

Short communication

Characterization of 109 Ah Ni–MH batteries charging with hydrogen sensing termination

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Received 5 April 2005; received in revised form 18 May 2007; accepted 26 May 2007

Available online 13 June 2007

Abstract

The use of Ni–MH batteries for traction applications in electric and hybrid vehicles is increasingly attractive and reliable. Besides the energy and power handling, and the cost issues, high tolerance to abuse is an important aspect of the Ni–MH technology. Thus, the ability to reduce charging time and to absorb regenerative braking is highly desirable in these traction applications. This requires an accurate control of the charge termination. To facilitate an easy and reliable charging control and to avoid battery premature failure or ageing it is very important to know the behavior of the battery under a range of charging conditions. In this paper, we described the performance of high capacity commercial Ni–MH traction batteries (12 V, 109 Ah modules) when subjected to different charging rates (0.1, 0.2, 0.5, and 1.0 C) from 100% depth of discharge (DOD). Changes in battery voltage and temperature during charging were monitored, with a particular emphasis on the detection of the presence of hydrogen near the battery. This unique hydrogen detection outside the battery was used as the method for the end-of-charge termination to prevent overcharging of the battery. Relevant parameters, such as charge acceptance, energy efficiency, and charging time, were analyzed for comparison. © 2007 Elsevier B.V. All rights reserved.

Keywords: Nickel–metal hydride battery; Charge acceptance; Traction application; Hydrogen evolution; Energy efficiency

1. Introduction

There is an increasing interest in energy efficiency and in reducing our dependency on fossil fuels. The progress in the introduction of modern electric and hybrid vehicles is an important step toward this goal. Batteries for electric traction applications play an important role in this case, as they provide the power and energy required for these applications. Ni–MH batteries are a viable option for these applications, as they exhibit high specific energy, high specific power and a long cycle life. Moreover, they are relatively benign to the environment [1,2].

Although a large-scale production might lead to a considerable price reduction, the high cost remains a barrier to traction applications for Ni–MH batteries. Furthermore, if charging time

could be considerably decreased, such batteries would likely become more acceptable for electric vehicle applications. Fast charging certainly can help to increase the mobility and the time of use of the vehicles and possibly reduce the need for spare batteries.

Fast charging may also have negative consequences to the battery. For example, fast charging may induce earlier oxygen evolution, which is often observed during overcharge. This phenomenon may produce higher rate of recombinant reaction and reduce charging efficiency. If the oxygen recombination rate is slower than that of oxygen evolution the internal pressure will increase. If the battery response to high charge rates is not rightly understood, and adequately monitored and controlled, the battery may be overcharged. Overcharging would lead to considerable temperature increase, excessive gas production, and eventual separator degradation, electrolyte loss, and premature failure [3].

To avoid these undesirable consequences, it is proposed that highly sensitive hydrogen sensor installed outside a battery during charging be used to detect the presence of hydrogen as a

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method for end-of-charge termination. This method permits the use of a wide range of charging rates to consistently terminate charging when hydrogen gas is detected near the safety valve. Compared to other methods that use pressure sensors to terminate charge [4,5], this approach offers an easier implementation in practical use, while retaining the necessary sensitivity. The particular hydrogen sensor used does not require a special fitting, and can detect hydrogen with high sensitivity (50 ppm). The detection can be performed outside the battery, allowing less dependency on the number of cells or modules in a pack, as long as a proper configuration is used. In contrast, a pressure sensor would need to be fit in a tight enclosure, typically in a specific cell or module; therefore, a pressure sensing system would be more complicated and potentially costly. The trade-off in the design is an interesting aspect of this work.

The reliability of Ni–MH battery performance under high rate charging is an important issue. There are many aspects that need to be considered in developing a proper charging strategy. If a battery charger is designed without due diligence to optimize battery performance, often battery life is shortened. Eventually, an optimum design of a battery charger relies upon in-depth knowledge of battery performance with respect to charging condition, but also largely depends on sensitive monitoring and control. Study of Ni–MH battery performance under different charging rates will facilitate implementation of a reliable charge control and monitoring system and the development of a better power control algorithm to precisely utilize such batteries for traction applications.

In this work the performance of Ni–MH batteries designed specifically for traction applications is discussed. A comparative analysis of the performance observed under different charging rates is made. The main focus of the study is to understand the behavior of battery voltage, temperature and gas evolution with respect to charge time, amount of charge input, charge acceptance, and energy efficiency as a function of charging rate. The impact on battery cycle life using this hydrogen sensing approach will be discussed elsewhere.

2. Experimental

Six Saft Ni–MH (Model # NH 12.4) modules designed for electric vehicle applications were used in our experiments. Each of them had ten cells connected in series to provide a nominal voltage of 12 V (1.2 V cell^{-1}) and a nominal capacity of 109 Ah (at 0.3 C rate discharged to 1 V cell^{-1} and at 23 °C). The physical dimensions of each module are 390 mm \times 120 mm \times 195 mm ($L \times W \times H$). All batteries were subjected to the same test condition. The behavior of the modules is quite consistent through the tests.

Battery performance largely depends on temperature, so all tests were commenced at an initial temperature of 23 °C in an electronically controlled environmental chamber. Although each battery has a built-in cooling system, it was not used during the tests in order to measure the battery temperature increases associated with different charging regimes. Battery temperature was measured with a thermistor attached to the cell at the center of the module. A programmable constant current source (Sorensen DHP60-220M1M9D) was used to charge the batteries. A Hewlett Packard HP 6050A programmable electronic load was used for battery discharge in the constant current mode.

Hydrogen emitted from the battery was detected by a Figaro TGS 821 high sensitivity hydrogen gas sensor. Two sensors were placed at different locations near the battery to detect hydrogen released from the open safety valve. This arrangement was used to verify if the hydrogen detection was sensitive to different locations on the battery.

The sensor was used mainly to detect hydrogen presence above a sensitivity level (50 ppm), and it was not intended to measure the concentration level. The output voltage signal from the sensor was used to trigger the end-of-charge termination.

The data acquisition was performed by a Hewlett Packard HP 34970A unit and the data was stored in a PC via an IEEE-488 interface connected to the battery test equipment. The data acquisition and instrumentation control were performed using a custom software application written in LabVIEW™. Fig. 1 shows the setup of the test bench used in the experiments.

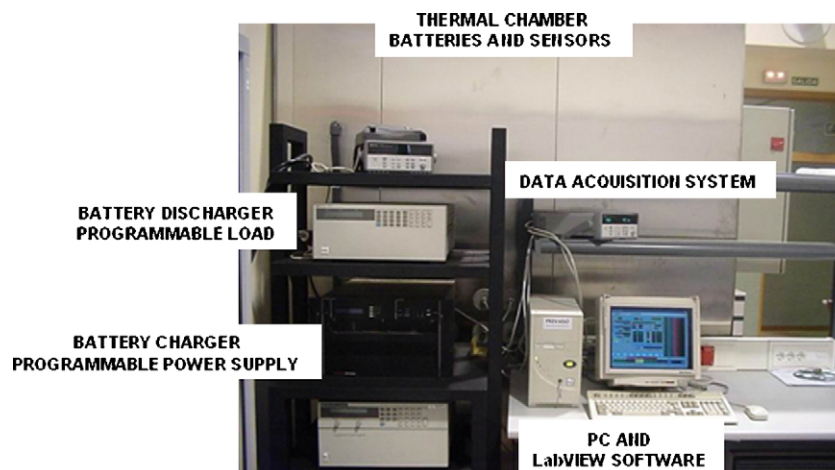


Fig. 1. Picture of experimental setup on the test bench.

Batteries were subjected to repetitive charge–discharge cycles so that their performance under different charge regimes could be studied. Each battery was initially conditioned following the instruction of the manufacturer. The protocol consisted of five cycles of charging at 0.1 C (14 h) and discharging at 0.3 C until 1 V cell⁻¹. The temperature was kept at 23 °C in the environmental chamber.

After conditioning, the batteries were subjected to 0.1, 0.2, 0.5, and 1.0 C charging, which corresponds to 11, 22, 55, and 109 A, respectively. Charging was always started from the totally discharged state (100% DOD). The batteries were sitting in the environmental chamber for sometime to reach 23 °C before commencing charging in all cases. Ten cycles per each charging rate were performed on each battery. Battery performance was reproducible, thus 10 cycles were enough to represent the battery behavior under each specific condition. However, it is difficult to display charge and discharge curves with standard deviations; therefore, in the presentation of the test results, we chose those that are representative with respect to the general trend of the module behavior as the examples in the figures.

The charging data obtained at 0.1 C was used as the benchmark for comparison. In this case the charge process was terminated when hydrogen gas was detected, which is different from the manufacturer suggested protocol.

The discharge rate for all tests was 0.2 C (22 A) and the end-of-discharge was set for the condition when the module voltage reached 10 V (i.e., 1 V cell⁻¹). Before commencing the discharge regime, the battery was sitting in the environmental chamber for a sufficient period of time to reach 23 °C. The temperature control protocol was designed to minimize any contributions from thermal effects. It should be noted that, with this protocol, the determination of capacity and charge acceptance might be affected by self-discharge during the thermal equilibrium.

Charge acceptance is the capacity that can be discharged from the battery versus the charge input supplied during charging as depicted by

$$\eta_c = \frac{\int I_d dt}{\int I_c dt} \times 100\%$$

where I_d is the discharge current and I_c is the charge current.

Energy efficiency is the energy released by the battery during discharge versus the energy supplied to the battery during charge as depicted by

$$\eta_e = \frac{\int (V_d \times I_d) dt}{\int (V_c \times I_c) dt} \times 100\%$$

where V_d is the battery voltage during discharge and V_c is the battery voltage during charge.

3. Results

Fig. 2 shows the battery voltage and temperature changes during a 0.1 C charge terminated by hydrogen detection. There is a marked temperature increase (about 9 °C) before termination by hydrogen detection. Both battery voltage and temperature

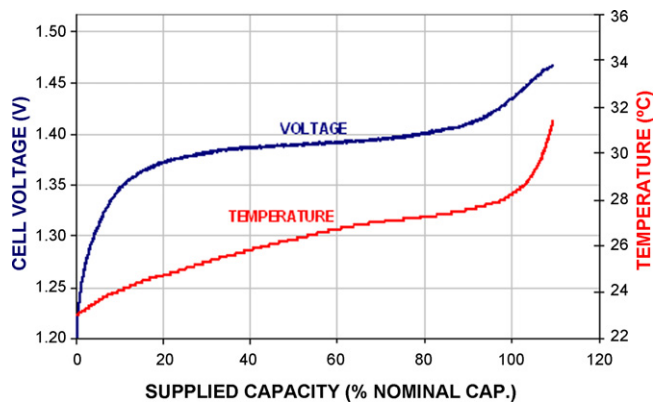


Fig. 2. Battery voltage and temperature curves at 0.1 C and 23 °C.

vary significantly at the end of charging. The end-of-charge voltage is slightly over 1.45 V cell⁻¹. About 10% overcharging to the battery at 0.1 C was measured before hydrogen detection termination. Almost 11 h were needed for charging.

Fig. 3 shows an example of the relationship between battery voltage and temperature at the charging rate of 0.5 C. In this figure, the voltage signal of the hydrogen sensor is also shown. In this experiment, the charging was terminated by the amount of charge input at about 25% overcharge, as it was intended to show the overcharge behavior. The result shows that the hydrogen detection coincides with a rapid battery voltage increase (near the onset of overcharge), and an increase in battery temperature change is noticed. There is a significant hydrogen evolution detected by the sensor right before the onset of overcharge. The charge acceptance before the detection of hydrogen was 96%. The charge acceptance for the entire charging process (with 25% overcharge) reduced to 80%.

Fig. 4 shows the charging curves as a function of charge input at different rates, where the end-of-charge condition was determined by hydrogen detection. Even though the end-of-charge condition is determined by hydrogen detection, the end-of-charge voltage for all cases is in the vicinity of 1.47 V. The amount of charge supplied to the battery under this end-of-charge condition decreases with increasing rate. Fig. 4 shows that the amount of charge supplied at 1.0 C rate is lower than

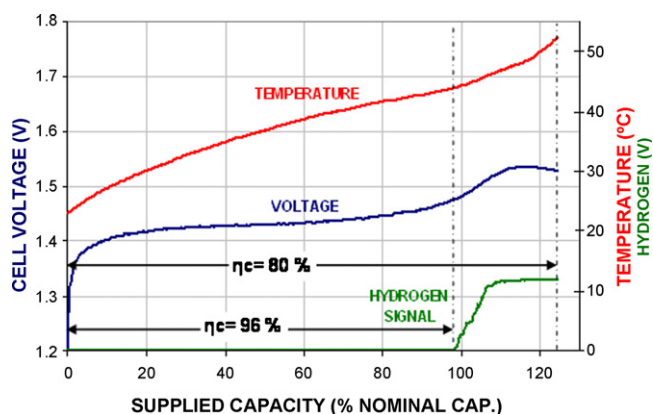


Fig. 3. Curves showing the battery voltage, temperature, and the output voltage signal of hydrogen sensor at 0.5 C and 23 °C. The result shows a 25% overcharge.

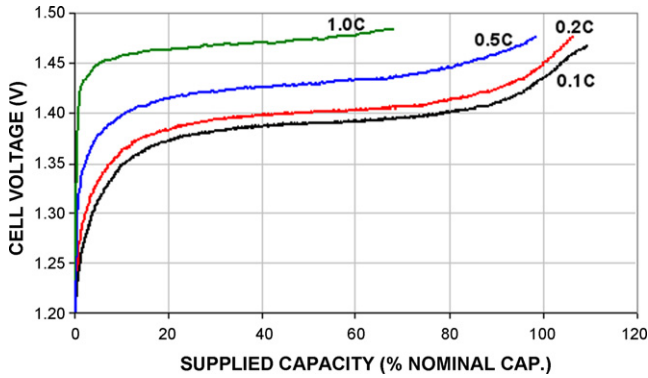


Fig. 4. Charging curves at 0.1, 0.2, 0.5, and 1.0 C, respectively. The initial temperature for all experiments is 23 °C.

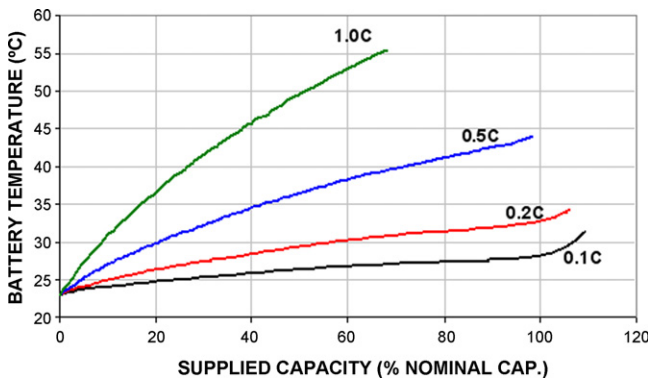


Fig. 5. Battery temperature changes during charging at 0.1, 0.2, 0.5, and 1.0 C, respectively. The initial temperature for all experiments is 23 °C.

70% of the battery nominal capacity, and the charge time is around 40 min.

Fig. 5 shows the temperature change of the battery at different charge rates. With an initial temperature of 23 °C, in all cases the temperature increases with the charge rate.

4. Discussion

Fig. 2 shows that even with this mild condition at 0.1 C rate, the module showed a temperature increase of more than 9 °C. Battery temperature is a major parameter to be considered if irreparable damages to premature failure or ageing are to be avoided. Unlike Ni–Cd, Ni–MH batteries involve more complicated thermal processes [6] that exhibit an overall exothermic phenomenon during charging which leads to a stronger thermal effect even at the rate as low as 0.1 C. This observation prompted the implementation of the thermal equilibrium process before commencing charging or discharging regimes to minimize temperature effect on the charging and discharging behavior. It is also worth noting that as the amount of charge was reaching the nominal capacity and during the overcharging, the temperature change accelerated, implying an increasing involvement of oxygen recombinant reaction, also evidenced by the increase of cell voltage. It should be noted that, to our surprise, hydrogen was detected at this slow rate, which implies that the oxygen recombinant reaction did not consume all the hydrogen evolved in

the negative electrode [7]. As such, the practice recommended by the manufacturer to charge the battery at this low rate for overnight might create adverse effect on battery life due to the loss of hydrogen to the ambient environment.

Fig. 3 illustrates that at 0.5 C the temperature increase was more profound (about 22 °C, if the charge termination were imposed with hydrogen detection). In this particular experiment, as the battery was overcharged, the rollover of the cell voltage typically observed in oxygen recombinant reaction is clearly seen. It is important to point out that conventional charge termination with the detection of dT/dt and/or dV/dt , in this case, will lead to overcharging of the cell substantially.

These experiments also clearly show that the hydrogen from the battery can be easily detected by the sensor. The sensitivity of the sensor can impose a very quick response time for charge termination. It is also possible to set charge termination at different level of hydrogen concentration by tuning the sensitivity level of the sensor, which is useful for optimization of the charging efficiency and for safety.

Fig. 4 shows the dependence of charge input with different rates using hydrogen detection to terminate charge. At slow rates such as 0.1 or 0.2 C the cell overcharging, was limited to less than 10%. At 0.5 C, the cell experienced nearly 100% of input charge, which eventually yielded an optimal charge acceptance close to 96% (Fig. 6). At 1.0 C the charge input was drastically reduced to less than 70%, although the charge acceptance remains high. The figure also shows the voltage changes during charging at different rates. It should be noted that the conventional charge control using dV/dt detection might not work well at higher rates.

Fig. 5 compares the temperature changes with different rates. It is important to point out again that even at the moderate rate of 0.5 C, the detection of dT/dt may no longer be useful for conventional charge control as overcharging will be a serious problem. It is also important to point out that temperature increase for Ni–MH batteries limits the application of high rate charging. Fig. 5 highlights the increase of temperature from the initial 23 to 55 °C (an increase of 32 °C) when hydrogen was detected for 1.0 C rate. This strong temperature increase could also limit the charge input due to the operating temperature limitation. As a matter of fact, the temperature limit given by manufacturer for

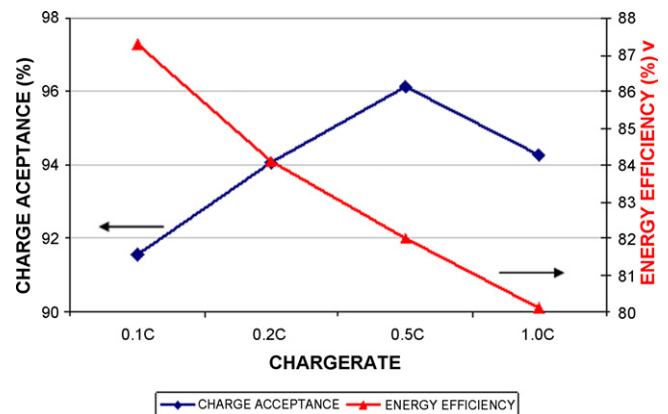


Fig. 6. Charge acceptance and energy efficiency for charging at 0.1, 0.2, 0.5, and 1.0 C and 23 °C.

normal operation condition is 45 °C. For a 1.0 C charge rate, this constraint was reached before hydrogen detection and only about 40% of input charge could be applied to the battery. This situation has deterred us from studying the battery performance at rates higher than 1.0 C.

Fig. 6 summarizes charge acceptance and energy efficiency for different charge rates with hydrogen detection termination. In the case of charge acceptance, the percentage of charge acceptance increases with rate up to 0.5 C then decreases. The optimal rate seems to be in the vicinity of 0.5 C, where the hydrogen detection termination provides the best combination of charge rate and reaction kinetics, when charged from 23 °C and low DOD. If the charge rate increases beyond this rate (e.g., 1.0 C), we suspect that the efficiency decreases because the contribution from the oxygen recombinant reaction might be increased.

In the case of energy efficiency, the trend shows that the efficiency generally goes down with increasing rate. This is consistent with the expectation that the contributions from the oxygen recombinant reaction and ohmic polarization are increasing with rate.

Fig. 7 exhibits the results showing how charging time, capacity and the temperature increase vary with rate. The charging time decreases, while the temperature change increases with rate. The capacity, on the other hand, does not change in proportion with the rate up to 0.5 C. Beyond 0.5 C, the decrease in capacity becomes more apparent. It should be noted that the 100% capacity used in the presentation of the data in the figure was the one obtained from 0.1 C charge, which is the same as the nominal capacity. The charging time (644 min) for the 0.1 C charging is used as the baseline (100% time); therefore, the charging time for other rates are given versus this 0.1 C charging time.

In comparison with charge termination techniques reported by others in the past [4,5], our approach offers some unique contributions. For instance, in comparison with the results reported by [5], we found that our hydrogen detection termination is capable of achieving high performance in terms of charge acceptance and energy efficiency, similar to those using pressure termination, even though the alloy compositions are quite different (AB₂

versus AB₅). For instance, at 1.0 C charging, the results in [5] showed a capacity return of 75% while in ours it is less than 70%. In this case, the charge acceptance reported in [5] was about 94%, almost the same as ours. The energy efficiency reported for 0.25 C in [5] was 82.7%, in comparison with ours at about 84% for 0.2 C charging. Some difference in the effect of temperature change was observed between the two experiments. However, it is difficult to assess the origin of these differences due to many unknowns in the measurements between the two experiments. It is possible that the result may merely reflect the difference in the alloy composition, not necessarily the difference in the termination conditions.

We believe that this hydrogen detection and termination technique brings to light some advantages to fast charging of Ni–MH batteries. For instance, it has been reported by Ikoma et al. [7] that the concentration of hydrogen in the gas mixture increases with charging rate. Furthermore, the hydrogen gas generated at the negative electrode contributes more rapidly to the internal pressure build-up as the charge rate increases. Therefore, this hydrogen detection and termination is particularly useful for high rate charging.

It is important to reiterate the importance and potential benefit of avoiding overcharging to improve battery performance and life. We have discussed previously the comparison in prospects of the overcharging issue between this technique and the conventional dT/dt and/or dV/dt methods. It is important to note that with this hydrogen detection and termination the safety valve was open and gas was released in order to enable hydrogen detection. Therefore, our results showed that even at a low charge rate such as 0.1 C, overcharge was present with our termination technique. Even though the overcharge at this rate is only about 10%, which may still have some undesirable impact on battery life, the results are still an improvement over conventional methods which often lead to higher overcharging. At higher rates, this hydrogen detection and termination technique can prevent overcharging, while the conventional techniques will experience significant overcharging under similar conditions.

5. Conclusion

A unique end-of-charge termination using sensitive hydrogen detection from a chemical sensor outside Ni–MH batteries was used in the evaluation of such batteries for electric vehicle applications. This hydrogen detection approach showed a simple, yet reliable, termination for battery charging at different rates (up to 1.0 C tested). High charge acceptance, energy efficiency, and moderate temperature rise are observed for all rates investigated. The 0.5 C rate was found to be the optimal rate for charging under this type of termination. We compared the benefits of this technique versus other charging methods. Thermal management remains a challenging issue at higher charge rates due to the negative effects they may have on the battery life.

Acknowledgements

The authors would like to thank the Spanish Ministry of Science and Technology (SMST) who provided the funding (Grant:

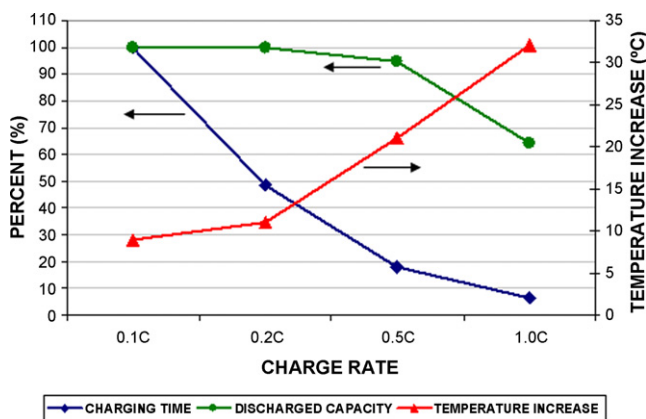


Fig. 7. Charging time for various rates in percentage vs. the charging time at 0.1 C, capacity in percentage vs. the nominal capacity (on the left), and the temperature increase of the battery for different rates from initial temperature of 23 °C (on the right).

MCT-02-TIC-03953) for this work and the State General Office for Universities in SMST for supporting JCV for a Postdoctoral Fellowship at the University of Hawaii from April 2006 to March 2008.

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