Research on Life Assessment of Ni-MH Battery through Orthogonal Experiment under Multiple Aging Factors

A.H. Chu¹,², X Chen³, Y.N. Yuan¹,², T Zhang³, H Yohei⁴, and G.C. Xu⁵

¹ Jiangsu University, Jiangsu Zhenjiang 212000, China;
² Soochow University, Jiangsu Suzhou 215006, China;
³ Corun CHS Technology co., LTD, Shanghai 201501, China;
⁴ Shonan Corun Energy co., LTD, Kanagawa 253-0014, Japan;
⁵ Hunan Co-power EV Battery co., LTD., Changsha 410205, China;
chueva@126.com

Abstract. The power battery is required to have the same service life as the hybrid vehicle. The cylindrical Ni-MH battery 600DC has been used in many HEVs, which was produced by Shona-Corun Energy Co., Ltd (Shona) in Japan. Recently, Shona has been acquired by Hunan Co-power EV Battery co., LTD (CPEV), and an improved and localized 600DE NiMH battery was produced in China. Therefore, it is necessary to study the cycle life of the battery according to the requirements of the real vehicle. The orthogonal experimental scheme based on characteristic conditions including battery temperature, SOC average value, DOD range and average current was designed. According to the periodic assessment during the aging cycle and the physio-chemical analysis after the aging cycle, it is proved that the depth of DOD has a significant impact on the life aging. The main factors of the performance degradation of the battery are the pulverization and corrosion of the negative alloy, the reduction of the active material Ni (OH)₂ and the production of the inert material Ni₂O₃H in the positive electrode.

1. Introduction
At present, due to short mileage and long charging time of pure electric vehicles (EV), and immature fuel cell vehicle (FCV) technology, hybrid electric vehicles (HEV) can overcome the shortcomings of both traditional internal combustion engine (ICE) vehicles and new energy vehicles, and considered to be the most feasible energy saving and emission reduction approach at the present stage (Hannan et al., 2014; Bauer et al., 2015; Kumar et al., 2014). Hybrid vehicles are the most comprehensive and rigorous application field for power batteries, in which NiMH battery has many advantages over Li-ion battery (K. Young et al., 2013; S. Yasuoka et al., 2006; M. Watada et al., 2006; H. Teraoka et al., 2015; M. Zelinsky et al., 2010). NiMH battery has the advantages of maturity, safe and long life. There is no case of burning or explosion caused by the battery in the market.

The cylindrical Ni-MH battery 600DC produced by Shona has been used in many HEVs, including Toyota Prius I, Honda Insight and Honda Civic. So far, about 600 thousand sets have been mass produced. Recently, CPEV has acquired Shona and started to produce an improved and localized 600DE Ni-MH battery with domestic materials. Because there is no large-scale production performance in the market, it is necessary to establish a multiple evaluation method to study the
degradation mechanism of cycle life through charge and discharge experiments under different conditions, so as to infer whether the battery life cycle meets the warranty requirements.

2. Aging mechanism of Ni-MH battery

A sealed Ni-MH battery cell is composed of four parts: a negative electrode (Metal Hydride, MH), a positive electrode (porous nickel oxy-hydroxide, Ni(OOH)$_2$), a separator (porous nylon material, typically) and a steel shell with sealing plate. Both electrodes are electronic conducting porous materials with constant porosity flooded with the electrolyte (concentrated KOH aqueous solution) which fully impregnates the separator as well. To improve the integration efficiency, a commercial L6 module, formed by welding five cells in series, were used. The shape of the battery cell and module are shown in Figure 1, and the electrical parameters of cells and modules are shown in Table 1.

![Figure 1. The structure of the battery cell and module.](image)

### Table 1. Basic performance parameters of the Ni-MH cell and module.

| Items                  | Cells            | L6 Modules       |
|------------------------|------------------|------------------|
| Size (mm)              | φ=33.0±0.5; H=60.8±1 | φ=34.8; L=397±1   |
| Weight (g)             | ~170g            | ~1020g           |
| Nominal capacity (Ah)  | 6                | ←                |
| Rated voltage (V)      | 1.2              | 7.2              |
| Power density (W/kg)   | >1200            | >1100            |
| Energy density (Wh/kg) | >43              | >42              |

2.1. Aging mechanism of positive electrode

There are two crystal forms of nickel hydroxide: α and β, and the products formed after charging also have two crystal forms: β-NiOOH and γ-NiOOH (H. BODE et al., 1966). The formation of γ-NiOOH causes the expansion of the nickel electrode, weakens the mechanical properties of the electrode substrate, causing the rupture of the nickel electrode substrate and the fall off of the active material (Y. Chen et al., 2001).

\[
\begin{align*}
\beta\text{-Ni(OH)}_2 & \xrightarrow{\text{charge/discharge}} \beta\text{-NiOOH} + H^+ + e^- \\
\alpha\text{-Ni(OH)}_2 & \xrightarrow{\text{charge/discharge}} \gamma\text{-NiOOH} + H^+ + e^-
\end{align*}
\]

At the same time, the γ-NiOOH and β-NiOOH phases show instability relative to the electrolyte at high temperature, which leads to the irreversible formation of Ni$_2$O$_3$H through reduction reaction, accompanied by dissolution and precipitation mechanism. Olivier guiader (O. Guiader et al., 2018) confirmed the correlation between the amount of Ni$_2$O$_3$H and the abnormal and irreversible battery capacity loss in his study.

\[
\text{NiOOH + Ni(OH)}_2 \xrightarrow{\text{>100°C}} \text{Ni}_2\text{O}_3\text{H} + \text{H}_2\text{O}
\]
2.2. Aging mechanism of negative electrode

The expansion of crystal lattice results in the increase of internal stress, the growth of microcracks in grains, the formation of hydrogen embrittlement, the fracture of grains, the pulverization of alloys and the decrease of hydrogen absorption and desorption capacity (X. Zhou et al., 2013; A. Durairajan et al.). On the other hand, due to the consideration of cost in battery production, most of the negative electrodes are made of rare earth hydrogen storage alloys. Because rare earth elements are not stable in strong alkaline solution, they are easy to corrode and form M(OH)₃, which is one of the reasons for the deterioration of hydrogen storage performance of the alloys. From the above analysis, it can be seen that the main reasons for the degradation of rare earth hydrogen storage alloys are the micronization and the corrosion of the alloys. The resistance to pulverization and alkaline corrosion of the alloy can be improved by adding a small amount of Co, Al, Mn, Cu and other alloying elements, and the cycle life of the alloy can be increased. Therefore, the degradation process can be predict by observing the precipitation amount of Ni, Co and Mn.

3. Life cycle experiment of 600DE battery

3.1. Orthogonal experiment scheme

The cycle life experiment is carried out under the condition of different combination of characteristic parameters, including battery temperature, SOC average value, DOD range and average current. The battery temperature includes three levels of 25°C, 35°C, and 45°C. The average SOC includes three levels of 40%, 60%, and 80%. The DOD range includes three levels of 10%, 20%, and 30%. The average current includes 15.5A, 30A, and 40A. In order to study the influence of single factor on life aging, the above experimental conditions are classified by orthogonal method. As shown in Table 2, nine groups of charge and discharge durability experiments need to be carried out under different conditions. ① ② ③ are for different temperatures, ① ④ ⑤ are for different SOC average values, ⑥ ⑦ ⑧ are for different DOD ranges, ① ⑧ ⑨ for different average current. In addition, for the convenience of reference, we design a naming rule according to the characteristics of conditions.

Table 2. The combination of nine experimental conditions and the naming rules of each experiment.

| Items | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------|---|---|---|---|---|---|---|---|---|
| Tbat | 25°C | 35°C | 45°C | 25°C | 35°C | 45°C | 25°C | 35°C | 45°C |
| SOC  | 60% | 60% | 60% | 40% | 80% | 40% | 60% | 60% | 60% |
| DOD  | 10% | 10% | 10% | 10% | 10% | 10% | 20% | 30% | 20% |
| Iavg | 15.5A | 15.5A | 15.5A | 15.5A | 15.5A | 15.5A | 15.5A | 30A | 40A |
| r    | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 900 |

Reference: Temperature | SOC | DOD | Current
24010-60-35 | 24010-60-25 | 24010-60-25 | 24010-60-25 | 24010-60-25 | 24010-60-25 | 24010-60-25 |

3.2. Procedure of experiment

All batteries in this research must come from the same batch. Each group of experiments uses two L6 modules connected in series to expand the number of samples appropriately. According to the specific conditions mentioned before, all battery modules are placed in a climate chamber with fixed...
temperature and are cycled with a programmable electrical tester, according to the specific conditions described before. The experimental environment is shown in Figure 2.

As shown in Figure 3, the first group (① 24010-60-35) is the reference for the other groups of experiments. Each cycle time was 3388s and a total of 12,000 cycles were performed to meet the requirement of vehicles. The aging cycle was separated by periodic assessment of capacity tests, which was suspended once every 1,000 cycles to test capacity of battery module. After 12000 cycles, disassembly and physio-chemical analysis of battery are performed to evaluate the corrosion and pulverization of the negative alloy, the metal dissolution in the electrolyte, and the element phase of the positive electrode. The items of electrical test and physio-chemical analysis are shown in Table 3.

| Catalog                  | Objects       | Tools  | Purposes                     |
|--------------------------|---------------|--------|------------------------------|
| Electrical tests         | Modules       | Charger| Capacity fade                |
|                          | Cells         | Charger| Impedance deviation         |
|                          | Positive electrode | XRD    | Ni$_2$O$_3$H phase          |
| Physio-chemical analyses | Negative electrode | VSM    | Dissolution of Ni           |
|                          | Separator     | SEM    | Alloy powdering              |
|                          |               | EDS    | Micro short circuit         |

4. Results of electrical experiment

4.1. Capacity deterioration of modules

The residual capacity and capacity reduction need to be recorded every 1000 cycles with the test conditions: 3A charge to 1.5V cut off voltage and 2A discharge to 1.0V cut off voltage per cell at 25 °C. As shown in Figure 4, DOD range has the greatest influence on the capacity loss, the maximum deterioration is over 10%, and the capacity deviation caused by different DOD is also obviously large.
4.2. DC-IR deviation between cells
After 12000 cycles, the module we disassemble into single battery cells, and then the impedance of all cells and the impedance deviation between cells were measured. The measurement results are shown in Figure 5. In each group of experiments, the impedance deviation between twelve cells of two L6
modules is not greatly affected by different SOC, but the deviation tends to increase due to the increase of load according to the influence of battery temperature, DOD range, average current, especially the increase of DOD range.

5. Results of Physio-chemical analyses

5.1. Degradation of negative electrodes

5.1.1. Observation of alloy pulverization

The pulverization of negative electrode was characterized by scanning electron microscopy (SEM). Figure 6 shows the SEM cross section photographs of the alloy after 12000 cycles. The DOD range at the maximum load 30% (7) was selected for comparison with the reference experimental conditions 1. The results show that all the alloys are powdered to a certain extent, but the overall phenomenon is not very serious.

![Figure 6. SEM observation (×300) of negative electrode.](image)

(a) 1 24010-60-25 (reference)  (b) 7 24030-60-35 (high DOD)

5.1.2. Observation of alloy corrosion

The corrosion of negative electrode was characterized by the vibrational sample magnetometer (VSM). Figure 7 shows the VSM value of the alloy after 12000 cycles. The corrosion products were formed on the alloy surface during the cycling process, and the increase of strong magnetism indicated that Ni or Co was formed in the process. Because Ni is quite stable in alkaline solution, VSM can be used as the indication of corrosion degree of alloy. The rise of VSM value is mainly affected by the temperature of the battery. The increment of VSM value from 25°C to 35°C is about 1.7wt%, and from 35°C to 45°C is 4.2wt%. The management of battery temperature has a great impact on battery life.
5.1.3. Chemical element analysis on separator

The corrosion of negative electrode was characterized by the Energy Dispersive X-Ray Spectroscopy (EDS). The separator corresponding to the highest impedance cell after cycle was used for element matching, and the precipitation amount of Co, Mn and Ni was observed. Figure 8 shows the EDS measurements on the surface of separator after 12000 cycles. The existence of Ni, Co and Mn on the surface of the separator was confirmed by X-ray fluorescence analysis, which indicated that the corrosion of the alloy in alkaline electrolyte had occurred. However, the mass of Co element in all experiment is about 10%, and the amount of precipitation does not induce micro short circuit.

5.2. Degradation of negative electrodes

As shown in figure 9, the positive electrode phases were also studied by analyzing the powder removed from the positive electrode by X-ray diffraction (XRD). Cells with obvious increase of impedance was selected for analysis after disassembly. For the positive electrode after 12000 cycles, the strength of Ni(OH)₂ on the positive electrode surface of group ⑦ (30% DOD range) was weak, and a new phase was unexpectedly formed on the positive electrode surface corresponding to Ni₂O₃H. Olivier Guiader confirmed that temperature is the first parameter in the formation mechanism of Ni₂O₃H. In this paper, it is proved that Ni₂O₃H can also be produced by enlarging the cycle depth of SOC at normal temperature. Ni₂O₃H is a rather moderate electronic conductor and is almost
electrochemically inactive, which leads to the decrease of the utilization rate of active substances, and the degradation and deviation of the electrical characteristics between battery cells.

6. Conclusion
In this paper, the orthogonal experimental scheme based on characteristic conditions including battery temperature, SOC average value, DOD range and average current was designed to evaluate the aging of battery life. According to the periodic assessment during the aging cycle and the physio-chemical analysis after the aging cycle, the following conclusions can be obtained:

1. Under different multiple conditions, the depth of DOD has significant influence on life aging. The maximum degradation of battery capacity was 10%, which does not reach the end of life threshold. It is proved that the 600DE battery meets the warranty requirements.

2. The main factors of the performance degradation of the battery are the pulverization and corrosion of the negative alloy, the reduction of the active material Ni(OH)2 and the production of the inert material Ni2O3H in the positive electron.

Acknowledgments
This paper was funded by China High-Tech Development Program (863) under Grant 2011AA11A207.

References
[1] Hannan M A, et al. (2014). ‘Hybrid electric vehicles and their challenges: A review’. Renewable and Sustainable Energy Reviews, 29, pp.135-150(Access 2014).
[2] Bauer C, et al. (2015). ‘The environmental performance of current and future passenger vehicles: Life cycle assessment based on a novel scenario analysis framework’. Applied energy, 157, pp.871-883(Access 2015).
[3] Kumar L and Jain S (2014). ‘Electric propulsion system for electric vehicular technology: A review’. Renewable and Sustainable Energy Reviews, 29, pp.924-940(Access 2014).
[4] Young K, et al. (2013). ‘Electric Vehicle Battery Technologies’. Electric Vehicle Integration into Modern Power Networks, 2013; pp. 15–56(Access 2013).
[5] Yasuoka S, et al. (2006). ‘Development of high-capacity nickel-metal hydride batteries using superlattice hydrogen-absorbing alloys’. J. Power Sources, 2006, 156, 662–666. (Access 2006)
[6] Watada M, et al. (2006). ‘Development trend of rechargeable nickel-metal hydride battery for replacement of dry cell’. GS Yuasa Tech. Rep., 2006, 3, 46–53. (Access 2006)
[7] Teraoka H, et al. (2015). ‘Development of Low Self-Discharge Nickel-Metal Hydride Battery’. Available online: http://www.scribd.com/doc/9704685/Teraoka-Article-En (accessed on 30 September 2015).
[8] Zelinsky M, et al. (2010). ‘Storage-Integrated PV Systems Using Advanced NiMH Battery Technology’. In Proceedings of the 5th International Renewable Energy Storage Conference, Berlin, Germany, 22–24 November 2010. (Access 2015)
[9] BODE H, et al. (1966). ‘To the Knowledge of the Nickel Hydroxide Electrode-I. Over the Nickel (II)-Hydroxide Hydrate’. Electrochim Acta, 1966, 11 : 1079(Access 1966)
[10] Guiader O, et al. (2018). ‘Understanding of Ni(OH)2 / NiOOH Irreversible Phase Transformations: Ni2O3H Impact on Alkaline Batteries. Journal of The Electrochemical Society, 165 (2) A396-A406 (Access 2018)
[11] Chen Y, et al. (2001). ‘Discussing of invalidation factors of Ni-MH battery at high charge and discharge rate’. Chin. J. Power Sources, 2001, 25, 142–145. (Access 2001)
[12] Zhou X, et al. (2013). ‘Degradation mechanisms of high-energy bipolar nickel metal hydride battery with AB5 and A2B7 alloys’. J. Alloys Compd, 2013, 580, S373–S377. (Access 2013)
[13] Durairajan A, et al. (2000). ‘Pulverization and corrosion studies of bare and cobalt-encapsulated metal hydride electrodes’. J. Power Sources, 2000, 87, 84–91. (Access 2000)