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Pulse Charging of Nickel Cadmium Batteries for Lost Capacity Recovery

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Abstract: This study presents an experimental investigation on the effectiveness of pulse recharging technique in recovering the lost capacity of nickel cadmium batteries (NiCad), through a comparison test with the conventional constant-current recharging technique. Scanning Electron Microscope (SEM) analysis has been carried out on the electrodes of both pulse recharged and conventionally recharged NiCad cells after a controlled experimental process to restore the lost capacity due to shallow cycling. The results show that the pulse recharging technique performed equally well with the conventional recharging method in improving the topologies of the cell electrodes and recovering the lost capacity of the NiCad cells. The causes of capacity loss in NiCad batteries have also been investigated and the results obtained established the claim that shallow cycling enhances large and dendritic crystalline growth on the cell electrodes.

Keywords: Capacity loss, conventional charging, nickel cadmium batteries (NiCad), pulse charging

INTRODUCTION

The Nickel Cadmium battery (NiCad) still retains its prominent role in certain niche applications that require very high discharge rates which are beyond the capacity of other battery technologies. Examples of such applications are in portable power tools, emergency lighting, alarm systems and medical instruments. NiCad batteries are normally recharged using conventional constant current rechargers, just like other rechargeable batteries. However, it has been reported that pulse recharging of batteries offers certain benefits over the conventional recharging method. For lead acid batteries, the pulse recharging method reduces the gas evolution rate during the gassing phase of recharging, which in turn leads to a decrease in the rate of battery plate deterioration as reported by James *et al*. (2006) and, Starkey and Lefley (2004). This ultimately extends the life cycle of the battery.

Lam *et al*. (1995) reported that pulse recharging of a lead acid battery offers a reduction in the recharging time by an order of magnitude (i.e., from ~10 h to 1 h) and an increase in cycle life by a factor of three to four. The pulse recharging technique has been found to be an effective means for delaying the crystallisation of the active material during cycling, a major cause of battery capacity loss. Additionally, the application of pulse recharging to a cycled lead acid battery with 80% of the initial ampère-hour capacity can evoke a recovery in the lost capacity.

Zhang *et al*. (2004) have confirmed experimentally that the pulse recharging technique is highly capable of lowering the internal pressure of sealed Nickel Metal Hydride batteries (NiMH) during recharge and overcharge. It was also observed that pulse recharging can slow down the capacity fade rate and prolong the battery life cycle. The advantages of pulse recharging are not limited to lead acid and NiMH batteries alone as it has been reported that the recharging method has positive impacts on the capacity characteristics of lithium-ion batteries. Li *et al*. (2001) reported that pulse recharging of the lithium-ion battery eliminates concentration polarisation and increases the power transfer rate. This lowers the recharging time and improves the active material utilisation, resulting in a higher discharge capacity and a longer cycle life.

In this study, a detailed report of the experimental investigation carried out on the causes of capacity loss in NiCad batteries is presented. Besides, the effectiveness of the pulse recharging technique in restoring the lost battery capacity through a comparative test with the conventional recharging method is also reported.

Causes of capacity loss in NiCad batteries: A number of factors, which are connected with the nickel-oxide electrode and the cadmium electrode, have been attributed to capacity loss in NiCad batteries. The prominent amongst these factors is the formation of crystals of growing size on the battery plates which is observed when the battery is recharged at a low current density in the

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plates. This crystal growth can be enhanced when the battery is subjected to repeated partial discharge and recharge and the recharge occurs at a moderate current rate. Increased crystal size leads to a reduced surface area of the active material which causes an additional voltage drop during discharge. Consequently, the voltage level of the whole discharge curve is reduced and the end-of-discharge voltage is reached earlier, which results in a reduced capacity (Berndt, 1997). Another cause of capacity loss in NiCad batteries with sintered electrodes is the formation of intermetallic compounds (Ni_2Cd_5 or Ni_5Cd_{21}) on the cadmium electrode according to Berndt (1997) and Simic *et al.* (2001). The presence of nickel in the active material is traceable to either corrosion reactions of the substrate during precipitation of the cadmium hydroxide into the sintered substrate, or it might have been added deliberately as a conducting aid and as an expander. A reduction of about 150 mV of the battery voltage during discharge occurs as a result of the intermetallic compounds which discharge at a more positive potential than the cadmium electrode.

Sato *et al*. (2001) reported that the development of γ-Oxy-nickel hydroxide (γ-NiOOH) on the nickel electrode in the charged state after repetitive shallow (charge-discharge) cycling of the cells or overcharging of the cells is also responsible for capacity loss in NiCad batteries. This γ-NiOOH is initially formed at the collector side of the electrode and it later grows into the electrolyte.

MATERIALS AND METHODS

The methodology adopted to carry out an investigation on the negative effects of repetitive partial discharge and recharge on the NiCad battery capacity and the performance of pulse recharging in recovering the lost capacity is divided into three steps:

Control system: This involves developing a control system to serve as a reference for healthy batteries i.e. without capacity loss. In a controlled experiment, ten 4Ah-NiCad D-size sealed cells were fully recharged at 0.5 C rate and discharged at 0.3ºC rate using a conventional battery recharger and constant current discharger. This process of full cycling was repeated three times and the microstructures of the discharged electrodes of a sample from the cells were studied using Scanning Electron Microscope (SEM).

Battery cycling: Twenty 4Ah-NiCad D-size sealed cells were subjected to four different repetitive patterns of shallow discharge and recharge for 1500 times in order to reduce the discharge capacity to 60% of its initial value of 4.63 Ah (which was higher than the nominal stated capacity of 4 Ah). The four shallow cycling patterns comprise the following discharge-recharge processes: 1 Ah to 2 Ah, 2 Ah to 3 Ah, 3 Ah to 4 Ah and 2 Ah to 4 Ah, as presented in Table 1. The cell cycling was carried out at 1ºC charge rate followed by 0.3ºC discharge using a conventional battery recharger and constant-current discharger. In addition, the SEM photographs of the discharged electrodes were captured to examine the level of dendritic crystalline growth, a visual evidence of the capacity loss.

Battery capacity recovery: The capacity loss due to repetitive shallow cycling can be considerably recovered by fully discharging and recharging the cell several times. This process of full recharge and discharge actually destroys the dendritic crystalline growth formed on the electrodes, which is responsible for the capacity loss. The recovery of the lost capacity was implemented using two different recharging techniques:

Conventional full charge and discharge method: Ten of the shallow-cycled cells were fully recharged and discharged five times using a conventional battery recharger and a constant-current discharger until the lost capacity was fully recovered. A recharge rate of 1ºC and discharge rate of 0.3ºC were used under this method which provides an experimental control and a comparison with the other method explained below.

Pulse charging method: The cell capacity recovery process was repeated using a pulsed-current recharger designed to inject a train of high current pulses into the battery at a peak rate of 12ºC and average rate of 1ºC. A second group of ten shallow-cycled cells were fully recharged with the pulse recharger at 1ºC charge rate and fully discharged at 0.3ºC rate.

Furthermore, the performance of the two recharging techniques in recovering the lost capacity of cycled cells was compared and the microstructures of the discharged electrodes were also examined under a scanning electron microscope.

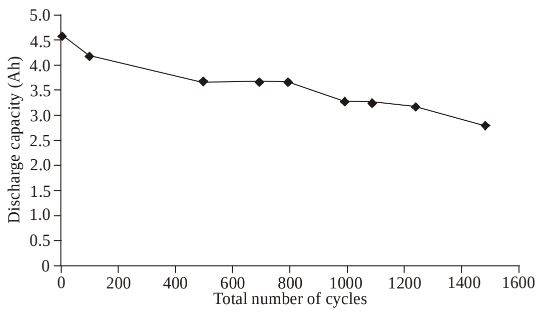
RESULTS AND DISCUSSION

Cell cycling results: Table 1 shows how the discharge capacity of the NiCad cells was gradually reduced to 60% of the initial value of 4.63 Ah by different repetitive patterns of shallow discharge and recharge.

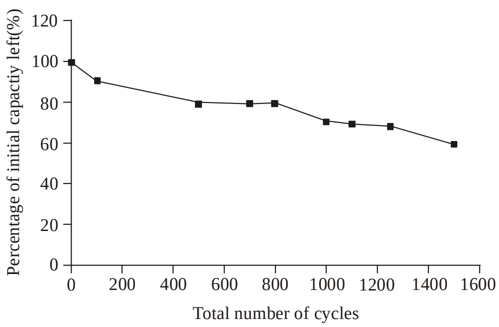
Table 1: Cell cycling results

Total Number Of Shallow Cycles	Cycling Pattern	Discharge Capacity (Ah)	Percentage Of Initial Capacity Left (%)
0	Not applicable	4.63	100
100	2⇔4Ah*	4.22	91
500	2⇔3Ah	3.71	80
700	3⇔4Ah	3.70	80
800	2⇔4Ah	3.69	80
1000	2⇔3Ah	3.30	71
1100	1⇔2Ah	3.25	70
1250	1⇔2Ah	3.20	69
1500	2⇔3Ah	2.80	60

2⇔4Ah* means that the batteries were recharged from 2Ah and discharged 4Ah to 2Ah



(a)



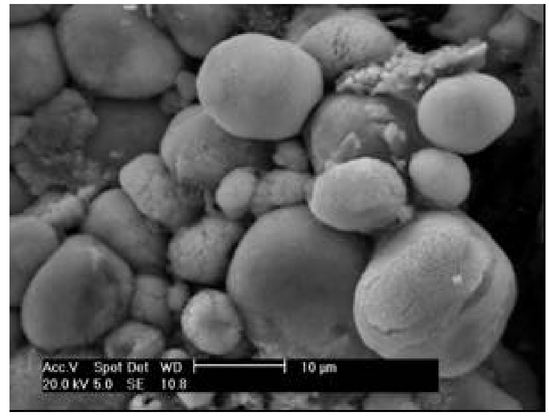
(b)

Fig. 1. Cycling characteristics of the NiCad cells showing, (a) the discharge capacity decreasing due to repeated partial discharge and recharge, (b) the percentage of initial capacity left after shallow cycling of the cells

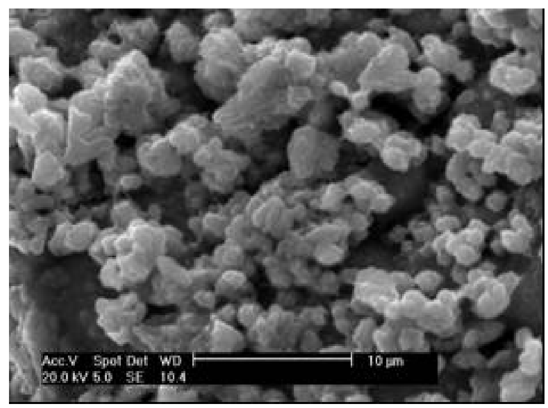
The cell cycling results presented above show a rapid drop in the discharge capacity of the cycled NiCad cells from 4.63 Ah down to 4.22 Ah (i.e., 91% of the initial capacity) after 100 cycles of shallow discharge and recharge. However, it took a further 400 shallow discharge and recharge cycles to reduce the cell discharge capacity to 80% of its initial capacity as shown in Fig. 1b. No additional reduction in the cell capacity was observed after cycling the cells 800 times as illustrated by the flatness of the curves in Fig. 1a. The results also show that a total number of 1500 cycles of partial discharge and recharge was able to reduce the cell capacity to 60 % of its initial value as shown in Fig. 1b.

SEM photographs of the shallow-cycled cells: Visual evidence of capacity loss in the cycled NiCad batteries is presented in Fig. 2 and 3, which show SEM (scanning electron microscope) photographs of the discharged electrodes captured after 1500 shallow cycles compared with the same healthy (un-cycled) electrodes.

Figure 2a shows the presence of nickel hydroxide crystals that have formed on the surface of the nickel electrode of the cycled cell. This crystalline growth is large and globular compared with that observed in the case of a healthy cell shown in Fig. 2b. A similar result was obtained with the cadmium electrodes as large size cadmium hydroxide crystals have formed in the cycled cells (Fig. 3a), compared with the fine crystalline growth in the cadmium electrode of a healthy cell (Fig. 3b).



(a)

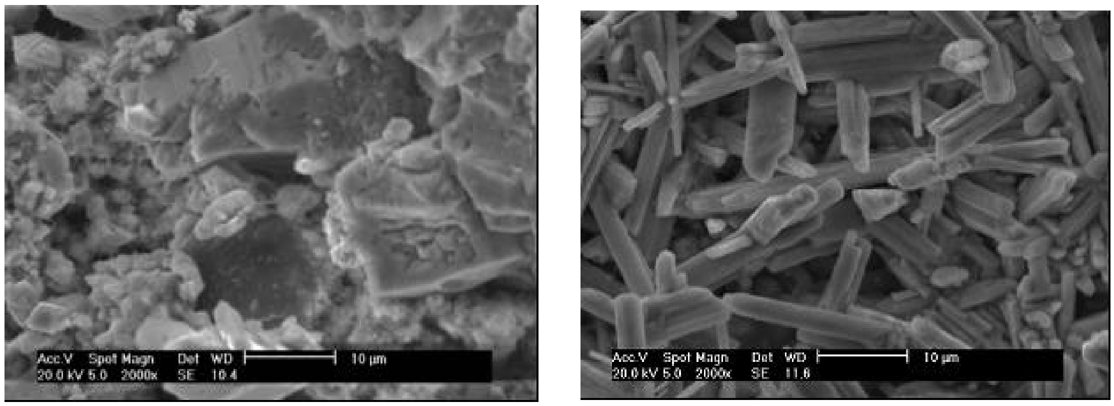


(b)

Fig. 2. SEM photographs of the nickel electrodes of, (a) a cycled cell and, (b) a healthy cell

Results of battery capacity recovery: Table 2 compares the performance of the pulse recharging technique with the conventional constant-current method in recovering the lost capacity of the cycled NiCad cells.

The pulse recharger and the conventional constant-current recharger were both able to fully recover the lost capacity of the shallow-cycled cells after five cycles of full discharge and recharge. Table 2 reveals no significant difference in terms of performance of the two charging techniques in rejuvenating the cycled cells. However, further analysis of the surface topologies of the electrodes of both sets of recovered cells is expected to give more insight into the effects of the two recharging methods on the cells.

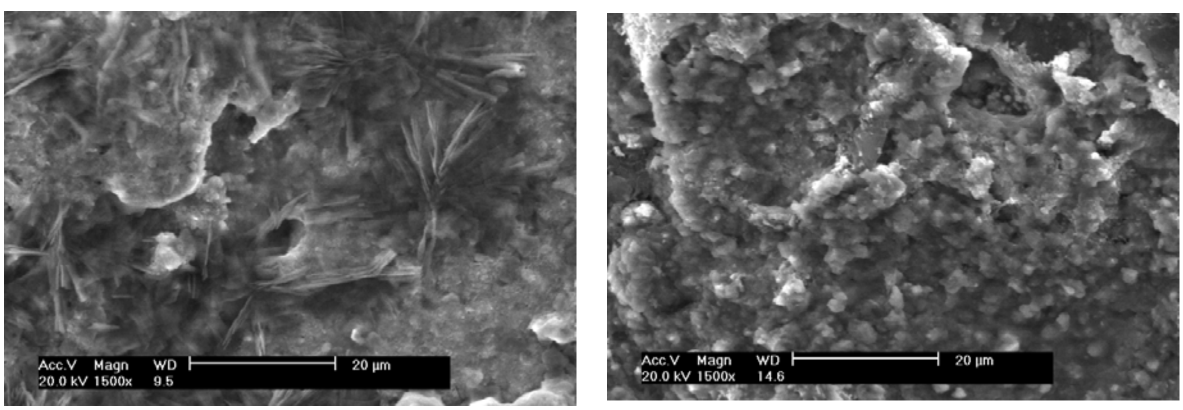


(a) (b)

Fig. 3. SEM photographs of the cadmium electrodes of, (a) a cycled cell and, (b) a healthy cell

Table 2 :Results of cell capacity recovery by pulse recharging and conventional recharging methods

	Pulse charging		Conventional charging	
Deep cycle	Discharge capacity (Ah)	Percentage of initial capacity recovered (%)	Discharge capacity (Ah)	Percentage of initial capacity recovered (%)
First	3.56	77	3.67	79
Second	3.95	85	4.09	88
Third	4.23	91	4.20	91
Fourth	4.52	98	4.50	97
Fifth	4.63	100	4.63	100



(a) (b)

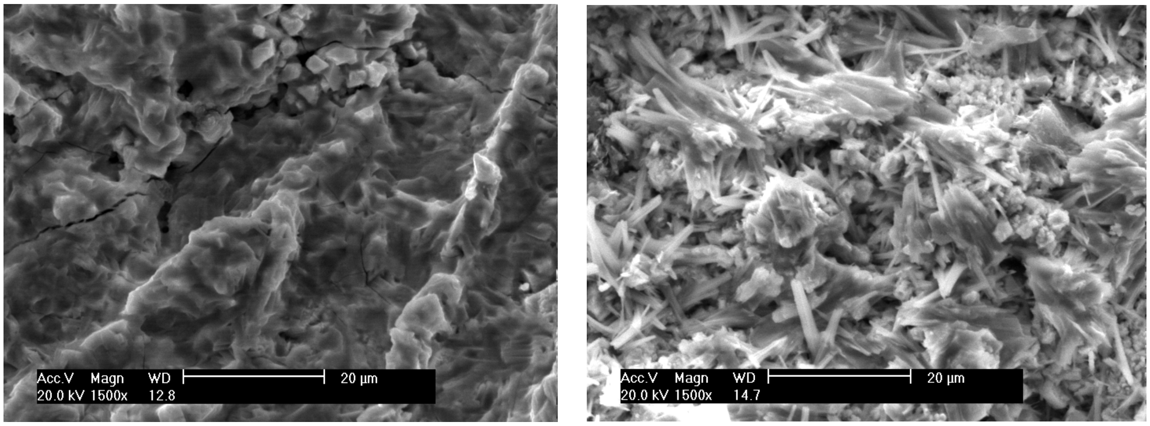
Fig. 4. SEM photographs of the nickel electrodes of, (a) a pulse recharged cell and, (b) a conventionally recharged cell

SEM photographs of the fully-cycled cells: The SEM photographs of the fully-cycled cells are presented in Fig. 4 and 5. A visual comparison can be made on the effectiveness of the pulse recharging and conventional recharging techniques in destroying the undesirable crystalline growth previously formed on the electrodes of the shallow-cycled cells.

The SEM photographs clearly show that the pulse recharging and conventional recharging techniques have considerably improved the electrode surface topologies of the shallow-cycled cells. In terms of performance, the pulse recharging technique compares very well with the conventional recharging technique in rejuvenating both the nickel and cadmium electrodes of the shallow-cycled cells.

CONCLUSION

The negative effects of repetitive patterns of shallow discharge and recharge of NiCad cells on the cell capacity have been presented in this paper. Moreover, the results of the experimental investigation carried out on the causes



(a) (b)

Fig. 5. SEM photographs of the cadmium electrodes of, (a) a pulse recharged cell and, (b) a conventionally recharged cell.

of capacity loss in NiCad cells confirmed that shallow cycling enhances large and dendritic crystalline growth on the cell electrodes. The effectiveness of the pulse recharging technique in recovering the lost capacity of NiCad cells has been analysed in comparison with the conventional recharging technique. The analysis of both the experimental results and the SEM photographs of the rejuvenated cells shows that the pulse recharging technique performed equally well with the conventional recharging method in recovering the lost capacity of the NiCad cells.

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