

Short Communication

Effect of Overcharge on Capacity below 1 V of Nickel/Hydrogen Cells

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The dependence of the capacity of a nickel/hydrogen cell below 1.0 V on the charge rate and temperature has been investigated. Data show that the capacity exhibits a step change for charge inputs in excess of 100%. It is postulated that both chemical and physical changes determine the capacity below 1.0 V.

Introduction

A programme to establish operating characteristics of nickel/hydrogen cells has been devised. This has involved the measurement of charge efficiencies at different charge rates and temperatures (to be reported elsewhere). Under normal circumstances, the discharge is terminated at 1.0 V, but it is well known, at least in qualitative terms, that such cells deliver considerable capacity below this voltage. Thus, discharges have been continued to about 0.5 V, at a lower discharge rate. The capacity below 1.0 V has been measured at different charge rates and different temperatures.

Experimental

Test were performed on a type HRN 36 nickel/hydrogen cell, of nominal capacity 36 A h, that was manufactured by SAFT, France. By fitting a transducer to the cell, the pressure could be monitored under all test conditions. The construction and design details of the cell are given in Table 1.

The cell was charged to 20, 40, 60, 80, 100, 140, 160 and 180% of the nominal capacity and then left on open circuit for 1 h before commencing the discharge. The cell was discharged at the $C/2$ rate (18 A) down to 1.0 V, and then at the $C/5$ rate (7.2 A) to 0.5 V.

Tests were conducted in a thermostatically controlled chamber maintained at 0, 15 or 30 °C. The cell temperature was held constant to within ± 1 °C by mounting the cell on a substantial heat-sink. At each temperature, experimental runs were conducted at charge rates of $C/15$, $C/10$, $C/5$ and $C/3$. In all cases, the discharge rate was that described above.

In this paper, the nominal capacity of the cell, *viz.*, 36 A h is denoted by the term C . All charge/discharge rates are referred to this capacity.

TABLE 1

Details of the nickel/hydrogen cell

Type	HRN 36
Capacity (nominal) (A h)	36
Capacity (actual) (A h)	42
Weight (g)	1090
<i>Positive electrode</i>	
Area (cm ²)	45
Thickness (mm)	0.92
Impregnation	Electrochemical
No. of plates	18
<i>Negative electrode</i>	
Area (cm ²)	45
Thickness (mm)	0.38
Catalyst	36 mg/plate of platinum
No. of plates	18
<i>Separator</i>	
Material	Non-woven polyamide felt
Thickness (mm)	0.32
<i>Electrolyte</i>	
Aqueous KOH	
Concentration (M)	7.3
Density	1.306
<i>Case</i>	
Inconel of 0.51 mm thickness	

Results and discussion

Figure 1(a) shows a plot of the capacity available below 1.0 V at 0 °C, with respect to charge input, given as a percentage of the cell actual capacity. The latter is defined as the capacity of the cell at 15 °C for an input of 180% of nominal ($C/10$ rate) when discharged to 1.0 V at the $C/2$ rate. It can be clearly seen from the data of Fig. 1 that the capacity below 1.0 V shows a marked increase at charge inputs around 100%. This behaviour is the same for all charge rates except that the sharp rise in capacity is delayed as the charge rate is lowered.

Figure 1(b) presents the capacity data collected at 15 °C. The behaviour is similar to that observed at 0 °C. However, the capacity delivered at 15 °C up to 100% charge input is slightly higher, and the influence of the charge rate on the incidence of the capacity step is less noticeable.

The capacities obtained at 0, 15 and 30 °C for a constant charge rate of $C/10$ are compared in Fig. 2. It can be seen that the capacity is highly temperature dependent. In particular, there is a greater difference in the capacity behaviour between 15 and 30 °C than there is between 0 and 15 °C.

There have been several reports in the literature of the formation of γ -NiOOH during overcharge of the positive electrode. This material discharges at considerably lower voltages than β -NiOOH [1 - 3]. It has also been

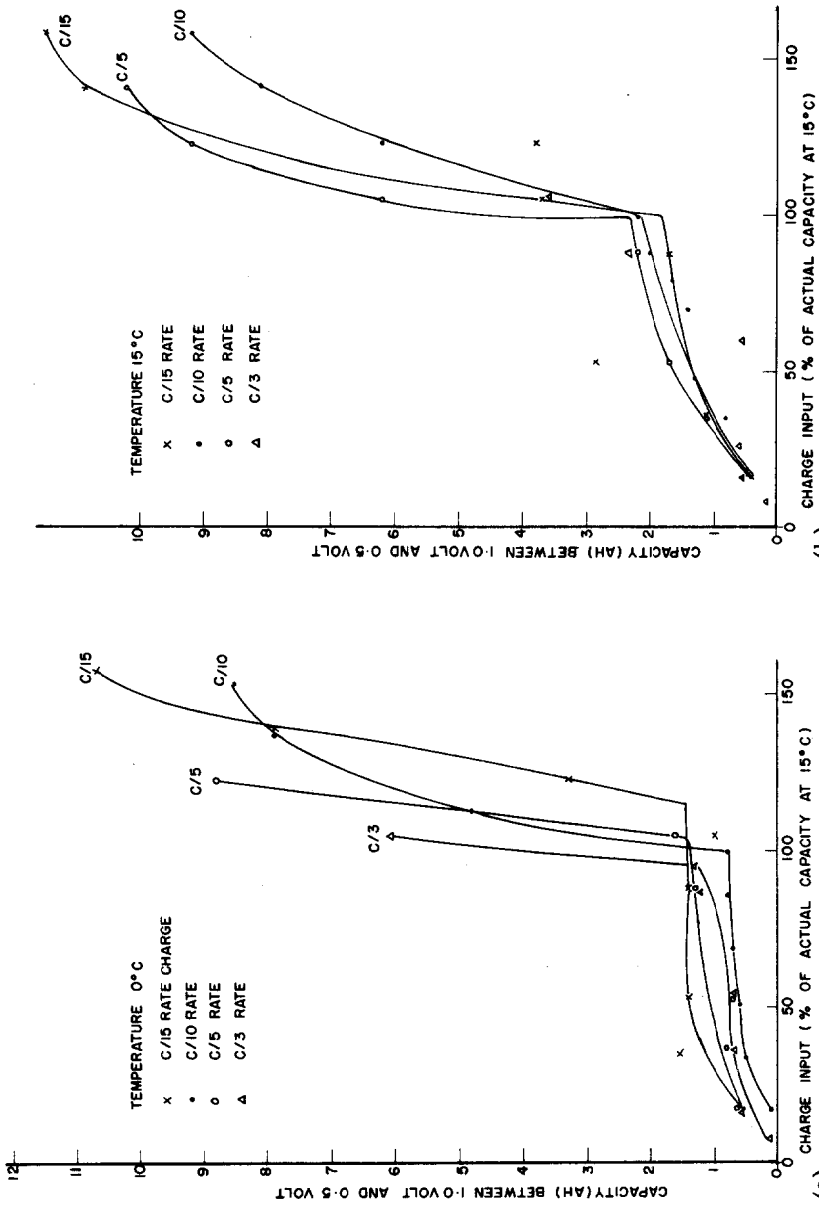


Fig. 1. Capacity between 1.0 and 0.5 V as a function of charge input for different charge rates: (a) 0°C; (b) 15°C.

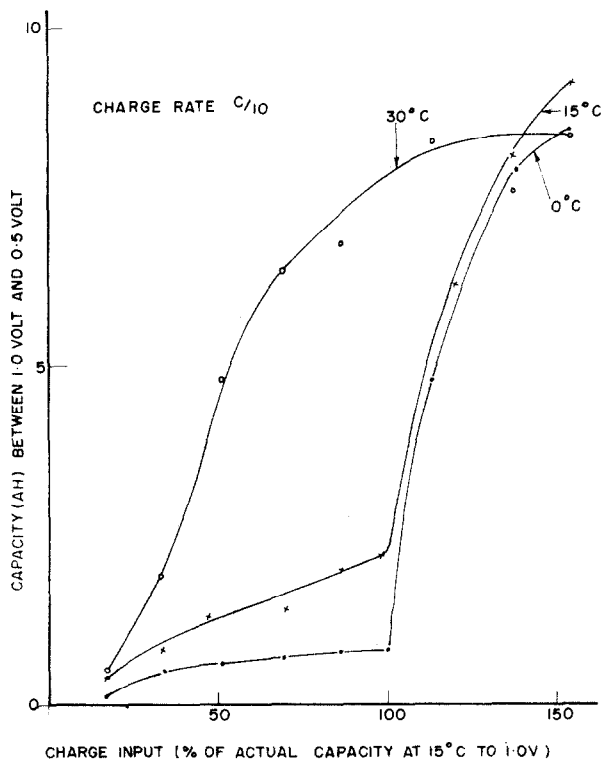


Fig. 2. Capacity between 1.0 and 0.5 V as a function of charge input for a charge rate of $C/10$. Temperature: 0, 15 and 30 °C.

suggested [4 - 5] that adsorbed oxygen, produced during overcharge, accounts for the capacity below 1.0 V. In the work reported here, it has been shown that the species contributing to capacity below 1.0 V have a definite trend in a complete cell. At 0 and 15 °C, the step increase in capacity at 100% charge input indicates that the species responsible do not form to any appreciable extent below this input. Further, since the charge efficiency is greater at higher charge rates, it is clearly obvious that the step should occur earlier, as shown by the data in Fig. 1.

More detailed experimentation is required to establish the identity of the species responsible for the capacity below 1.0 V. However, it is noted that the studies reported in ref. 5 indicate that these species have a low stability and decay rapidly on open-circuit standing.

Another observation that can be made from Figs. 1 and 2 is that the capacity below 1 V approaches a constant value for charge inputs $>100\%$. This suggests that an equilibrium is established between the different species, i.e., β -NiOOH, γ -NiOOH and oxygen.

The end-of-discharge pressures to 1.0 and 0.5 V are plotted as a function of the charge input ($C/10$ rate) for temperatures of 0, 15 and 30 °C

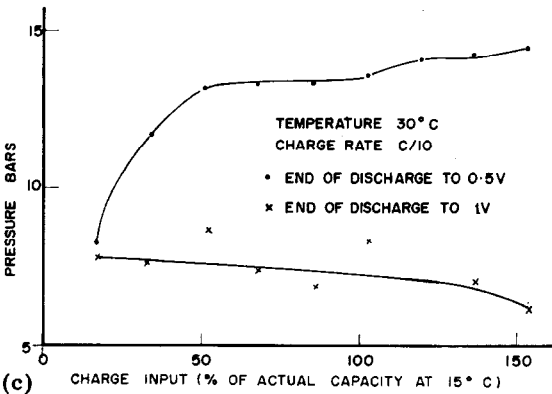
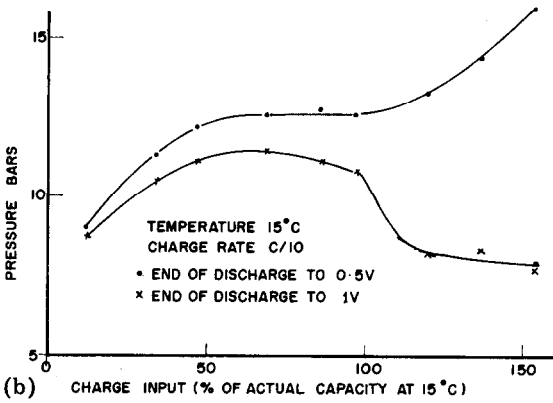
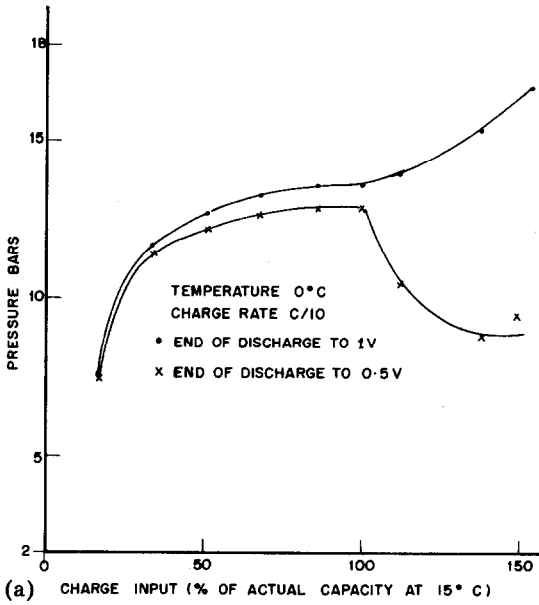


Fig. 3. End-of-discharge pressure at 1.0 and 0.5 V as a function of charge input: (a) 0°C; (b) 15°C; (c) 30°C.

in Fig. 3(a), (b), and (c), respectively. At each temperature, the pressure at 1.0 and 0.5 V increases at about the same rate up to a charge input of 100%. However, beyond this value, the pressure at 1.0 V continues to increase (sharply at 0 and 15 °C), whereas that at 0.5 V decreases (again sharply at 0 and 15 °C). This latter difference in behaviour reflects the difference in cell capacity witnessed earlier (*i.e.*, Fig. 2). However, it is surprising that the pressure at 0.5 V was found to decrease. It could be argued that the pressure was, in fact, constant, and that the capacity between 1.0 and 0.5 V was entirely due to chemical species formed during overcharging of the cell. In this case, the reduction in pressure at 0.5 V indicates that the cell internal polarization is lowered at high charge inputs. This reduction in polarization could be due to various physical changes in the active materials, *e.g.*, finer grains, better adhesion to the base nickel, or better conductivity. Thus, the effect of overcharge should not be attributed exclusively to the formation of different chemical species, but rather the possibility of physical changes in the electrode material should also be considered.

Nickel/hydrogen batteries now being used in satellites are expected to give longer service lives than their nickel/cadmium counterparts. The better performance of nickel/hydrogen batteries is attributed to a greater resistance to abuse from overcharge and or overdischarge. This study shows that much care should be exercised in the overcharge of nickel/hydrogen batteries. For example, γ -NiOOH is known to have a low density, and if produced in large quantities, weakens the sinter reducing life.

Conclusions

From tests on a complete nickel/hydrogen cell, it has been demonstrated that there is a step increase in the capacity below 1.0 V for charge inputs beyond 100%. The dependence of this step on both the charge rate and the temperature has been examined. More detailed investigation is needed to establish the species responsible for this behaviour. However, a notable conclusion is that overcharge may cause physical as well as chemical changes in the active material. These may be responsible for the capacity obtained below 1.0 V.

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