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Mathematical characterization of internal pressure variation of Ni-MH batteries

Zhong-qiang Shan · Wei Hu · Zheng Chen · Jian-hua Tian

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Abstract The internal pressure variations of different Nickel-metal hydride batteries were studied. The relationship between the deflection of a battery shell and internal pressure can be determined by thin elastic shell theory, and also by experimental methods. A DNY-2 was specially designed to measure indirectly the pressure inside the battery shell without damage to any battery parts. The internal pressure variations were simulated by the Boltzmann function when the batteries were charged with a low current density. The parameters in the simulating function have definite physical meanings, and a special parameter *k*, which is the variability of internal pressure with the charge state or the charge time of the battery in the region of inflexion of this simulation function can be used to estimate the cycle life of batteries. The result shows that batteries with a smaller *k* value have a longer cycle life.

Keywords Nickel-metal hydride battery · Internal pressure · Cycle life · Mathematical model

Z.-q. Shan · W. Hu · Z. Chen · J.-h. Tian (✉)
School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P.R. China
e-mail: jhtian@126.com

W. Hu
Department of Basic Medical Science, Binzhou Medical College, Yantai, Shandong 264000, P.R. China

1 Introduction

Nickel-metal hydride (Ni-MH) batteries are one of the most promising future vehicular power systems because of advantages such as high specific energy, high specific power, long cycle life and use of no poisonous heavy metals [1, 2]. Extensive efforts are being made to develop Ni-MH batteries to meet the stringent requirements of electric vehicles [3, 4].

One of the important factors which affects the charge-discharge cycle life and safety of Ni-MH batteries is the battery internal pressure, which may increase excessively during charging, especially during a rapid charge process. If a Ni-MH battery is considered to be a sealed electrochemical reactor, the battery internal pressure is the operating pressure of this reactor. The behavior of electrochemical reactors has been modelled mathematically, and a valid model can play an important role in identifying reactor-limiting mechanisms and predicting reactor performance for design, scale-up and optimization [5]. Therefore, mathematical modelling is the most appropriate way of simulating the internal pressure changes.

In this work, change of internal pressure for different Ni-MH batteries was measured by using a new type of instrument specifically designed to meet the requirement of internal pressure measurements without destruction of the battery. On the basis of the experimental data, a mathematical model of the internal pressure changes was created, with one parameter in the simulating function indicating the relationship between the internal pressure and the cycle life.

2 Experimental

2.1 Principles of experiments

The basic principles of the experiments include:

1. The deflection (or strain) of a battery shell, caused by the internal gas pressure, has a special relation to the internal pressure under certain conditions.
2. The relationship between the deflection and internal pressure of a battery shell can be ascertained by both thin elastic shell theory and experimental methods.
3. A precise micrometer sensor can accurately measure the micro-deformation of the battery body caused by the internal pressure.
4. Computing software permits in situ treatment of a large amount of internal pressure data and analyzing the influence of parameters related to the internal pressure on performance of the battery by mathematical modeling.

2.2 Mechanical model of cylindrical battery shells

Deformation of a battery occurs when the internal pressure is changed, which is the basis for the indirect measurement of internal pressure. The following assumptions were made from the characteristics of a cylindrical battery and the mechanical model as shown in Fig. 1: (i) the radial deformation of shell could be neglected; (ii) the internal pressure of the battery was evenly distributed; and (iii) the base of the battery shell was considered to be a slab of uniform thickness.

According to this model, the bottom of a battery shell can be simplified as a disk slab with fixed periphery. On the basis of the slab theory [6], the greatest deformation occurs at the center of the disk when a pressure P is exerted. The deflection at the centre can be expressed as:

$$\omega = \frac{3(1-\mu^2)D^4P}{256Eh^3} \quad (1)$$

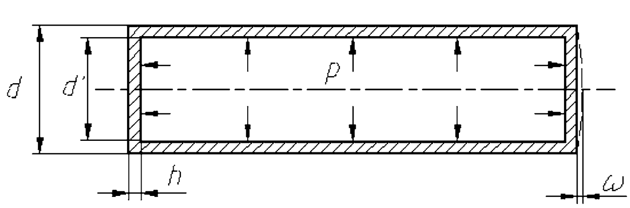

Fig. 1 Mechanical model of a cylindrical battery with expandable ends d and d′, outer and inner radius of the battery shell; h, thickness of the shell; P, internal pressure; ω, deflection of the battery bottom center

where ω(mm) is the deflection of the center of the slab (i.e. the battery bottom); D(mm) is the average diameter of the shell, i.e. $D = 0.5 \times (d + d')$, where d and d' are the outer and inner radii of the shell, respectively; P (MPa) is the internal force of the shell (i.e. the internal pressure of the battery); h (mm) is the thickness of the shell; μ is the Poisson ratio of the battery shell materials and E (MPa) is their elastic modulus. In general, the parameters for an AA# battery with a stainless steel shell can be set as $D = 14.0$ mm, $h = 0.3$ mm, $E = 2 \times 10^5$ MPa and $\mu = 0.3$, respectively, and the value of ω was therefore 75.9 μm assuming P being 1.0 MPa. The maximum value of radial deformation ($\triangle d$) of a battery shell can be calculated as just 1.39 μm according to Eq. (2) [7]. Hence, the radial deformation of the shell was negligible compared to that of ω.

$$\triangle d = D^2Ph^{-1}E^{-1}(1-0.5\mu)/2 \quad (2)$$

When equation (1) is rearranged, the corresponding internal pressure can be calculated, where the deflection of the center of the battery bottom can be measured.

$$P = 256Eh^3\omega(1-\mu^2)^{-1}\mathrm{D}^{-4}/3 \quad (3)$$

2.3 Method for measurement of battery internal pressure

Two methods are normally used to measure the internal pressure of Ni-MH batteries, i.e. direct and indirect methods. Generally, direct testing methods cannot obtain the internal pressure data without destroying the battery, because the battery must be directly linked to a manometer. For example, a tube joined to the manometer can be embedded into a battery, before the battery sealing, and then the internal pressure measured while the battery is charged. In addition to the sealed battery, an open battery may be pressure tested in a sealed vessel by measuring the air pressure variation in the vessel. Nevertheless, the indirect and nondestructive testing method for battery internal pressure is preferred, where micro-variations in battery shape caused by the changes in internal pressure are measured by a micrometer sensor, which converts the deflection into an electrical signal that is transformed into internal pressure information [5].

A DNY-2 designed in this laboratory was used as the experimental instrument to acquire the internal pressure data. As shown in Fig. 2, the DNY-2 system

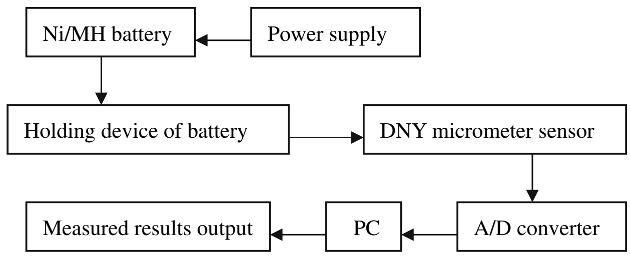

Fig. 2 Schematic diagram of the DNY-2 system

consisted of a micrometer capacitor sensor to relay the micro-deformation of the battery shell, a holding device for the AA# battery, an A/D converter, a personal computer and software for the internal pressure calculation. The deflection ω was computed from the capacitance data, and the internal pressure curve was calculated using Eq. (3).

Additionally, it is important that the cycle life of the battery can be evaluated from the internal pressure information, because the battery is not destroyed when the DNY-2 is employed.

2.4 Operating conditions

The batteries employed in this measurement were sealed AA# Ni-MH batteries. The current density was controlled at 0.2 C (time-rate) during the charging process and all batteries were charged to 120% of capacity. Measurement of the internal pressure was carried out during charging, after which, the battery was discharged at 1 C.

3 Results and discussion

Figure 3 shows the typical internal pressure curve measured during charging at 0.2 C. The curve comprises three regions, the plateaus of the internal pressure P at the beginning and end of the charging process (steps 1 and 3, respectively), and the region of rapid change (step 2). The plateau of P in region 1 (Fig. 3) is attributed to the negative and positive electrode reactions (4) and (5), respectively. At the negative electrode, H_2O is reduced to hydrogen atoms, which are absorbed into the hydrogen storage alloy electrode, and no hydrogen gas is released [8]. At the positive electrode, Ni^{2+} is oxidized to Ni^{3+}, and no oxygen gas is released.

$$M + xH_2O + xe^- \rightarrow MH_x + xOH^- \quad (4)$$

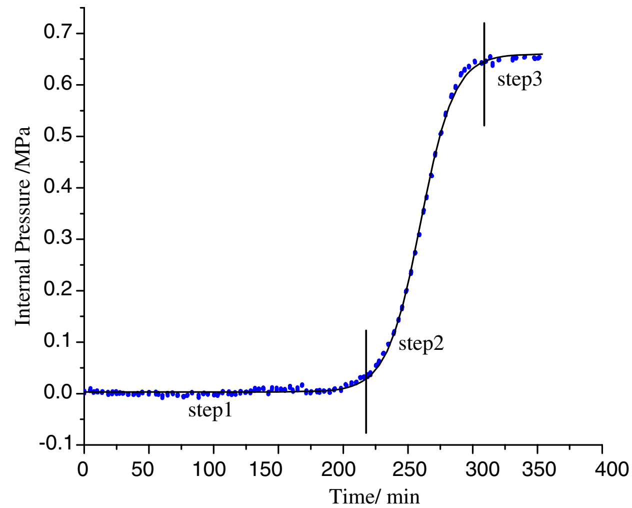

Fig. 3 Typical internal pressure curves of Ni-MH batteries Scattered data (**a**), measured curve; Solid line (**b**), simulated curve

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \quad (5)$$

During the rapid change region for P in Fig. 3, region 2, the diffusion velocity of H atoms is reduced with increasing concentration of hydrogen atoms at the MH electrode. As a result, a large amount of hydrogen atoms accumulate on the negative electrode surface rather than being absorbed by the hydrogen storage alloy to produce MH. Thus, a large amount of hydrogen gas (H_2) is produced as shown in reaction (6). At the same time, the oxygen evolution reaction (7) takes place at the positive electrode so that the internal pressure increases rapidly as shown in Fig. 3, curve (a).

$$2H_2O + 2e^- \rightarrow 2OH^- + 2H_2\uparrow \quad (6)$$

$$4OH^- \rightarrow O_2\uparrow + 2H_2O + 4e^- \quad (7)$$

The oxygen produced at the positive electrode is able to permeate through the diaphragm into the negative electrode, and subsequently react with hydrogen via catalysis with MH to produce water, as shown in Eq. (8). It is also possible for the oxygen to react with MH or water as illustrated in Eqs. (9) and (10). On the other hand, the hydrogen from the negative electrode can also diffuse to the positive electrode surface and be consumed through reactions (11) and (12). Consequently, some of the gas produced is consumed inside the battery.

$$2H_2 + O_2 \rightarrow 2H_2O \quad (8)$$

$$4MH_x + xO_2 \rightarrow 4M + 2xH_2O \quad (9)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (10)$$

$$H_2 + 2NiOOH \rightarrow 2Ni(OH)_2 \quad (11)$$

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad (12)$$

The internal pressure variation results from the competition between production and consumption of gases inside the battery. At the beginning of the battery charging process, the amount of gas produced is much greater than that consumed. The gases accumulate rapidly inside the battery and thus lead to an increase in internal pressure. In the final stages of the process, the increase in pressure accelerates the gas consumption reaction, and gradually slows the pressure buildup. The internal pressure levels and reaches the second plateau as shown in Fig. 3, where the gas producing and consuming rates are equivalent.

The Boltzmann function is a good option for precisely simulating the internal pressure changes during charging at low current density. As illustrated in Eq. (13), four parameters are relevant to this function, i.e. P_1, P_2, dt and t_0, where P_1 and P_2 are the initial and terminal values of the internal pressure, respectively; t represents the charging time; t_0 is the inflexion of the function, or the value of t when P is at $(P_1 + P_2)/2$; and dt is the width where the P value changes acutely, e.g. the width of region of $(t_0\text{-}dt, t_0\text{+} dt)$.

$$P(t) = P_2 + \frac{(P_1 - P_2)}{1 + \exp\left(\frac{(t-t_0)}{dt}\right)} \quad (13)$$

The curve (b) in Fig. 3 is the simulation result according to the Boltzmann function (13). It is seen that the simulation matches the measured internal pressure curve (a) in Fig. 3.

In order to relate the parameters of the Boltzmann formula (13) with cycle life, a group of Ni-MH batteries were prepared with different compositions, such as different amounts of electrolyte (2.45 ~ 2.65 *g*), different mass ratios between the negative and positive electrode materials (1.6 ~ 0.85) etc. The battery samples were expected to have different inner pressure characteristics because of the different diffusion and absorption rates, and different gas product ratios [9]. Twelve batteries were randomly chosen from the group for testing (marked as 1# ~ 12# in Table 1).

Figures 4–7 show the trends of the internal pressure P with t for the twelve battery samples at the fifth charge of 0.2 C. Relevant parameters obtained from

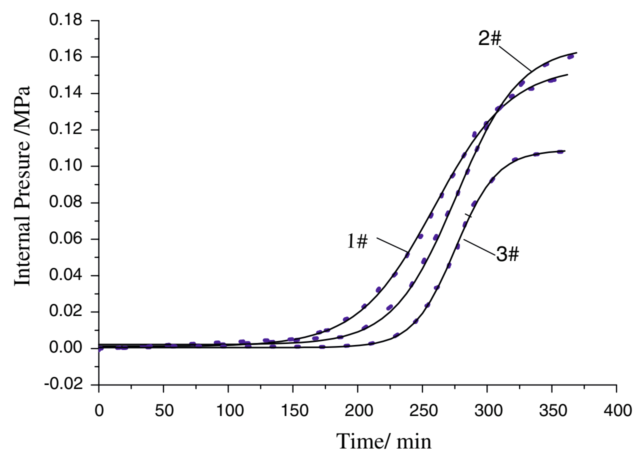

Fig. 4 Internal pressure curves of Ni-MH battery samples 1#, 2# and 3# Scattered data, measured curves; Solid line, simulated curves

Table 1 Related parameters of the simulating function for the internal pressure of a battery

Batteries	10^2P_1 /MPa	P_2 /MPa	t_0 /min	dt /min	n^a	10^2k /MPa min^{-1}
1#	0.5035	0.1568	258.3	33.96	344	1.041
2#	0.2168	0.1663	276.3	24.57	284	1.368
3#	0.2110	0.1225	273.3	14.64	256	1.467
4#	0.7334	0.1545	280.2	19.34	240	1.785
5#	0.1890	0.2112	299.1	25.11	200	1.728
6#	0.8329	0.2199	270.9	27.45	198	1.777
7#	0.4667	0.2084	277.5	24.69	177	2.103
8#	0.2594	0.6005	293.4	13.08	156	2.322
9#	0.4189	0.2732	283.8	17.52	145	3.525
10#	0.1409	0.5912	295.2	19.83	132	7.059
11#	0.7608	0.9052	285.6	19.14	95	9.639
12#	1.4607	0.8666	285	34.8	53	12.966

n^a is the cycle number of times when the discharge capacity drops down to the 60% of the initial battery capacity

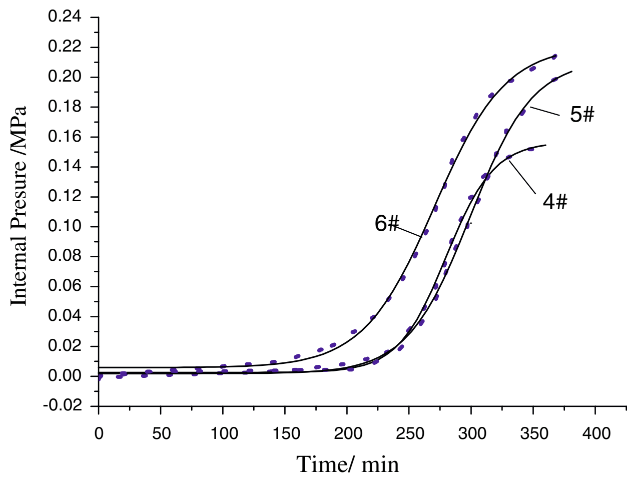

Fig. 5 Internal pressure curves of Ni-MH battery samples 4#, 5# and 6# Scattered data, measured curves; Solid line, simulated curves

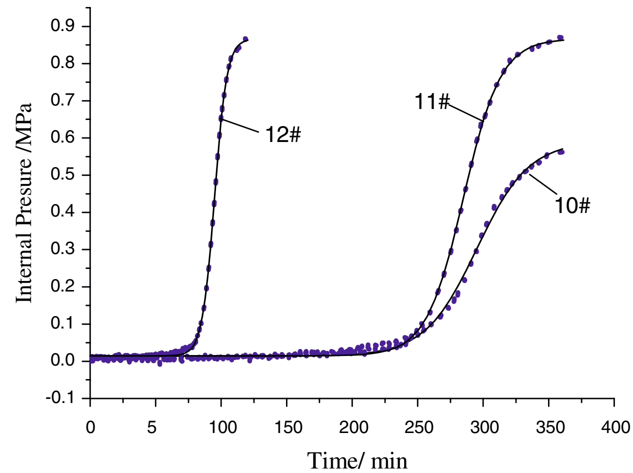

Fig. 7 Internal pressure curves of Ni-MH battery samples 10#, 11# and 12# Scattered data, measured curves; Solid line, simulated curves

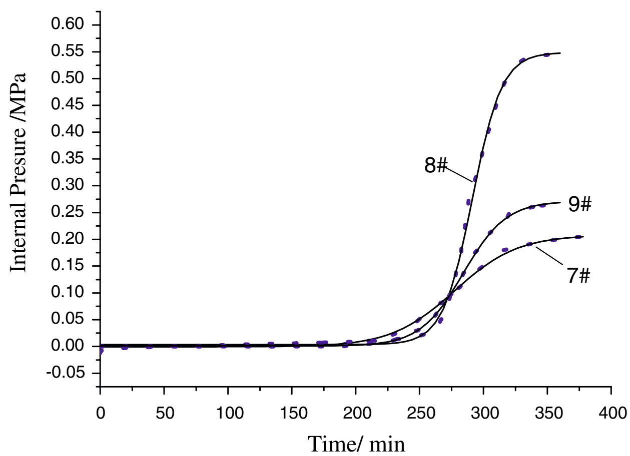

Fig. 6 Internal pressure curves of Ni-MH battery samples 7#, 8# and 9# Scattered data, measured curves; Solid line, simulated curves

the simulated curves, along with the cycle life, are listed in Table 1. A low charging current density (e.g. ≤ 0.2 C) was used in these experiments. The cycle life is defined as the number of charge-discharge cycles (expressed as n in Table 1) to a discharge capacity equivalent to 60% of the initial battery capacity.

It is generally accepted that a battery operating at a lower internal pressure exhibits better performance, including a longer cycle life; however, this is not always the case according to the results in Table 1. For example, although the final internal pressure (P_2) of 1# and 4# batteries are almost the same, the cycle lives are significantly different. On the other hand, batteries having similar cycle lives (7# and 8#) have different final internal pressures as shown in Fig. 6.

Therefore, it is necessary to determine a pressure-related parameter which contributes to the evaluation of the charge-discharge cycle performance. The variation regularity of the inner pressure of battery samples 1#~ 12# shown in Figs. 4–7 reveals that a new parameter, k, indicates the variability of the internal pressure with the charge state or the charge time in the region of t_0, defined by Eq. (14). It is clear from the definition that k varies approximately linearly with $P(t)$ in the region of $(t_0 - dt, t_0 + dt)$.

$$k = \frac{P(t_0 + dt) - P(t_0 - dt)}{2dt} \tag{14}$$

It is clear that k is related to battery cycle life n, as seen from Table 1 or Figs. 4–7. In general, a battery with a low k displays a long cycle life. All battery samples behaved in accordance with this principle except battery 4#. This demonstrates that the variability of internal pressure is an important factor affecting performance. Typically a battery with significantly higher internal pressures (P_1 and P_2) yields a lower cycle life (or high k value), e.g. samples 11# and 12# in Fig. 7.

The accuracy of the calculated k is related to the precision of measurement of the internal pressure. The battery samples #5 and 6# have similar n and k values, 200 and 198, and 0.01728 and 0.01777, respectively, with the negligible difference in k indicating an acceptable level of precision.

The experiments applied to evaluate the cycle life of a battery are time-consuming, thus it is significant that the parameter *k* can be used as a predictor for cycle life.

4 Conclusion

A DNY-2 device specifically designed in this laboratory was used to indirectly measure the internal pressure inside a battery shell without damage to the battery. The pressure variation inside a Ni-MH battery was simulated by the Boltzmann function during charging at low current density. The parameters in the simulation function have definite physical meanings including the special parameter *k*, which was used to estimate the cycle life of the battery. *k* is the variability of the internal pressure with state of charge or the charge time of the battery in the inflexion region of the simulating function. A battery with a lower *k* displayed a longer cycle life.

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