_2, thus reducing its activity. Moreover, oxygen generated during overcharge reduces the MH capacity.

Figure 3 shows an increasingly rapid decline. This decline in capacity may be attributed to volume expansion and the poor contact among MnO_2 particles [8]. Poor contact occurs increasingly among the MnO_2 particles and the particles of conductive material in the electrode, which causes an increase in the cell internal resistance, and thus decreases the MnO_2 utilization. Some MnO_2 particles peel off from the electrode during prolonged cycling. The porosity of the electrode may then decrease, and therefore, the utilization of the electrode active material may be reduced further. In a previous paper [1], we suggested that the addition of $Ni(OH)_2$ to the MnO_2 electrode of the MH/MnO_2 rechargeable battery can prevent overcharge of the MnO_2 electrode, decrease the imbalance in the charge/discharge states of the positive and negative electrodes, raise the working voltage of the MH/MnO_2 cell, and prevent the formation of Mn_3O_4. In this study, according to the XRD results on the formatted MnO_2 electrode, greater advantage is proven by the addition of $Ni(OH)_2$ to the MnO_2 electrode. The XRD results show an obvious peak of γ-NiOOH. The formation of γ-NiOOH is associated with the volume expansion of the cathode in the MH/MnO_2 rechargeable cell as discussed in the previous section. However, the existence of a small amount of γ-NiOOH can stabilize the MnO_2 lattices due to an isomorphic effect because γ-NiOOH and MnOOH are isomorphous substances [9]. The phase transformation of $\gamma\text{-NiOOH} \rightarrow \beta\text{-Ni(OH)}_2$ may occur only on discharge [10], but the β(II)-phase produced from this reduction was found to preserve the textural features of its precursor γ(III)-phase. Thus, the isomorphic effect always existed during charge/discharge cycles.

3.4. *Influence of the charging regime*

The previous charging method of the MH/MnO_2 cell was to charge the cell at 1.55 V for 12 h, which unavoidably led to overcharge. Mn(VI) may be produced first and then Mn_3O_4 is formed during consequent cycling. Overcharge leads to the generation of O_2 and, therefore, to electrolyte loss. Moreover, the overcharge may promote the production of γ-NiOOH and the volume expansion of the MnO_2 electrode. Figure 4 shows the influence of the charging regime on the discharge curves. It can be seen that the cell with the modified charging regime had a better performance; its discharge capacity can be 3.5 A h after 180 cycles, while that of the cell without modification of its charging regime delivered only 2.2 A h.

4. Conclusion

The following can now be stated:

(i) Improvements in the cell construction and the separator can prevent the separator and the anode surface from 'drying-out', which results from the volume expansion of the electrode and gas emission.

(ii) Improvements in the charging regime and the formation procedure can prevent overcharging of the MH/MnO_2 rechargeable cell, relieve the capacity loss, and thus improve the battery performance.

(iii) Seven steps with a multicycle formation procedure can match the anodic discharged state with the cathodic charged state perfectly, and prevent the MH electrode deteriorating during formation.

(iv) The use of a laminated separator can provide good capability of electrolyte absorption and strong mechanical strength.

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