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# Gas Consumption Reactions and Cycling Characteristics of Improved Sealed Ni-Cd Batteries

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Conventional sealed Ni-Cd cells were improved for high-rate applications by mixing metal hydride (MH) alloy powder with Cd/CdO active materials. Experimental results demonstrated that the presence of MH alloy powder, such as $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$, improves the performance of conventional Ni-Cd cells as they are capable of consuming hydrogen and catalysing the recombination reactions of hydrogen and oxygen by both chemical and electrochemical routes. As a result, the safety of Ni-Cd batteries is significatly enhanced, particularly when they are operated under high-rate charge/discharge processes. The addition of MH alloy powder also slows down the capacity fade rate and extends the operation lifetime.

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**Keywords:** Ni-Cd battery; Internal pressure; Gas consumption reactions; Metal hydride; Cycling characteristics

## 1. INTRODUCTION

In past decades, Ni-Cd batteries have played an important role in the rechargeable battery market. Their ability to perform at high rates, whilst maintaining a long cycle lifetime and being able to operate in a broad range of temperatures has given them a considerable advantage over other conventional available batteries [1-7]. For this reason, Ni-Cd batteries have been extensively utilized in a vast range of applications [8-12]. It reports that over 1.5 billion Ni-Cd batteries have been produced annually since 2000 [13]. So researchers are still making a large amount of efforts to improve their safety [14, 15], memory effects [16, 17] and environmental compatibility [18, 19]. The basic principle of the sealed Ni-Cd battery is the realization of the so-called "oxygen cycle" by the "positive-electrode-limited" capacity during the stage of overcharge [20-22]. However, hydrogen can possibly evolve within the sealed cell under either of the following circumstances [14]: (1) When the potential of the negative electrode or local potential of some part of the negative electrode is polarized to a value more negative than the hydrogen evolution potential as the result of high rate of charging or overcharging; (2) When the ratio of the amounts of electro-active materials contained in the positive and the negative electrodes is improper (i.e., capacity of the cell is not “positive-electrode-limited”, as the result of improper cell design or faster degradation rate of the negative electrode); (3) When there is a mismatch between the “state-of-charge” of the negative electrode and that of the positive electrodes (as the results of unbalanced loss of electro-active materials or irreversible redox processes such as corrosion of the electrode or current collector, oxidation of separator or a constituent in the electrolyte, etc.). What would happen if some hydrogen is generated at the negative electrode during the charge/overcharge process? Lee and his coworkers [23, 24] reported that the rate of hydrogen oxidation at the positive electrode (namely NiOOH) is usually a relatively slow process, at least two orders of magnitude slower than the normal rate of the charging process. After N. Sac Epée and his coworkers [25, 26] investigated the interactions between hydrogen and β, γ-NiOOH phases, they found that the possible hydrogen consuming reactions include (i) the direct oxidation of hydrogen by γ-phase NiOOH and (ii) electrochemical catalytic oxidation of hydrogen at the positive electrode, but the hydrogen oxidation rate is very slow and corresponds with the self-discharge rate. In principle, if hydrogen evolution takes place in sealed Ni-Cd batteries, it will accumulate and result in a high internal pressure. The internal pressure accumulation is a serious problem for battery safety, which is known to be the main cause for cell leaking, cracking or exploding. Yang and coworkers [27] explored the possible use of ferrocyanide as a redox additive for the prevention of electrolyte decomposition in overcharged nickel batteries. However the addition of ferrocyanide in electrolyte may deteriorate the self-discharge of battery. Masahiko reported that hydrogen occlusion alloy could improve quick-charge characteristics and capacity of Ni-Cd batteries [28]. In our previous studies [14], we found that only oxygen can be consumed at the negative electrode of the sealed Ni-Cd battery, while the negative electrode of the Ni-MH battery possesses the additional ability to consume hydrogen and catalyse the recombination reaction of hydrogen and oxygen.

In this paper, we have attempted to improve conventional Ni-Cd batteries for high-rate applications by combining the unique advantages of sealed Ni-Cd and Ni-MH batteries. The experimental results for improved sealed Ni-Cd cells when charged or overcharged at high currents are also presented.

## 2. EXPERIMENTAL

### *2.1. Preparation of improved Ni-Cd cells*

The improved AA-type Ni-Cd cells (nominal capacity 700 mAh) were prepared in Hunan Corun Hi-Tech Co. Ltd (Hunan, China) by mixing Cd/CdO powder, metal hydride (MH) alloy $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ powder, acetylene black and polytetrafluoroethylene (PTFE). In comparison to production processes of conventional Ni-Cd cells, 15% w/w of Cd/CdO powder was replaced by MH powder for the improved Ni-Cd cells. The resulting cells were formatted by the following activation scheme: Step 1: Cells were charged at 0.1C for 300 minutes, then stored at 45 $^{o}$C for 24 hours; Step 2: Cells was charged at 0.2C for 300 minutes, rested for 10 minutes, and then discharged at 0.2C down to 1.0V; Step 3: Cells was charged at 0.5C for 150 minutes, rested for 10 minutes, and then discharged at the current of 0.5C down to 1.0V. This step was repeated 5 times.

### *2.2. Internal pressure measurements*

A specially designed set-up was employed for gas pressure measurements in the sealed battery system [14, 27]. The basic unit comprised a stainless steel pressure container, which can host an AA-sized testing cell. The container was also equipped with a pressure sensor. Prior to enclosing the cell in the pressure container, the top of the cell was removed.

### *2.3. Charge/discharge cycling*

A computer-controlled Neware battery testing system (Guangdong, China) was employed to control the cycling experiments. The gas pressure, charging/discharging battery voltages and currents were recorded at 1 minute intervals. All experiments were performed at room temperature.

## 3. RESULTS AND DISCUSSION

### *3.1. Influence of MH alloy on the inner pressure of Ni-Cd cells*

Figure 1 shows typical profiles of internal pressure changing over time when conventional and improved Ni-Cd cells were charged at 2C for 60 minutes, rested for 300 minutes and then discharged at 0.5C down to 1.0V. The results clearly indicated that the internal pressures remain negligible in both systems during the initial charging period, but start to increase when the charging process is almost completed and then rise rapidly in a short time. The internal pressure in the conventional cell attains 2.3 MPa at the end of overcharge process, whereas the internal pressure in the improved cell only attains 1.6 MPa, approximately equivalent to 70% of the former. After rested for 300 minutes, the internal pressure in the conventional cell remains at 1.0 MPa (about 43% of its maximum), while that value in the improved cell reduces to 0.1 MPa (about 6% of its maximum). After the discharge stage, the internal pressure in the conventional Ni-Cd cell is maintained and remains at this value for a long period of time. For the improved cell, the internal pressure returns to the initial value. The different behaviors in the two systems can be attributed to the hydrogen evolution during charge and overcharge process [14]. As it is well understood that nothing can effectively adsorb hydrogen or catalyze the recombination reaction of hydrogen and oxygen in a conventional Ni-Cd battery [21-24], the evolved hydrogen cannot be reduced promptly [25, 26]. After hydrogen storage alloy powder is mixed into the negative electrodes of conventional batteries, it significantly improves the gas consumption process in a sealed Ni-Cd cell.

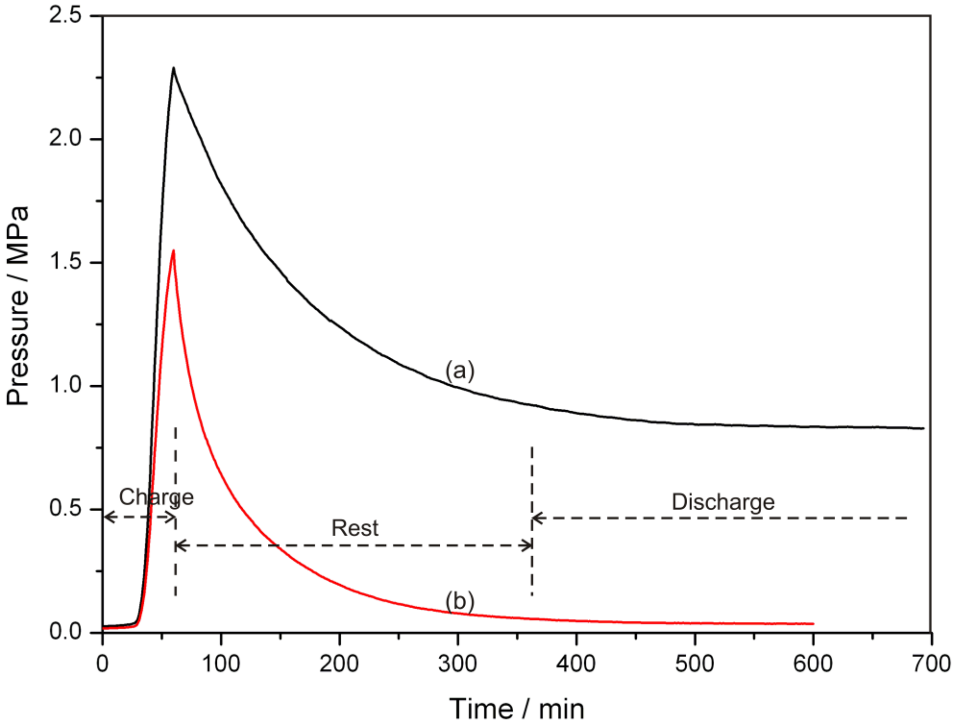

**Figure 1**. The profiles of changes of internal pressure over time when the conventional (a) and improved (b) Ni-Cd cells were charged at 2C for 60 minutes, rested for 300 minutes and then discharged at 0.5C down to 1.0 V.

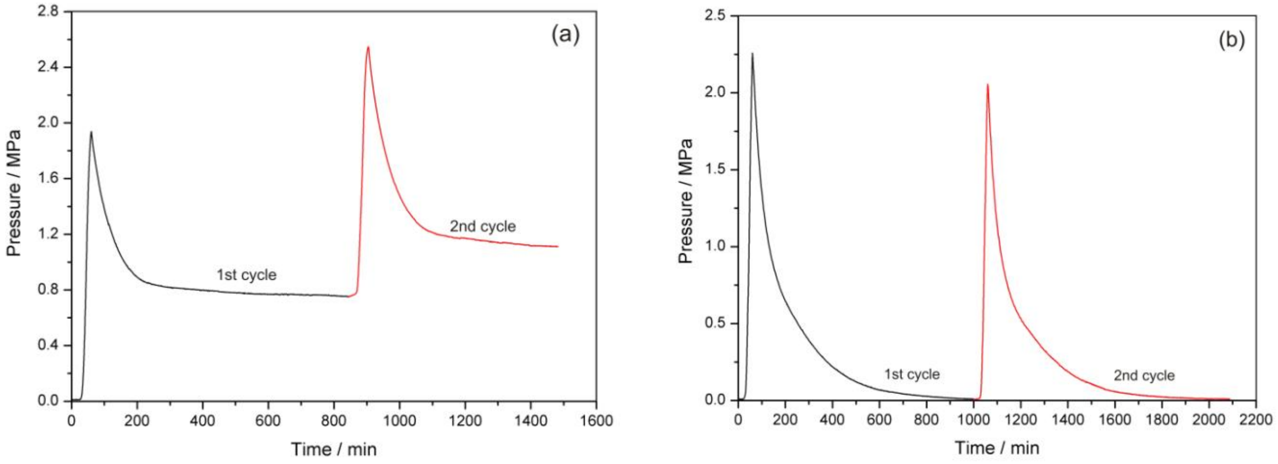

**Figure 2**. Changes of internal pressure over time when the conventional (a) and the improved (b) Ni-Cd cells were cycled at the following regime: charged at 2C for 60 minutes, then rested for 300 minutes and discharged at 0.5C down to 1.0 V.

Figure 2 shows the changes of internal pressure over time when the conventional and improved Ni-Cd cells were cycled. We can see that for the conventional cell, the peak and residual pressure are 2.0 MPa and 0.75 MPa respectively in the first cycle. In the second cycle, both peak and residual pressures get larger, reaching 2.5 MPa and 1.25 MPa respectively. In contrast, the changes of internal pressure in the improved cell are quite different. The residual pressures returns to their initial values although the peak pressures attain 2.25 MPa and 2.0 MPa in both cycles. Obviously the internal pressure accumulates with cycling in conventional cells, but the "accumulation effects" does not occur in improved Ni-Cd cells. As a result, the introduction of metal hydride alloy remarkably improves the safety of Ni-Cd cells, especially when operated under high-rate overcharge/discharge processes. Overall, the experimental results have demonstrated the ability of improved Ni-Cd cells to consume the hydrogen gas evolved under charge/overcharge processes.

### *3.2. Analysis of gas consumption reactions in improved Ni-Cd cells*

In order to understand how the metal hydride alloy powder helps consume the internal gases, we investigated the possible gas consumption reactions by modifying conventional Ni-Cd cells. Figure 3 shows the profile of changes of internal pressure during charge/discharge process after a piece of activated MH electrode foil ($10\times10\times0.3$ mm$^3$) was inserted into a conventional Ni-Cd cell and contacted with the Cd/CdO electrode. The activated MH electrode foil was taken from an activated Ni/MH cell. At the initial stage, the internal pressure is very low, but increases rapidly after the charging process is almost completed. After rested for 300 minutes, the internal pressure reduces to 0.05 MPa, equivalent to approximately 3.5% of its maximum. After the discharge process, the internal pressure further reduces to a value close to its initial value prior to charging. The results clearly indicated that the modified cell exhibits the similar gas consumption behaviors as the improved Ni-Cd cells.

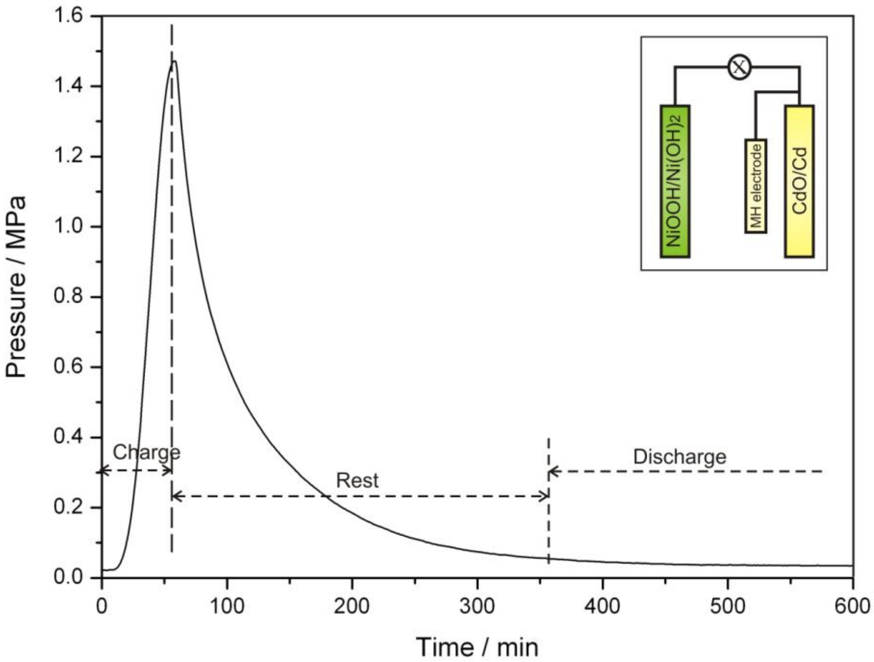

**Figure 3**. The profile of changes of internal pressure over time when a modified conventional Ni-Cd cell was charged at 2C for 60 minutes, rested for 300 minutes and then discharged at 0.5C down to 1.0 V. Inset: Schematic electrode connection in the modified conventional Ni-Cd cell.

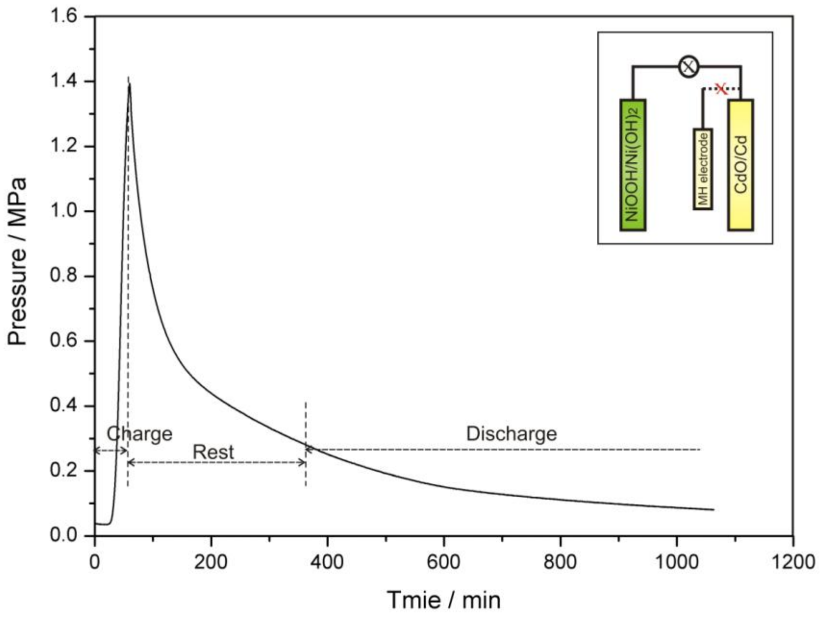

**Figure 4**. The profile of changes of internal pressure over time when the sealed Ni-Cd cell with a isolated alloy electrode was charged at of 2C for 60 minutes, then rested for 300 minutes and discharged at 0.5C down to 1.0 V. Inset: Schematic electrode connection in the modified conventional Ni-Cd cell.

Figure 4 shows the typical profile changes of internal pressure over time when a Ni-Cd cell modified with a piece of isolated MH alloy electrode foil was charged at 2C for 60 minutes, rested for 300 minutes and then discharged at 0.5C down to 1.0V. Since the alloy electrode foil did not contact with the Cd/CdO negative electrode, electrochemical reactions cannot occur at the alloy electrode. As shown in Fig. 4, the internal pressure still remains about 21% of its maximum after rested for 300 minutes. Compared to the changes of internal pressure shown in Fig 1, the attenuation rate of internal pressure is much greater than that observed in a conventional Ni-Cd cell, but slower than that in an improved Ni-Cd cell. Importantly, the internal pressure in the Ni-Cd cell modified with a piece of isolated MH alloy foil could eventually return to the initial value after discharge, but this does not occur in a conventional cell. The presence of a separated alloy electrode can improve the gas consumption process in the sealed system, but the gas consumption rate is slower than that in an improved cell. Thus we infer that some gas consumption reactions must chemically take place in this sealed system besides the oxygen cycling reaction [14, 27]. The possible gas consumption reactions in this sealed system are expressed as follows:

(1) reduction of oxygen at the negative electrode;

$$O_2+2Cd+2H_2O\longrightarrow 2Cd(OH)_2 \quad (1)$$

(2) hydrogen adsorption by the unsaturated hydrogen storage alloy;

$$2M+H_2 \rightarrow 2MH \quad (2)$$

and (3) the oxygen reacts with the metal hydride alloy.

$$4MH+O_2 \longrightarrow 4M+2H_2O \quad (3)$$

The overall reaction for (2) and (3) at the separated alloy electrode is

$$2H_2+O_2 \xrightarrow{MH} 2H_2O \quad (4)$$

Compared to conventional Ni-Cd cells, the cell modified with an isolated alloy electrode has the ability to consume hydrogen and catalyse the recombination reaction of hydrogen and oxygen by chemical routes. In order to further investigate the possible electrochemical gas consumption reactions in the improved Ni-Cd battery, a piece of alloy electrode was inserted in between the positive and negative electrodes of a conventional cell without contact to these two electrodes. However the connecting wire of the alloy electrode was leaded to outside of the pressure container. The Ni-Cd cell was charged at 2C for 60 minutes and first rested for 120 minutes. The alloy electrode was then connected to the negative electrode. After rested for 180 minutes, it was discharged at 0.5C down to 1.0 V. Figure 5 demonstrates the changes of internal pressure over time in this sealed system. By comparison with the changes of internal pressure shown in Fig. 4, we can observe an inflexion at 180 minutes. The attenuation rate of internal pressure becomes faster after this point, indicating that the gas consumption rate has increased. As a result, we believe there must be an extra gas consumption reaction occurring by electrochemical routes.

The equilibrium potential of $Cd/Cd(OH)_2$ is –0.81 V (vs. SHE) [14], slightly more positive than that of $MH/H_2O$ –0.83 V (vs. SHE) [11, 29], which provides the thermodynamical possibility to consist of a local primary cell. In fact, current could be observed during the rest period if an amperemeter was connected in series with the Cd negative electrode and the alloy electrode (here the positive terminal of the amperemeter was connected to the Cd electrode), indicating that the electrochemical reactions were occurring on the alloy electrode and the Cd electrode. Herein the Cd electrode acts as the positive electrode and the alloy electrode as the negative electrode in the local “cell” [30]. Thus the possible gas consumption reactions can be expressed as follows [14]:

(1) hydrogen adsorption by the unsaturated hydrogen storage alloy;

$$2M+H_2 \rightarrow 2MH \quad (5)$$

(2) then the alloy and the Cd electrode construct a primary cell. The electrode reactions can be described as

$$2MH+2OH^{-}-2e \rightarrow 2M+2H_2O \quad (6)$$

$$Cd(OH)_2+2e \rightarrow Cd+2OH^{-} \quad (7)$$

Accordingly, the overall battery reaction for (6) and (7) is:

$$2MH+Cd(OH)_2 \rightarrow 2M+2Cd+2H_2O \quad (8)$$

By combining the reaction (5) and (8), the following reaction may be obtained, which can unlikely take place in conventional sealed Ni-Cd cells.

$$H_2+Cd(OH)_2 \rightarrow Cd+2H_2O \quad (9)$$

Obviously after MH alloy electrodes are introduced into conventional sealed Ni-Cd cells, the evolved gases (especially hydrogen) can be consumed by both chemical and electrochemical routes.

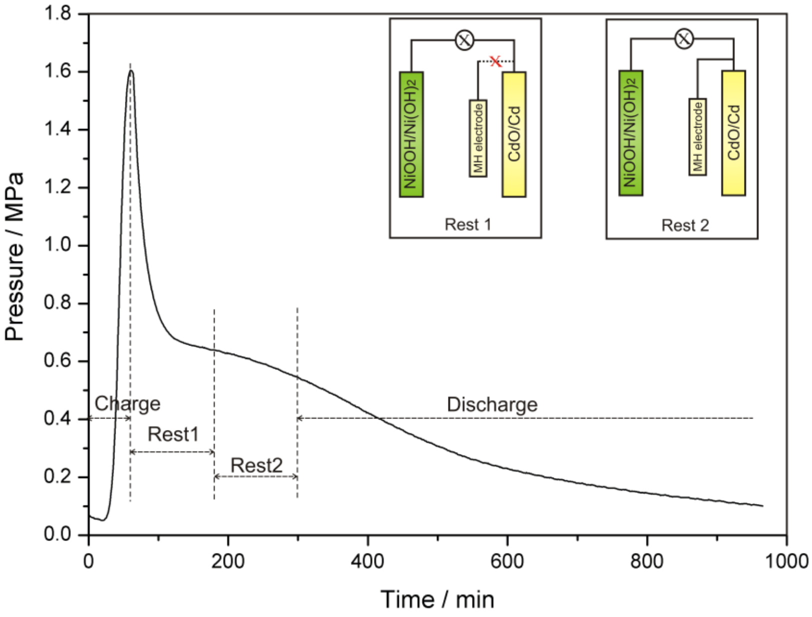

**Figure 5**. The profile of changes of internal pressure over time when a modified Ni-Cd cell with a separated alloy electrode was charged at 2C for 60 minutes, and first rested for 120 minutes. Then the alloy electrode was connected to the negative electrode. After rested for 180 minutes, the cell was discharged at 0.5C down to 1.0 V. Inset: Schematic electrode connection in the modified conventional Ni-Cd cell.

### *3.3. The cycling characteristics of the improved Ni-Cd cells*

After conventional Ni-Cd batteries were improved by introducing metal hydride alloy, it is important to investigate their cycling characteristics. The discharge capacities of the conventional and improved Ni-Cd cells as a function of the cycle number are shown in Fig. 6. Both of the initial discharge capacities are higher than the nominal capacity (700 mAh). The initial capacity is about 750 mAh for the conventional cell, but the discharge capacity has decreased to only 690 mAh at the 150th cycle, about 92% of the initial capacity. Compared to the cycling characteristics of the conventional cell, the discharge capacity of improved cell still keeps 720 mAh at the 150th cycle, about 98% of its initial capacity. Obviously, the improved cell shows a slower capacity fade rate. Figure 7 shows the charge/discharge voltage curves of the conventional and improved cells at the 150th cycle. According to the figure, the charge/discharge polarization in the improved Ni-Cd cell is smaller than that of the conventional cell. The possible reason may be that the presence of MH alloy improves the gas evolution and consumption process in the sealed system, which slows down the degradation of electrode microstructures, therefore enhancing the lifetime performance of Ni-Cd batteries.

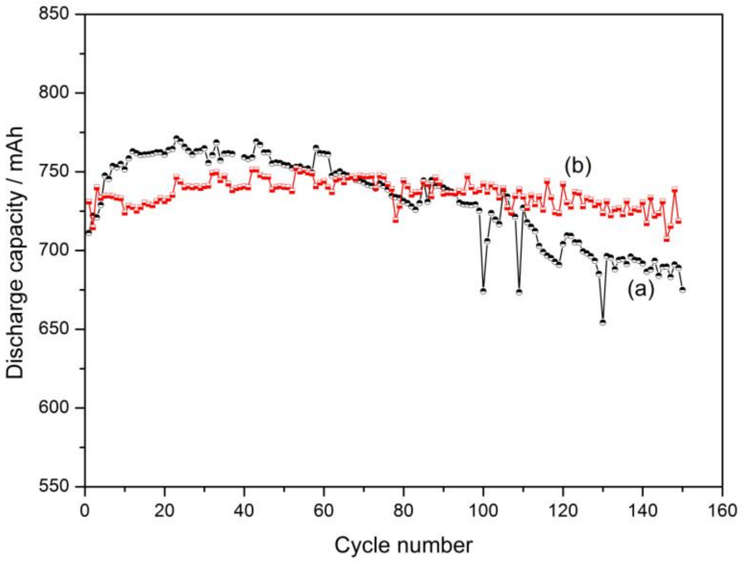

**Figure 6**. Cycling characteristics of the conventional (a) and improved (b) Ni-Cd cells. Ni-Cd cells were charged at 1C for 72 minutes and discharged at 1C down to 1.0 V.

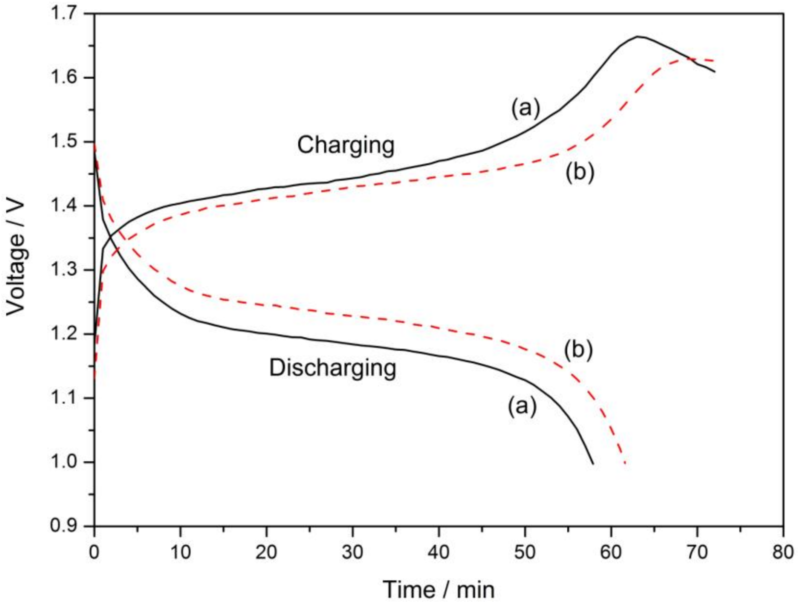

**Figure 7**. The charge/discharge voltage curves of the conventional (a) and improved (b) Ni-Cd cells at the 150th cycle.

## 4. CONCLUSIONS

The addition of hydrogen storage alloy powder is an effective approach to improve the gas consumption process in sealed Ni-Cd batteries and raise the safety especially under high-rate charge/discharge applications. Moreover the presence of MH alloy powder can slow down the capacity fade rate and extend the operation lifetime.

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