

Comparative experimental study of gas evolution and gas consumption reactions in sealed Ni–Cd and Ni–MH cells

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Abstract

The behavior of the sealed Ni–Cd and Ni–MH systems are compared experimentally with regard to their ability to consume gaseous products generated during the overcharge stage of these systems. It was found that the Ni–Cd system could only consume oxygen, while the Ni–MH system possesses the additional ability to adsorb hydrogen and to catalyze the recombination reaction of hydrogen and oxygen. The internal pressure within both sealed Ni–Cd cells and sealed Ni–MH cells can be kept well under control during the charge/overcharge processes if the rate of overcharge is not too high and if there is sufficient surplus of charging capacity at the negative electrodes. However, the internal pressure can rise to dangerously high levels if the rate of overcharge is too high or there is a deficiency of the charging capacity at the negative electrodes. The various factors that may affect the surplus of charging capacity of the negative electrodes are also discussed. © 2003 Elsevier B.V. All rights reserved.

Keywords: Sealed Ni–Cd cell; Sealed Ni–MH cell; Gas generation; Gas consumption; Battery overcharge

1. Introduction

There are five main types of aqueous secondary cells, namely, the Ni–Fe, Ni–Cd, Ni–MH (metal hydride), Ni–Zn and Pb–acid batteries. No serious attempt has ever been tried to seal the Ni–Fe battery, apparently due to the high rate of self-discharge of the negative electrode and the vigorous gas evolution reactions accompanying the charge and overcharge processes of this type of secondary battery. The Ni–Zn and Pb–acid batteries can only be designed to operate as “valve-regulated”. The valve-regulated battery performs mainly as a sealed battery, but its design would allow occasional purge of gas from the battery when the internal pressure exceeds a certain threshold. Only the Ni–Cd and Ni–MH systems are available as completely sealed aqueous secondary batteries.

One of the basic design principle for both the valve-regulated and the completely sealed batteries is the realization of the so-called “oxygen cycle” during the stage of overcharge of the battery. Thus, the relative amounts of electro-active materials employed in the fabrication of the positive and the negative electrodes are usually so adjusted that the charge–discharge capacity of the battery is

“positive-electrode-limited”. Oxygen starts to evolve at the positive electrode in the late stage of charging when the normal charging process of the negative electrode is still going on. Then the oxygen evolved at the positive electrode is transferred through the gas phase and electrolyte phase to reach the negative electrode and reduced to hydroxyl ion or water to complete the “oxygen cycle”, leaving the composition of the battery practically unchanged during the overcharging process.

However, situations would become drastically complicated if hydrogen were produced within the sealed cell, either as the product of self-discharge of the negative electrode or as the by-product of the charging reaction of the negative electrode. A vast amount of experimental evidences obtained from direct reaction rate measurements by micro-calorimetric [1,2], XRD/TEM [3] and electrochemical [4] techniques, together with huge amount of experiences accumulated in works associated with Ni–H₂ batteries [5] and Pb–acid batteries [6], clearly indicates that the rate of oxidation of hydrogen at the positive electrode (NiOOH or PbO₂) is usually a relatively slow process, at least two orders of magnitude slower than the normal rate of the charging process. Therefore, the prerequisite for the successful construction of a completely sealed aqueous secondary battery system would be that at least one of the following two circumstances could be realized within the sealed cell:

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- (1) very slow rate of hydrogen production at the negative electrode, including both self-discharge reaction of the negative electrode and hydrogen production as by-product of the charging process;
- (2) hydrogen produced at the negative electrode can be consumed effectively within the cell.

Apparently neither of these two circumstances can be effectively realized within the Ni–Zn and Pb–acid cells, so these two types of aqueous secondary batteries can only be designed as “valve-regulated”, not completely sealed.

In this paper, we are going to show the results of experimental studies concerning what normally happens in sealed Ni–Cd and Ni–MH cells, and what may happen when something goes wrong.

2. Experimental

In the literature, the gas generation and gas consumption reactions within sealed cells were usually studied by placing a punctured cell in a specially designed autoclave, equipped with pressure sensor and means of withdrawing gas samples from the free space above the punctured cell. The variation of pressure during the charge–discharge processes is monitored with the pressure sensor, and often the composition change of the gas phase also monitored by GC analysis of gas samples intermittently withdrawn from the autoclave [7,8]. Results obtained from such experiments are in general informative. Nevertheless, with such type of experimental set-ups it is not easy, and sometimes even impossible, to calculate the rates of evolution and consumption of individual gas species from experimental data. Therefore, we tried to improve the situation by adding a third electrode, the gas-evolving electrode, to the conventional experimental system.

The experimental set-ups employed in our works are schematically shown in Figs. 1 and 2. The basic unit is a stainless steel pressure container, which can just host an AA-sized cell. The container is equipped with a pressure sensor. A nickel foam foil (20 mm × 5 mm × 0.1 mm) is inserted in between the positive and negative electrodes of the cell to serve as a gas-generating auxiliary electrode, which is connected in parallel with the negative electrode of the cell. The charging/discharging current passing through the negative electrode (I_1) and that passing through the auxiliary electrode (I_2) can be adjusted and recorded separately (see Fig. 2); and the current passing through the positive electrode is the sum of I_1 and I_2 . The only cathodic process that could take place effectively at the auxiliary electrode is the hydrogen evolution reaction:

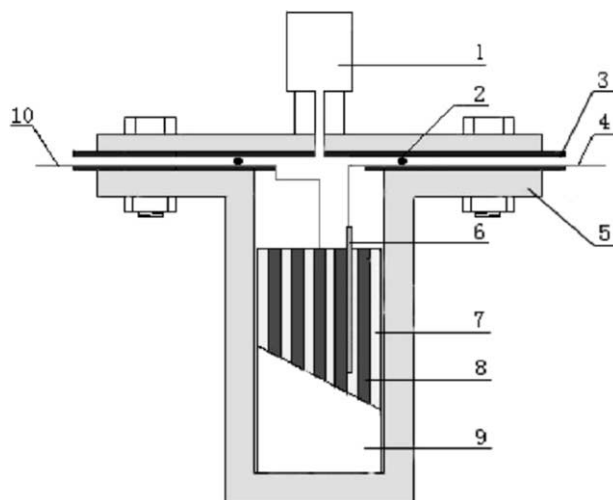
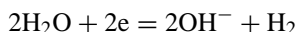


Fig. 1. Pressure container for testing AA-sized cell. (1) Pressure sensor, (2) O-ring, (3) cushions, (4) connecting wire to the gas-evolving (“third”) electrode, (5) stainless steel cylinder, (6) the gas-evolving electrode, (7) negative electrode, (8) positive electrode, (9) the punctured AA-sized cell (the cell can serve also as connection to the negative electrode) and (10) connecting wire to the positive electrode.

Therefore, the auxiliary electrode serves as a hydrogen injection electrode, and the rate of hydrogen injection can be accurately controlled by adjusting I_2 .

AA-type Ni–Cd (nominal capacity 700 mAh) and Ni–MH (nominal capacity 1200 mAh) cells used in our studies were kindly donated by B.Y.D. Battery Co. (Shenzhen, Guangdong) and J.J.J. Battery Co. (Jiangmen, Guangdong). These batteries were subjected to a few 0.1–0.2 C charge–discharge cycles to verify their normal capacities and behavior before employed in experimental studies. Either the top of the cell was removed or a small hole was drilled at the top of the cell before the cell was placed in the pressure container.

A computer-controlled battery testing system (manufactured in Guangdong, China) was employed to control the experiments. The pressure within the pressure container, the cell voltage, and the currents I_1 and I_2 were recorded every minute. All experiments were performed at room temperature.

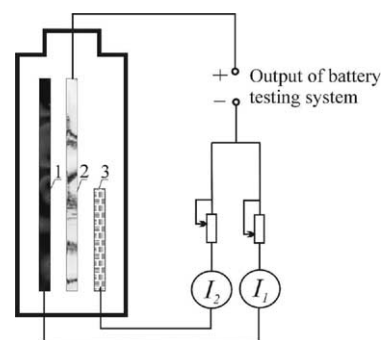


Fig. 2. Schematic circuit for testing. (1) Negative electrode, (2) positive electrode and (3) the gas-evolving (“third”) electrode.

3. Results and discussion

3.1. Ni–Cd cells

Fig. 3 shows the typical profile of changes of internal pressure with time when a Ni–Cd cell is charged and then overcharged with different charging current. The internal pressure remains negligible during the initial period of charging, but it starts to increase when the charging process is almost completed, and then shoots up rapidly to reach a limiting value (P_{\max}) which is a linear function of the charging current (see cut in Fig. 3).

If we assume that the current efficiency of oxygen evolution at the positive electrode is 100% in stage of overcharge and the rate of consumption of oxygen is a first-order reaction with respect to the partial pressure of oxygen (P_{O_2}), then the variation of P_{O_2} with time must be related to the difference between the rate of oxygen generation at positive electrode and the rate of oxygen consumption at negative electrode, so it can be written as [9]

$$\frac{dP_{O_2}}{dt} = A_0I - k_O P_{O_2} \quad (1)$$

in which I is the overcharging current, A_0 is a constant derived from the Faraday constant and volume of free space within the pressure container, and k_O is directly proportional to the kinetic rate constant of oxygen consumption.

When the steady-state of internal pressure has been reached, $dP_{O_2}/dt = 0$ and $P_{O_2}(\text{MPa}) = P_{O_2\max} = P_{\max} - 0.08 = A_0/k_O$, (P_{\max} is the maximum total pressure, and 0.08 MPa is the partial pressure of nitrogen), so Eq. (1) can

be transformed to

$$\frac{dP_{O_2}}{dt} = k_O(P_{\max} - 0.08 - P_{O_2}) \quad (2)$$

from which we obtain

$$\ln(P_{\max} - 0.08 - P_{O_2}) = -k_O t + \text{constant} \quad (2a)$$

or

$$\ln(P_{\max} - P_i) = -k_O t + \text{constant} \quad (2b)$$

in which $P_i = P_{O_2} + 0.08$, is the total pressure inside the cell container.

Similarly, the attenuation of internal pressure after cut-off of overcharging current can be written as

$$-\frac{dP_{O_2}}{dt} = k_O P_{O_2} \quad (3)$$

from which we obtain

$$\ln P_{O_2} = -k_O t + \text{constant} \quad (3a)$$

or

$$\ln(P_i - 0.08) = -k_O t + \text{constant} \quad (3b)$$

Eqs. (2b) and (3b) indicate that both $\ln(P_{\max} - P_i)$ (in stage of overcharge) and $\ln(P_i - 0.08)$ (after cut-off of overcharging current) should be linear function of time. Examples of such linear relationships found in experiments are depicted in Fig. 4a and b, which clearly suggest that the oxygen consumption reaction is kinetically a first-order reaction. The slightly different values of the slopes of these curves are apparently due to difference of cell temperature after the cell

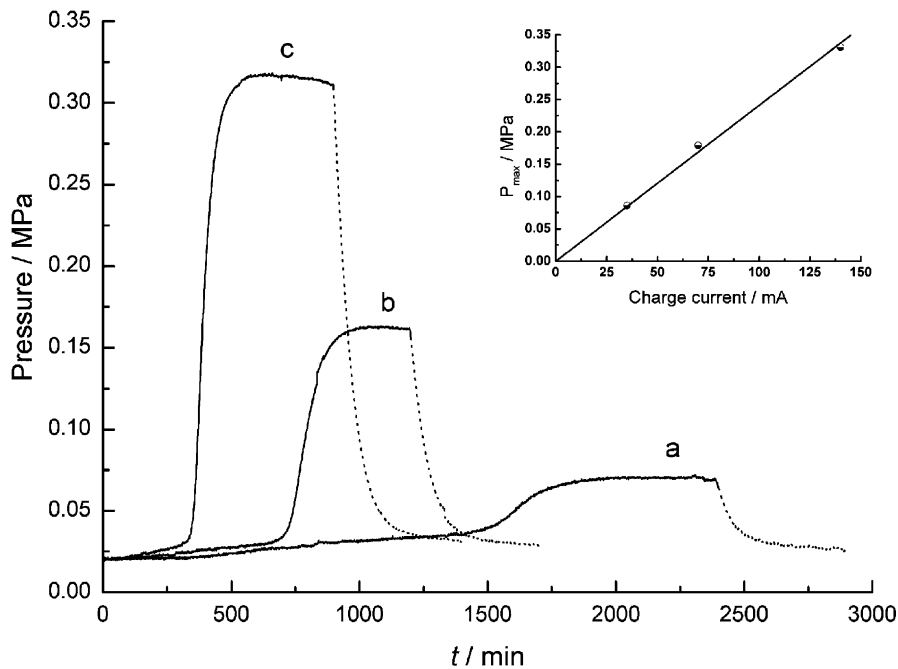


Fig. 3. Variation of internal pressure in a 700 mAh sealed Ni–Cd cell during charge/overcharge and after cut-off of the charging current (I). (a) $I = 35$ mA (0.05 C); (b) $I = 70$ mA (0.1 C); and (c) $I = 140$ mA (0.2 C).

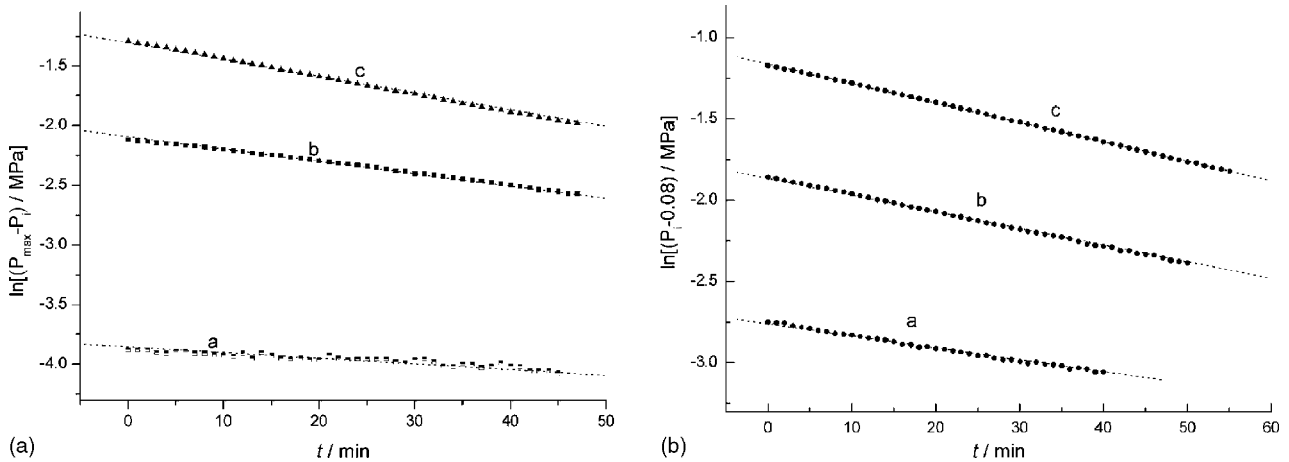


Fig. 4. Logarithmic analysis of internal pressure variations with time shown in Fig. 3. (a) During overcharge; and (b) after cut-off of charging current.

was subjected to different rate of overcharge. The higher the rate of overcharge, the higher the cell temperature and the higher the rate constant of gas consumption.

These experimental results seem to verify that, in case of sealed Ni–Cd cells, the ideal oxygen cycle mechanism can actually be realized quite satisfactorily when these cells are subjected to low-rate overcharge. Besides, the limiting P_{\max} values were found to be not too high and the attenuation of internal pressure rather sufficiently rapid after cut-off of charging current, indicating satisfactory rapid kinetic rates of the oxygen-consuming reaction within the sealed Ni–Cd cells.

However, all the above-stated experimental results were obtained with well-designed new cells and relatively slow rates of charge/overcharge (0.05–0.2 C). What would happen if some hydrogen were generated at the negative electrode during the charge/overcharge process? In principle, evolution of hydrogen may take place within the sealed cells under either of the following circumstances:

- (1) when the potential of the negative electrode or local potential of some part of the negative electrode is polarized to value more negative than the hydrogen evolution potential as the result of too high rate of charging (evidence will be presented in later section);
- (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 some constituent in the electrolyte, etc.).

In order to simulate the effect of hydrogen evolution at the negative electrode, hydrogen was injected amperometrically into the sealed cell by employing the auxiliary electrode shown in Fig. 2. Fig. 5 depicts the effects of hydrogen injection on the internal pressure of the sealed Ni–Cd cell in stage of overcharge. The internal pressure was found to shoot up almost linearly after start of hydrogen injection, and show no tendency of reaching a limiting value after 9 h. Besides, the internal pressure was found to attenuate very slowly after the cut-off of the charging current (compare with Fig. 3).

Fig. 5 can serve also as evidence for the almost ideal realization of oxygen cycle in the stage of normal overcharge of sealed Ni–Cd cells. If noticeable amount of hydrogen were produced during normal overcharging, there should be no limiting values of internal pressure on the P – t curves shown in Fig. 3. Besides, it is also clear from Fig. 5 that nothing

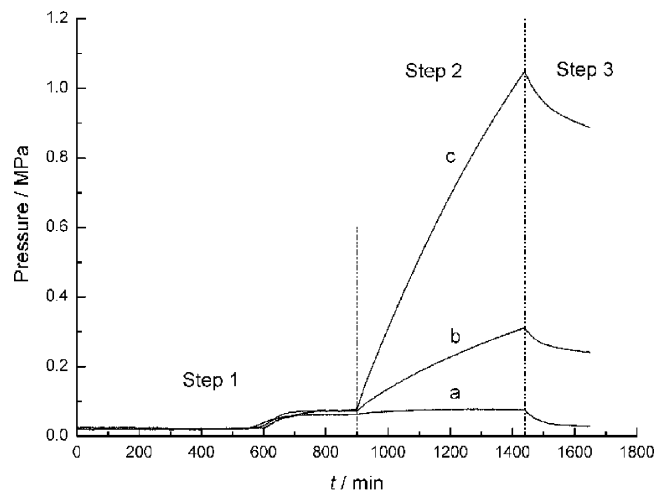


Fig. 5. Effects of hydrogen-injection on the internal pressure of sealed Ni–Cd cell. Step 1: normal charge/overcharge; step 2: effect of hydrogen injection, (a) $I_1 = 70 \text{ mA}$, $I_2 = 0$; (b) $I_1 = 70 \text{ mA}$, $I_2 = 10 \text{ mA}$; (c) $I_1 = 70 \text{ mA}$, $I_2 = 20 \text{ mA}$; and step 3: after cut-off of charging current.

within the sealed Ni–Cd system can effectively catalyze the recombination reaction of hydrogen and oxygen, since apparently no gas consuming reaction happened when hydrogen was injected into an oxygen-rich environment.

These experimental results show unambiguously that the consumption of hydrogen within a well-charged sealed Ni–Cd cell is actually a slow process. Neither the electro-oxidation of hydrogen at the positive electrode nor the recombination of hydrogen with oxygen at some place within the sealed cell could serve as a sufficiently rapid path for the attenuation of hydrogen pressure within the sealed cell. Therefore, dangerously high internal pressure can be created within a sealed cell if noticeable hydrogen evolution reaction proceeds in parallel with the charging or overcharging processes. For example, if the capacity of the sealed cell were erroneously designed to become “negative-electrode-limited”, sharp increase of internal pressure would take place after the completion of the charge of the negative electrode.

Fig. 6 shows the results obtained with a normal Ni–Cd cell from which a part of the negative electrode has been removed to make the capacity of the cell “negative-electrode-limited”. After the completion of the charging process of the negative electrode, the cell pressure starts to increase linearly with time due to the evolution of hydrogen at the completely negative electrode and accumulation of hydrogen in the free space within the cell container. In this “first stage” of overcharge, $dP_{H_2}/dt = A_H I$.

However, the rate of pressure increase starts to slow down after the completion of the charging process of the positive electrode. In this stage (“second stage”) of overcharge, oxygen evolves at the fully charged positive electrode and a part of it becomes reduced at the negative electrode. Therefore, the cathodic current is consumed in two different processes:

$$\text{oxygen reduction : } I_{O_2, \text{redn}} = k' P_{O_2} \quad (1)$$

$$\text{hydrogen evolution : } I_{H_2, \text{evoln}} = I - I_{O_2, \text{redn}} = I - k' P_{O_2} \quad (2)$$

in which $k' = k_O/A_O$, and the rates of hydrogen and oxygen partial pressure increase can be express as:

$$\frac{dP_{H_2}}{dt} = A_H I_{H_2, \text{evoln}} = A_H (I - k' P_{O_2}) \quad (4a)$$

and

$$\frac{dP_{O_2}}{dt} = A_O (I - I_{O_2, \text{redn}}) = A_O (I - k' P_{O_2}) \quad (4b)$$

therefore

$$\frac{(dP_{H_2}/dt)}{(dP_{O_2}/dt)} = \frac{A_H}{A_O} = 2 \quad (4c)$$

The solutions of Eqs. (4a) and (4b) are:

$$P_{O_2} = P_{O_2, \text{max}} [1 - \exp(-kOt)] \quad (5a)$$

$$\begin{aligned} P_{H_2} &= P_{H_2}^0 + 2P_{O_2} \\ &= P_{H_2}^0 + 2P_{O_2, \text{max}} [1 - \exp(-kOt)] \end{aligned} \quad (5b)$$

$$\begin{aligned} P_i &= P_{H_2} + P_{O_2} + 0.08 \\ &= P_{H_2}^0 + 0.08 + 3P_{O_2, \text{max}} [1 - \exp(-kOt)] \end{aligned} \quad (5c)$$

and

$$P_{i, \text{max}} = P_{H_2}^0 + 0.08 + 3P_{O_2, \text{max}} \quad (5d)$$

In these equations $P_{O_2, \text{max}} = I/k' = A_O I/k_O$, t is measured from the time of completion of the charging process of the positive electrode; and at $t = 0$, $P_{H_2} = P_{H_2}^0$ and $P_{O_2} = 0$. Fig. 7 shows the theoretical $P-t$ plot for the overcharge stage of the “negative-electrode-limited” Ni–Cd cell. In the first stage of the process ($t < 0$), only hydrogen is introduced into the gas phase; while in the second stage of the process ($t > 0$), equivalent (2:1) mixture of oxygen and hydrogen are produced (Eq. (4c)). When steady-state of overcharge has been reached, $dP_{H_2}/dt = dP_{O_2}/dt = 0$, and from Eqs. (4a) and (4b) it is clear that $I_{H_2, \text{evoln}} = 0$ and $I_{O_2, \text{redn}} = I$, indicating that ideal oxygen cycle can still be

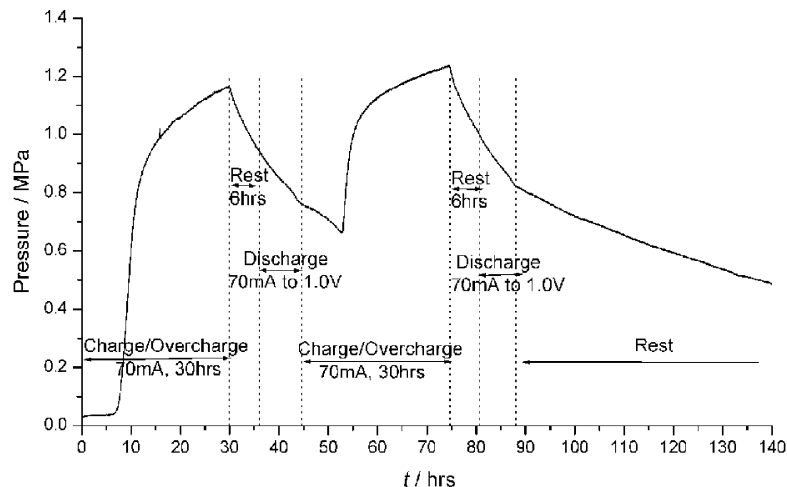


Fig. 6. Variation of internal pressure of a sealed AA-sized Ni–Cd cell from which a part of the negative has been removed.

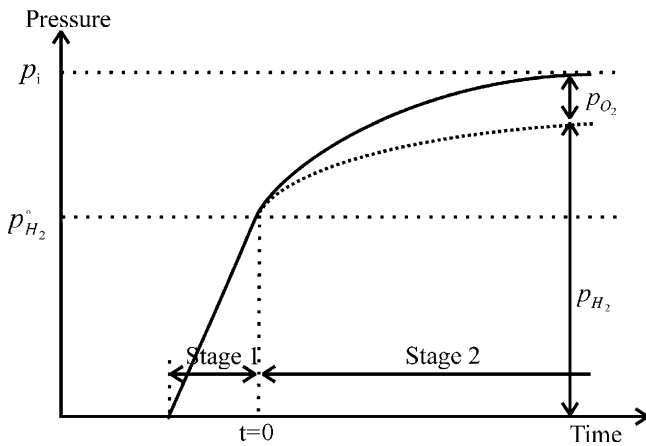
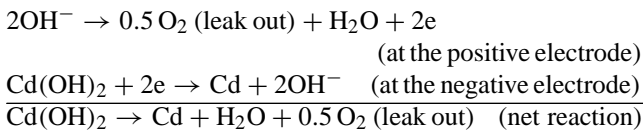


Fig. 7. Theoretical P_1-t curve of a “negative-electrode-limited” cell.

realized at steady-state of overcharge. However, since only oxygen can be effectively removed from the gas phase after the cut-off of the charging current, the attenuation of internal pressure within a “negative-electrode-limited” Ni–Cd cell after overcharge is a slow process, as shown in Fig. 6.

Another possible circumstance in the real world is the presence of micro-outlets (micro-cracks, micro-leaks, etc.) in the cell structure due to faulty design or manufacturing processes, so gas could slowly leak out from the inside of the sealed cell to environment. Leaking-out of oxygen would mean that the amount of reactant (oxygen) is insufficient to complete the oxygen cycle during the stage of overcharge, so the state-of-charge of the negative electrode has to increase (i.e., reduction of $\text{Cd}(\text{OH})_2$ to form more metallic Cd and water) gradually to compensate for the loss of oxygen:



The gradual increase of the state-of-charge of the negative electrode could only subside when hydrogen evolu-

tion starts to take place at the negative electrode. In other words, as the result of oxygen leak out, a properly designed “positive-electrode-limited” sealed cell could be transformed into a cell in which both the positive and negative electrodes can exist in the fully charged state when the cell is overcharged. By similar reasoning we could expect also that, if irreversible electro-oxidation of the separator or some constituents in electrolyte solution could take place at the positive electrode, their effects on the state-of-charge of the negative electrode would be similar to that of loss of oxygen. Apparently, under such circumstances the probability of hydrogen evolution would be significantly increased when the cell is subjected to overcharge, especially high-rate overcharge.

In order to simulate the effect of oxygen leaking on the behavior of Ni–Cd cells, a small hole was drilled on the top of the test cell before it was subjected to charge–discharge cycles. In Fig. 8 the charge–discharge voltage–time curves of the normal sealed cell are compared with that obtained with a punctured cell in open environment (i.e., not in pressure container). The most striking difference between these two sets of curves is that the punctured cell, after a deep overcharge–discharge cycle, exhibits sharp peak of charging potential at the beginning of next charging process. This seems to indicate that, as oxygen leaks out from the punctured cell, the negative electrode becomes deeply charged during the overcharge process; and then, due to the excess of discharge capacity of the negative electrode, the positive electrode becomes thoroughly discharged during the next discharge process, accompanied by significant increase of the resistivity of the powder matrix (due to very low concentration of Ni^{3+} sites). Therefore, the initial charging potential can be raised to significantly higher values. The charging potential gradually returns to normal value as more Ni^{3+} sites appear in the matrix during the charging process. Such overcharge–deep-discharge cycles are very harmful to the cyclic life of the cells. In Fig. 9 the deterioration rates of the sealed cell and the punctured cell are compared.

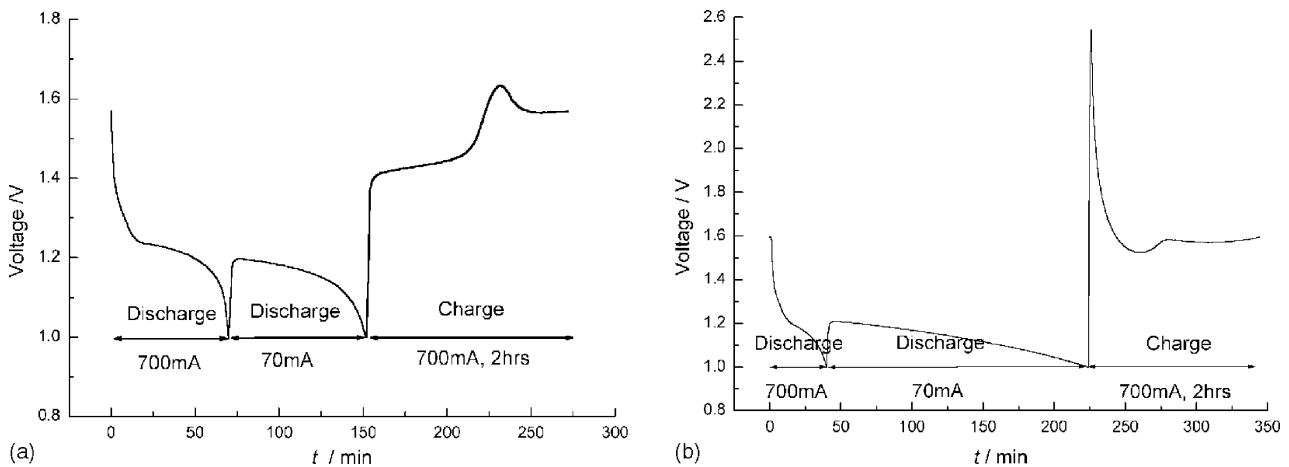


Fig. 8. Comparison of the discharge/charge characteristics of (a) a normal sealed Ni–Cd cell with that of (b) a punctured Ni–Cd cell.

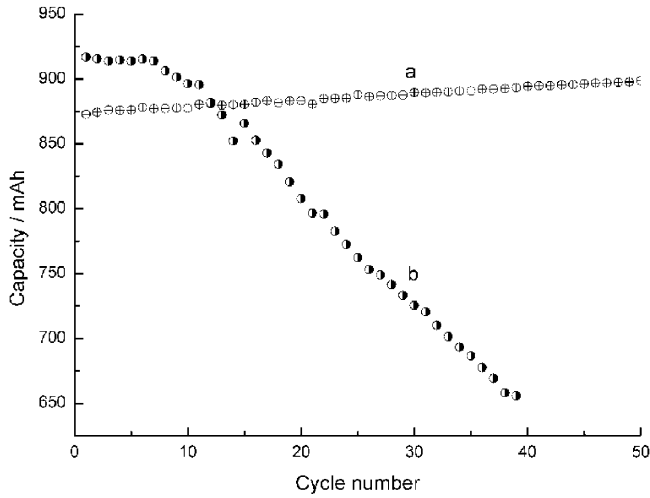


Fig. 9. The capacity degradation curves of (a) the sealed Ni–Cd cell; and (b) the punctured Ni–Cd cell.

In case of actual Ni–Cd cells, the loss of oxygen due to micro-leaks is usually a very gradual process, so its effects can be apparent only after many charge–discharge cycles. In other words, the above-stated experiments designed to simulate the effect of oxygen loss were definitely too brutal and exaggerated. Nevertheless, the basic conclusions obtained from results of these experiments should be applicable to interpretate the behavior of actual cells.

3.2. Ni–MH cells

Fig. 10 shows the variations of internal pressure with time when a Ni–MH cell is charged and then overcharged at various rates.

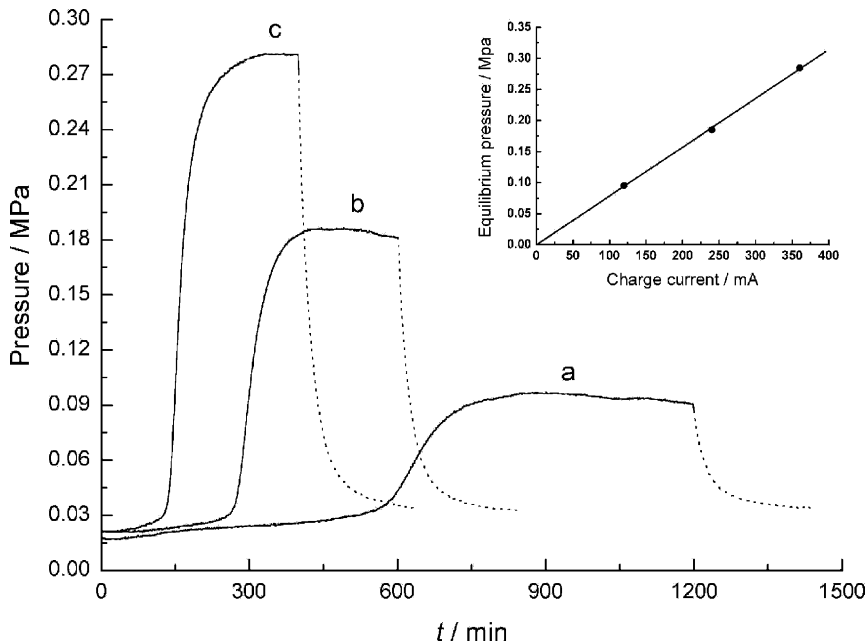


Fig. 10. Variation of internal pressure in a 1200mAh sealed Ni–MH cell during charge/overcharge and after cut-off of the charging current (I). (a) $I = 120$ mA (0.1 C); (b) $I = 240$ mA (0.2 C); and (c) $I = 360$ mA (0.3 C).

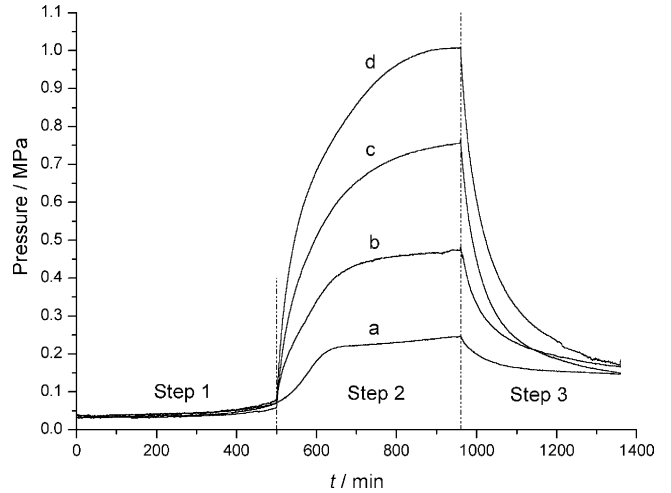


Fig. 11. Effects of hydrogen injection on the internal pressure of sealed Ni–MH cell. Step 1: normal charge/overcharge, $I = 120$ mA; step 2: effect of hydrogen injection, (a) $I_1 = 120$ mA, $I_2 = 0$; (b) $I_1 = 80$ mA, $I_2 = 40$ mA; (c) $I_1 = 40$ mA, $I_2 = 80$ mA; (d) $I_1 = 0$ mA, $I_2 = 120$ mA; and step 3: after cut-off of charging current.

Fig. 10 shows the variations of internal pressure with time when a Ni–MH cell is charged and then overcharged at various rates. Curves shown in Fig. 10 are in general similar to those depicted in Fig. 3, but the limiting values of pressure are somewhat lower in cases of Ni–MH cell, indicating higher rate of gas consumption. Besides, the P_{max} values shown in Fig. 10 were also found to vary linearly with the intensity of charging current (see cut in Fig. 10).

Fig. 11 shows the effect of hydrogen injection on the internal pressure of Ni–MH cell. Comparing these curves with those shown in Fig. 5, it is immediately clear that the Ni–MH system behaves quite differently from the Ni–Cd

system concerning their abilities of hydrogen consumption. In cases of Ni–MH cells, the internal pressure could gradually reach limiting values, even if the current efficiency of hydrogen evolution at negative electrode is 100% (curve d in Fig. 11). Besides, the internal pressure built-up during overcharge could subside rather quickly (compare with Fig. 5) after cut-off of the charging current.

Generally speaking, there are three possible mechanisms of hydrogen consumption within a sealed Ni–MH cell:

- (1) electro-oxidation of hydrogen at the positive electrode,
- (2) recombination with oxygen to form water at certain catalytically active surfaces within the sealed cell, and
- (3) hydrogen adsorption by the unsaturated hydrogen storing alloy (M, which is the reduced form of the electro-active material of the negative electrode).

Since in case of sealed Ni–Cd cells we have not observed consumption of hydrogen (see Fig. 5), there seems to be no reason to assume rapid electro-oxidation of hydrogen at the positive electrode (the same NiOOH electrode) in sealed Ni–MH cells. Thus, what we need to do is to verify the possibility of realizing the other two mechanisms. To serve such a purpose, we tried to inject hydrogen at an early stage of charging, i.e., at a stage prior to oxygen generation at the positive electrode. Fig. 12 show the results of such experiments, which clearly show that the consumption of hydrogen within the sealed Ni–MH cell does not necessarily involve oxygen. In other words, adsorption by hydrogen storage alloy seems to be a practically realizable mechanism of hydrogen consumption in sealed Ni–MH cells. The P_{\max} values are linear function of hydrogen injection current (see cut in Fig. 12), and analysis of experimental data shows that the consumption of hydrogen is a first-order reaction (Fig. 13).

It would be difficult to deduce from the general shapes of the pressure–time curves whether hydrogen generation actually takes place when the normal Ni–MH cell is overcharged, since hydrogen generation at negative electrode in

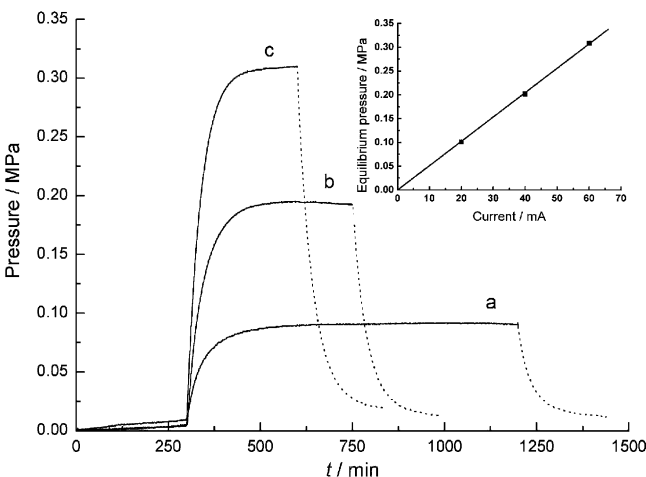


Fig. 12. Effect of hydrogen-injection on the internal pressure of a sealed Ni–MH cell when the injection was started far before the completion of charge of the positive electrode.

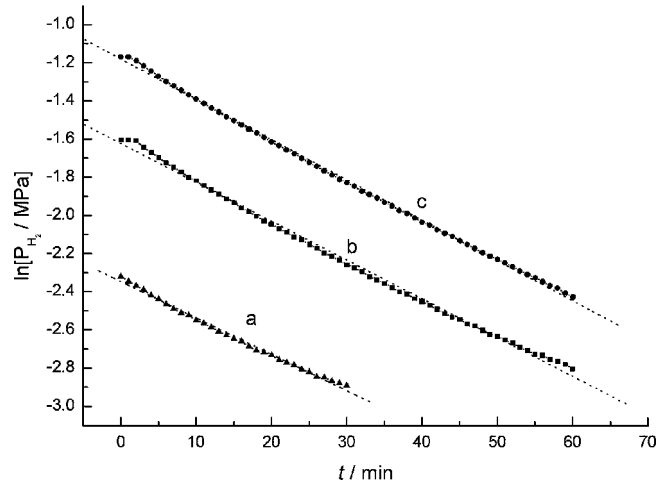
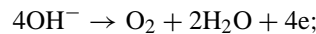


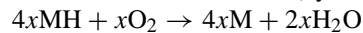
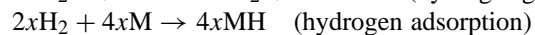
Fig. 13. Logarithmic analysis of the kinetics of internal pressure build-up shown in Fig. 12.

sealed Ni–MH cells can exhibit pressure–time relationships similar to those caused by oxygen cycle (compare Figs. 3 and 12). However, it has been frequently reported in literature (for example, [7,8]) that the partial pressure of hydrogen within the sealed cell was found to increase significantly when the Ni–MH cell is charged or overcharged. Therefore, very probably the reactions taking place within the normal sealed Ni–MH cell in steady stage of overcharge are the following:

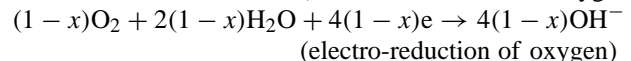
- (1) at the positive electrode,



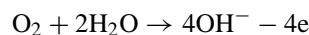
- (2) at the negative electrode (in the following x is the fraction of charging current consumed in hydrogen generation, and $(1-x)$ that of the electro-reduction of oxygen),



(chemical reduction of oxygen)



(electro-reduction of oxygen)



(net reaction at the negative electrode)

An important aspect of the above-stated mechanism is the involvement of unoccupied hydrogen adsorption sites (the reduced form of the electro-active material of the negative electrode, M) in the cyclic mechanism; so the mechanism could work only when there is an surplus of M, or in other words, only when the state-of-charge of the negative electrode is not 100%. If the negative electrode exists in totally reduced state (MH), hydrogen would not be consumed any more.

Fig. 14 shows the results obtained with a normal Ni–MH cell from which a part of the negative electrode has been cut-off to make the capacity of the cell “negative-electrode-

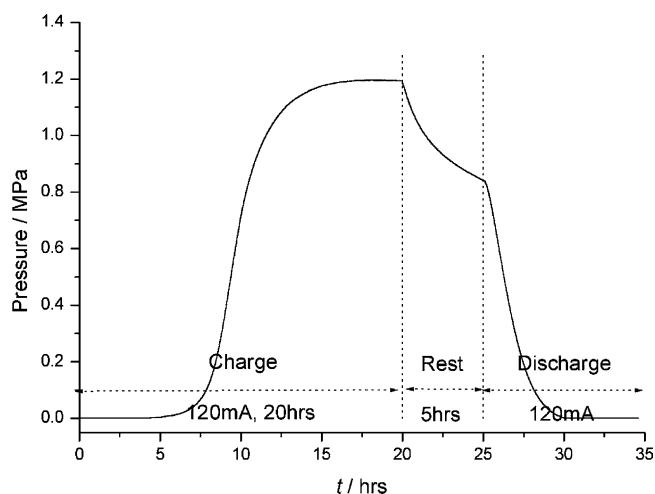


Fig. 14. The variation of the internal pressure of a sealed Ni–MH cell from which a part of the negative electrode has been removed.

limited”. It is clear that build-up of excess pressure is possible after the complete change of the negative electrode. In general, the curve shown in Fig. 14 is quite similar to that shown in Fig. 6, but there is a noticeable difference between these curves. In Fig. 6 the internal pressure subsides only slowly after cut-off of charging current and in the discharge stage following overcharge, since hydrogen generated during overcharge can not be effectively consumed in Ni–Cd cells; while in Fig. 14 the internal pressure drops to lower value after the cut-off of the charging current, and excess of pressure was found to diminish very quickly in the discharge stage, indicating that hydrogen can combine with oxygen at the fully charged MH electrode, and hydrogen can be very effectively eliminated from the gas phase when the negative electrode of the Ni–MH cell has been partially discharged.

Fig. 15 depicts the results of amperometric injection of hydrogen-oxygen (2:1) mixture into a fully charged normal Ni–MH cell. The internal pressure quickly approaches a limiting value after gas injection, and attenuates very swiftly

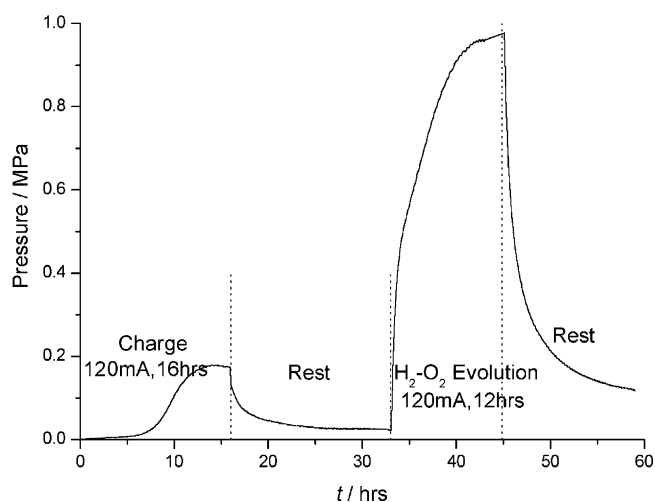
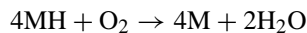


Fig. 15. Effect of evolution of 1:2 oxygen–hydrogen mixture and its consumption on the internal pressure of the sealed Ni–MH cell.

after cut-off of injection current. The mechanism of recombination at the MH electrode might be the following conjugated processes:



Usually the sealed Ni–MH cells are so designed that the electro-active materials of the negative electrodes are 30–50% in excess, in order to assure that the capacity of the cells is always “positive-electrode-limited”. However, the surplus of the charging capacity of the negative electrode could be lost as the result of reactions such as:

- (1) dissolution (corrosion) of the hydrogen storage alloy (or some constituents of the alloy) in alkaline electrolyte accompanied by hydrogen evolution;
- (2) irreversible electro-oxidation of the separator, the positive electrode current collector, or some constituents of the electrolyte.

The dissolution of hydrogen storage alloy is probably the most serious reason for loss of surplus charging capacity of the negative electrode, since both alloy dissolution and hydrogen generation reactions could raise the state-of-charge of the negative electrode. Such cases have already been reported in [7,10]. As the results of alloy dissolution and hydrogen generation, the state-of-charge of the negative electrode was found to raise to such an extent that terribly high partial pressure of hydrogen can be built-up within the sealed Ni–MH cell during the charging process.

3.3. Comparison of the behavior of sealed Ni–Cd and Ni–MH cells

From the above-stated experimental results and discussions it is clear that the Ni–Cd and Ni–MH systems behave quite differently in their ability to deal with gaseous products generated during the overcharge process. In the sealed Ni–Cd system only oxygen can be consumed at the negative electrode; while the negative electrode of the Ni–MH system possesses the additional ability to consume hydrogen and to catalyse the recombination reaction of hydrogen and oxygen. Nevertheless, the internal pressure within both the sealed Ni–Cd cells and the sealed Ni–MH cells can be kept well under control during the charge/overcharge processes if there is sufficient surplus of charging capacity at the negative electrode (i.e., the state-of-charge of the negative electrode always kept significantly smaller than 100%) and the rate of charge/overcharge is not too high (to avoid significant polarization and non-homogeneous polarization within the powder matrix).

In normal sealed Ni–Cd cells the oxygen cycle works almost ideally when subjected to not too high rate of overcharge. Since the equilibrium potential of the Cd electrode in equilibrium with “active” $\text{Cd}(\text{OH})_2$ and HCdO_2^{2-} in pH 14 alkaline solution is -0.804 V [11] (-0.821 V when in contact

with anhydrous CdO), slightly more positive than that of the reversible hydrogen electrode (RHE) in pH 14 alkaline solutions (-0.827 V), and the overvoltage of hydrogen evolution at the Cd electrode is rather high; so generation of hydrogen at the negative electrode is both thermodynamically improbable and kinetically seriously handicapped. On the contrary, in normal sealed Ni–MH cells, generation of hydrogen during charge/overcharge is usually unavoidable, since the potential of the MH electrode is slightly more negative than that of the Cd/Cd(OH)₂ and the overvoltage of hydrogen evolution at the MH electrode is usually low. Nevertheless, the internal pressure of sealed Ni–MH cells could also be kept under control, since the negative electrode of the Ni–MH system has the ability to consume hydrogen effectively.

On the other hand, for both sealed Ni–Cd and Ni–MH systems, the internal pressure within the sealed cells could raise to dangerously high levels if there is a deficiency of charging capacity of the negative electrode. Such a circumstance can be the result of deterioration of electrode materials (self-dissolution, passivation, pulverization, etc.) or raise of the state-of-charge of the negative electrode as the results of auxiliary irreversible electro-oxidation reaction at the positive electrode (such as corrosion of the positive electrode or current collector, oxidation of separator or some constituent in the electrolyte, etc.) or loss of oxygen. Simple calculation shows that 50 mAh deficiency of the charging capacity of the negative electrode could induce the generation of more than 20 ml (STP) of unconsumable hydrogen. If we assume that the effective volume of free space is less than 1 ml in AA cell, the pressure generated by 20 ml hydrogen would be more than 20 atm!

A parameter that should be carefully controlled in the manufacturing of sealed Ni–MH cells is the degree of reduction of the hydrogen storage alloy employed in the fabrication of the negative electrode before the sealing and subsequent charging of the sealed cells. In some practice, the hydrogen storage alloy electrodes are subjected to “activation” in highly reducing environment (such as immersion in boron hydride [12] or hot alkaline [13] solution) in order to facilitate more efficient intake of atomic hydrogen and higher rate of initial activation process. However, the state-of-charge of the MH electrode after such treatment must be carefully monitored to assure that there is still sufficient surplus of charging capacity of the MH electrode when the cell becomes fully charged.

The situations could be more complicated when the sealed cells are subjected to higher rate of overcharging mainly for two reasons:

- (1) Electrochemical polarization of the negative electrode becomes more severe when the current density increases, so evolution of hydrogen may take place at the Cd/Cd(OH)₂ electrode and the rate of hydrogen evolution at the metal hydride electrode will be more vigorous.
- (2) Distribution of current density becomes more and more non-homogeneous within powder electrode when the cur-

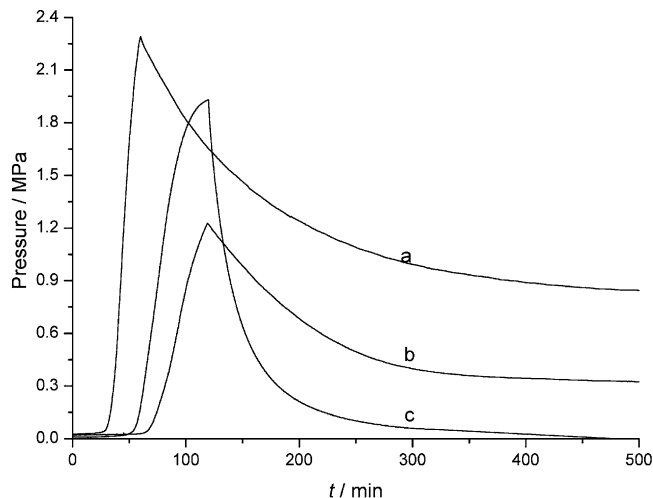


Fig. 16. The variation of internal pressure within sealed Ni–Cd and Ni–MH cells when they are overcharged at higher rate. (a) Ni–Cd cell, 100% overcharged at 2 C; (b) Ni–Cd cell, 100% overcharged at 1 C; and (c) Ni–MH cell, 100% overcharged at 1 C.

rent density increases, so local parameters (electrode potential, state-of-charge, etc.) can be quite different from the average values.

Fig. 16 shows the internal pressure variations within sealed Ni–Cd and Ni–MH cells when these cells are overcharged at higher rates. Perhaps the most significant characteristic of these curves is that the internal pressure within the sealed Ni–Cd cells does not deteriorate quickly to low value (as in the case of low rate of overcharging) after cut-off of the charging current, but gradually approaches a still quite high limiting value. This seems to indicate that significant hydrogen partial pressure has been built-up within the sealed Ni–Cd cell during the high-rate overcharging process, and the Ni–Cd system is not capable of coping with this situation effectively. On the other hand, the internal pressure within a sealed Ni–MH cell drops quickly to very low value after cut-off of the charging current, indicating that both oxygen and hydrogen can be consumed rapidly by the Ni–MH system.

4. Conclusions

From the above-stated experimental results and discussion it is clear that, in order to avoid the build up of high internal pressure within sealed cells, it seems very important to stick to the following principles:

- (1) The charging capacity of the negative electrode must be well above that of the positive electrode, and the state-of-charge of the negative electrode must be well beneath that of the positive electrode.
- (2) The deteriorating rate of the negative electrode should not be significantly higher than that of the positive electrode.

From both thermodynamic and kinetic points of view, the stability of the Cd/Cd(OH)₂ electrode in alkaline solution is far better than that of the MH electrode. Therefore, the rate of deterioration of the former should be slower, and there should be less chance for the loss of surplus of the state-of-charge of the negative electrode in case of sealed Ni–Cd cells. This seems to be at least part of the reasons for why the sealed Ni–Cd system is generally considered as more reliable and usually has longer cycle lives.

However, hydrogen production in sealed Ni–Cd cells is possible when they are subjected to prolonged high-rate overcharging. Such possibility must be seriously considered in manufacture and manipulation of seal Ni–Cd cells designed for high-rate applications.

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