PULSE POWER TESTS ON NICKEL OXIDE ELECTRODES FOR NICKEL–ZINC ELECTRIC VEHICLE BATTERIES

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Summary

In the development of non-sintered nickel oxide electrodes for Ni–Zn electric vehicle (EV) batteries, maintaining adequate power performance was of particular concern. In the systems studied, the power output was limited by the nickel oxide electrodes. Simple pulse power tests were useful in characterizing the power performance in such cells. Although the cell impedance was not a simple resistance, the effective impedance at the end of a high rate discharge pulse had a resistive nature. This simplified the test procedures so that an accurate estimate of peak power could be obtained from one measurement. Measurements of the dependence on state of charge showed that the power output at 50% depth of discharge was representative of the power capability available during discharge.

A method was devised to project power performance expected in a Ni–Zn cell from Ni–Cd cell tests. This was useful in testing the durability of nickel oxide electrodes free from complications due to the degradation of zinc electrodes.

Introduction

Nickel–zinc batteries have been under development at General Motors for electric vehicle (EV) and other automotive applications. Non-sintered nickel oxide electrodes have shown promise as a replacement for more costly sintered nickel oxide electrodes [1]. These electrodes have good specific energy characteristics typically matching or exceeding those for sintered nickel oxide electrodes. However, EV specific power goals are more difficult to meet with this type of electrode. Thus, much research and development effort has been focused on improving the power performance and durability.

This paper focuses on the characterization of the power performance achieved with practical nickel oxide electrodes in nickel–zinc electric vehicle batteries. Power performance can be characterized arbitrarily in a number of

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ways. For example, driving profile testing with the EPA–Urban driving cycle would be a relevant test for the EV application. These tests are experimentally complicated, however, and the data are difficult to analyze. Simpler tests can fulfill important functions needed for the research and development of nickel oxide EV electrodes:

(ii) compare power capability of different electrode types
(ii) monitor any deterioration in power capability during cycling
(iii) estimate the maximum specific power output.

A simple way to achieve these goals is to measure the power output at the end of a constant current, high rate discharge pulse. Such tests have been used to test automotive SLI batteries [2] as well as EV batteries [3, 4]. The present work focuses on how these pulse power tests can best be used to characterize the power capabilities of nickel oxide electrodes.

The power performance of nickel oxide electrodes must be measured in a complete cell. Since these electrodes are being developed for nickel–zinc cells, it is most realistic to test them against zinc electrodes. However, zinc electrodes deteriorate during cycling due to shape change and dendrite shorting. To circumvent these difficulties, it is sometimes useful to substitute more stable negative electrodes such as sintered cadmium electrodes. Power test results from both nickel–zinc and nickel–cadmium cells are discussed here.

Experimental

Power tests were performed with several types of nickel oxide electrodes in several types of cells. Nickel oxide electrodes tested included sintered electrodes (obtained from GE), pasted–rolled-type non-sintered electrodes with expanded metal current collectors, and pasted–rolled electrodes with stabbed-foil current collectors. The fabrication of the pasted–rolled electrodes has been described previously [4]. The nominal capacity of the nickel oxide electrodes was about 10 A h. Electrode dimensions were 16 cm × 16 cm, yielding a surface area of about 250 cm^2 on each side, totalling 500 cm^2 per electrode.

Counter electrodes included zinc electrodes, as described previously [5], and sintered cadmium electrodes obtained from GE. Trielectrode cells with one nickel oxide electrode between two counter electrodes and penta-electrode cells with two nickel oxide electrodes interspersed amongst three counter electrodes were both tested. Cell construction details are given elsewhere [4]. The electrolyte used was 25 wt.% KOH. The formation procedure and cycle regimen were conventional, as described elsewhere [4].

Two types of reference electrodes were used to measure the polarization contributions from the positive and negative electrodes during power testing: cadmium electrodes and Hg/HgO electrodes. The cadmium references were charged 16 cm × 16 cm sintered electrodes placed on the outside of the electrode stack. The Hg/HgO references were external to the cell

making electrical contact through a Teflon tube inserted in the side of the electrode stack.

Direct resistance measurements were performed with a 100 Hz a.c. milliohmeter (Hewlett-Packard Model 4328A) with four point probes attached to electrode tabs.

Results and discussion

The pulse power test

During the pulse power test, a constant current, high rate discharge pulse is drawn from the cell and the power output is calculated from the voltage measured at the end of the pulse. Power output depended on the duration of the pulse and the relaxation time between pulses. Therefore, the pulse length was set at 20 s, a reasonable acceleration time for EV applications. With 20 s current pulses, a 2 min relaxation time between pulses was required to obtain reproducible results.

The cell voltage declined during a discharge current pulse. Figure 1 shows the typical voltage response during a current pulse along with the calculated power output. In this case, the cell polarization increased during the pulse causing the voltage and power output to drop 40% in 20 s. After the pulse, the cell voltage can revert to its initial value only if a sufficient relaxation period is allowed. This time dependent polarization was observed in both nickel–zinc and nickel–cadmium cells. Reference electrode measurements showed it originated primarily in the nickel oxide electrode with the cells studied here. It was observed with each type of nickel oxide electrode. The cause of the time dependence was not determined.

Power profiles

Measurements from one high rate current pulse give the cell power output at that current. However, power output depends greatly on the current drawn. A more complete characterization of power performance is

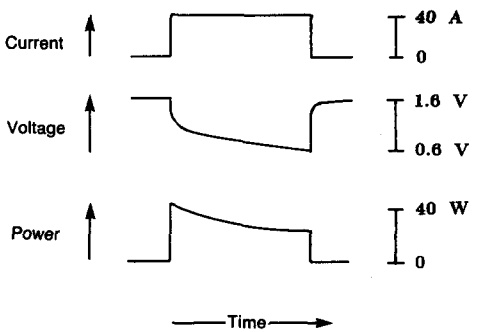

Fig. 1. Typical voltage response and power output during a high rate discharge pulse of 20 s duration. The cell was a trielectrode Ni–Zn cell with a pasted–rolled nickel oxide electrode.

a power profile curve of power plotted as a function of current. Power profile plots can be obtained from a series of pulse power tests at various currents. Examples of such power profile plots are shown in Figs. 2 - 4.

Power profiles obtained here for sintered and pasted–rolled nickel oxide electrodes in Ni–Zn and Ni–Cd cells were all qualitatively similar; they were parabolic in shape. Rates as high as 10 C (1/10 h rate) were required to attain peak power levels. As a result, the power output measured at low rates was not very characteristic of the cell power performance. For example, the peak power of sintered and pasted–rolled electrodes in Fig. 2 differed by about 40%. Yet, the power outputs of the two electrodes at 20 A were essentially identical. Because of the parabolic shape of the power profile plots, the peak power output was characteristic and descriptive of the overall power performance. It will be shown below that the peak power output can be indirectly derived from one pulse power measurement.

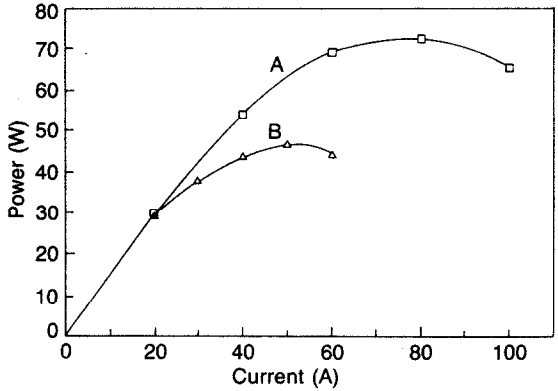

Fig. 2. Initial power profiles for trielectrode Ni–Zn cells at a 50% state of charge. Curve A with a sintered nickel oxide electrode. Curve B with a pasted–rolled nickel oxide electrode.

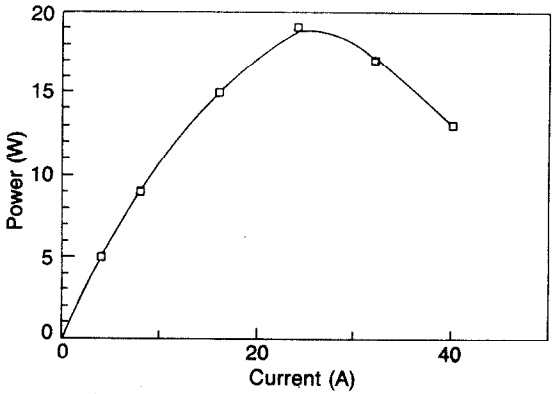

Fig. 3. Initial power profile for a trielectrode Ni–Cd cell with a pasted–rolled nickel oxide electrode at a 50% state of charge.

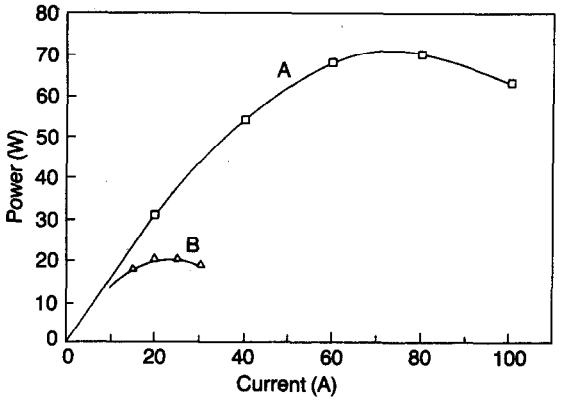

Fig. 4. Power profiles for a pentaelectrode Ni–Zn cell with pasted–rolled nickel oxide electrodes after: A, 1 cycle, B, 82 cycles. Depth of discharge was 50%.

Current–voltage plots

Instead of plotting the power obtained from a series of current pulses to obtain a power profile, the data can be presented in the more basic form as a current–voltage plot where the voltage at the end of the 20 s pulse is plotted directly as a function of current drawn. The open circuit voltage can be plotted at zero current. The results of Fig. 4 are replotted as current–voltage plots in Fig. 5. Other typical current–voltage plots are shown in Figs. 6 and 7.

The shape of a current–voltage plot is diagnostic of the source of polarization losses in a cell [6]. Three cases can be distinguished: rate control by activation overpotential, by mass transport limitations, and by ohmic losses. Linear current–voltage behavior is characteristic of ohmic losses. In this study, the Ni–Zn and Ni–Cd cells with both sintered and pasted–rolled nickel oxide electrodes all showed linear current–voltage curves, as shown in Figs. 5 - 7. Thus, the high rate behavior of these cells exhibited character-

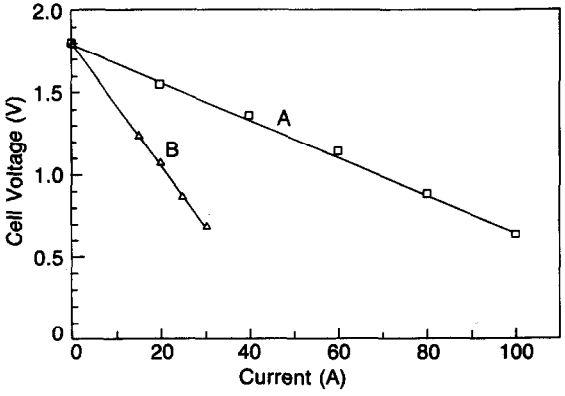

Fig. 5. Current–voltage plots for a pentaelectrode Ni–Zn cell with pasted–rolled electrodes after: A, 1 cycle, B, 82 cycles. Depth of discharge was 50%.

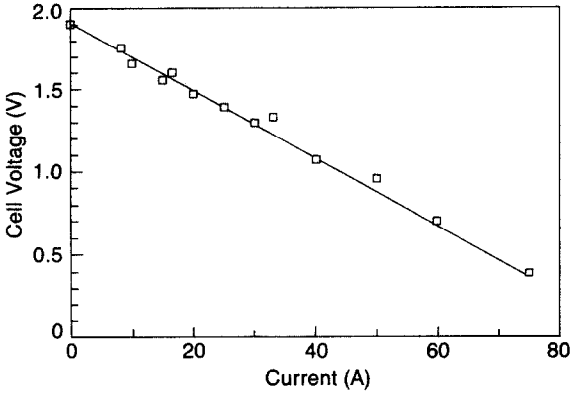

Fig. 6. Current–voltage plot for a trielectrode Ni–Zn cell with a sintered nickel oxide electrode in the fully charged state.

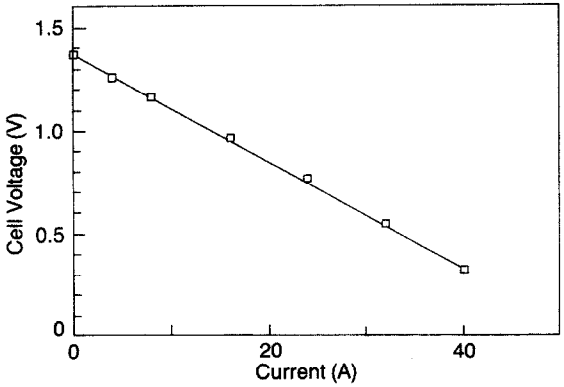

Fig. 7. Current–voltage plot for a trielectrode Ni–Cd cell with a pasted–rolled nickel oxide electrode at a 50% state of charge.

istics of rate control by resistive losses. The cell impedance was not a simple resistance, however, because it was time dependent during the current pulse. Nonetheless, the effective cell impedance at the end of the 20 s current pulse behaved like a resistance.

There were two conditions where the current–voltage curves deviated from linearity. First, if the relaxation time between pulses was too short, measurements during each succeeding pulse reflected a lower overall power performance. For example, when a "staircase" pulse waveform was applied (no relaxation time), the current–voltage plot exhibited a definite downward curvature [7]. A second deviation from linearity occurred in cells at a low state of charge. The power performance of such cells was strongly dependent on state of charge. Thus, successive pulse power tests reflected the declining power capability resulting as additional capacity was withdrawn during the power tests.

Peak power capability

It was possible to calculate the peak power capability from one pulse power test because of the ohmic behavior exhibited in the current–voltage curves. With a purely resistive load, the maximum power output is given by:

$$P_{max} = E^2/4R \quad (1)$$

where E is the open circuit voltage and R is the effective resistance. The effective resistance (the inverse of the slope in the current–voltage plots) can be determined from the open circuit voltage and the voltage at the end of one pulse power test. The maximum power output can then be calculated according to:

$$P_{max} = E^2I/4(E - V) \quad (2)$$

where I is the current drawn during the pulse and V is the voltage measured at the end of the pulse.

For cells of the type in this study, eqn. (2) provided a good estimate of peak power from one pulse power measurement. It was an excellent approximation when the pulse current was chosen so that the actual power output is near the maximum (*i.e.*, the voltage drops to half the open circuit value). Obtaining the peak power from one pulse measurement is simpler and quicker than a complete set of power profile measurements. Another advantage is that the capacity discharged during one pulse is less. This is especially useful in measuring the dependence of power on the state of charge. Peak power determinations from one current pulse using eqn. (2) were also very useful in measuring the deterioration in power capability during cycling where numerous tests were required.

Direct resistance measurements

The cell impedance was clearly not a simple resistance. Nonetheless, the ohmic nature of the effective impedance at the end of the discharge pulse suggested that direct resistance measurements with a milliohmeter might provide a useful characterization of the cell power capability if only for comparison purposes. To examine this, the cell resistance was measured directly with a milliohmeter and compared with the effective resistance exhibited in the pulse power tests as calculated from eqn. (1). A comparison of these results is given in Table 1. The resistance as measured with the milliohmeter was, in all cases, significantly lower than the effective resistance derived from pulse power tests. Furthermore, the trends were not the same and a significant deterioration in power output after extended cycling was not as apparent in the milliohmeter results. These discrepancies are another indication that the cell impedance is not a simple resistance. As a result, the power capability cannot be determined accurately from direct resistance measurements with a milliohmeter.

Reference electrode measurements

In the Ni–Zn and Ni–Cd cells studied here, the strong dependence of power capability on the type of nickel oxide electrode suggested that that

TABLE 1

Direct milliohmeter resistance measurements compared with resistances calculated from power tests

Cell	Cycles	Peak power (W)	Resistance (ohms)	
			Calculated	Measured
NiZn-1	10	45	18	13
NiZn-2	10	44	18	15
NiZn-3	10	49	17	13.5
NiZn-4	10	37	22	14
NiZn-5	100	18	45	18.5
NiZn-6	100	18	45	20

electrode determined the cell power performance. Reference electrode measurements have confirmed this. The polarizations at the nickel oxide electrode and the counter electrodes were measured against two types of reference electrodes: sintered cadmium electrodes and Hg/HgO electrodes. The result was the same for sintered and pasted-rolled nickel oxide electrodes in the variety of Ni–Zn and Ni–Cd cells tested here; the polarization was highest at the nickel oxide electrodes indicating that they were limiting the power output.

Typical polarization measurements are shown in Figs. 8 and 9. Figure 8 shows that the polarization at the nickel oxide electrodes was higher than the polarization at the zinc electrodes in a pentaelectrode Ni–Zn cell. At the 50 A peak power current, the nickel oxide electrode polarization was over 6 times that of the zinc electrode polarization. Figure 9 shows, likewise, that the nickel oxide electrode polarization was substantially higher than that of the cadmium electrode polarization in a trielectrode Ni–Cd cell.

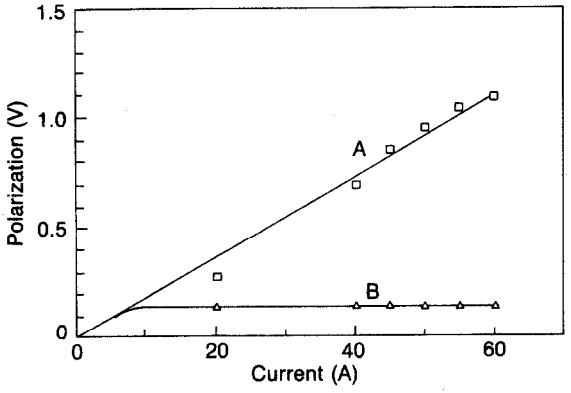

Fig. 8. Polarization measurements in a pentaelectrode Ni–Zn cell for the nickel oxide electrode, A, and the zinc electrode, B, using a sintered Cd reference.

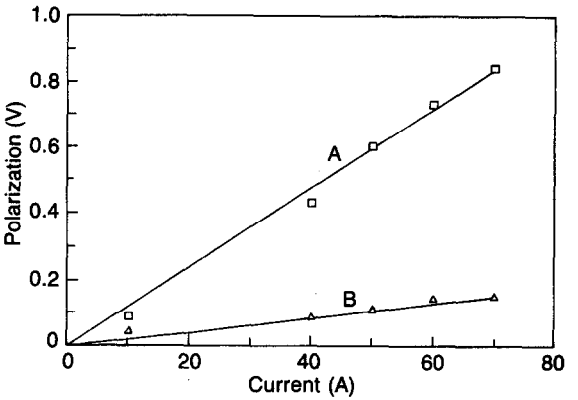

Fig. 9. Polarization measurements in a trielectrode Ni–Cd cell for the nickel oxide electrode, A, and the cadmium electrode, B, using an Hg/HgO reference.

Comparing Ni–Cd results

While reference electrode measurements were useful in determining that the nickel oxide electrode limited the power output of our cells, the best way to determine the power capability for our applications was to measure this directly in Ni–Zn cells. However, some power measurements were carried out in Ni–Cd cells to avoid complications due to the zinc electrodes. When tests were carried out with these cells, it was useful to estimate the power the nickel oxide electrodes could generate in a Ni–Zn cell for comparison purposes.

In the last section, it was shown that the impedances of the zinc and cadmium counter electrodes were similar and small in comparison with the nickel electrode impedances. Thus, the higher power generated by nickel oxide electrodes in Ni–Zn cells is primarily due to the cell voltage being 0.40 V higher than in comparable Ni–Cd cells. The power that a nickel oxide electrode could generate in a Ni–Zn cell can be calculated by so-adjusting the cell voltage upward. Adjusted power profile results projected for a Ni–Zn cell are compared to the Ni–Cd results in Fig. 10. Note that the parabolic shape is retained while both the peak power and the current required to produce the peak power are shifted upward. The peak power that could be generated in a Ni–Zn cell can also be calculated directly from Ni–Cd peak power results. Equation (2) shows that these peak powers ratio as the squares of the open circuit voltages according to:

$$\frac{P_{max}(\text{Ni–Zn})}{P_{max}(\text{Ni–Cd})} = \frac{E^2(\text{Ni–Zn})}{E^2(\text{Ni–Cd})} = \frac{1.7^2}{1.3^2} = \sim 1.7 \qquad (3)$$

where the open circuit voltages can be estimated to be 1.7 and 1.3 V for Ni–Zn and Ni–Cd cells, respectively.

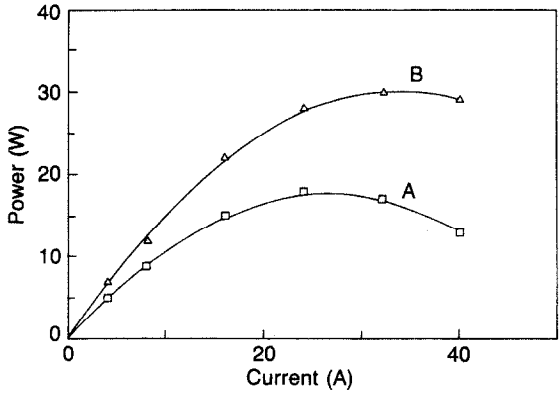

Fig. 10. Projection of power to be generated in a trielectrode Ni–Zn cell, B, estimated from Ni–Cd results, A.

State of charge effects

The power capability of nickel oxide electrodes in Ni–Zn and Ni–Cd cells declined during discharge. This dependence on state of charge was most pronounced with non-sintered type nickel oxide electrodes. Typical plots of peak power *versus* depth of discharge are shown in Figs. 11 and 12. These plots resemble discharge curves and the most rapid drop in power output is near the end of discharge. Not only did the power output depend on the state of charge, but there was also an hysteresis in this dependence. For example, a cell with a 50% charge input will give a higher power output than one that has been discharged 50% of its capacity. This is illustrated in Fig. 13.

Results here show that the state of charge must be carefully specified and controlled to get meaningful power results. If measurements are to be taken at one state of charge, the 50% depth of discharge is recommended

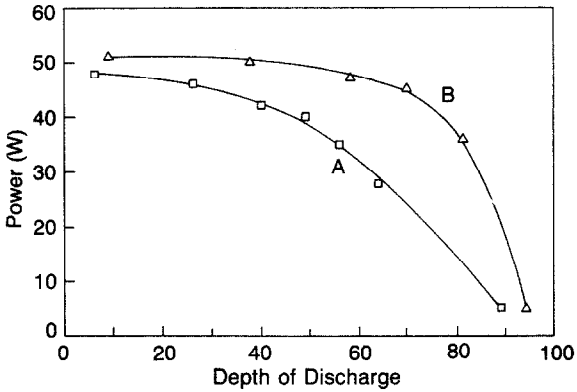

Fig. 11. Peak power output as a function of depth of discharge for trielectrode Ni–Zn cells: with a pasted–rolled nickel oxide electrode, A, with a sintered nickel oxide electrode, B.

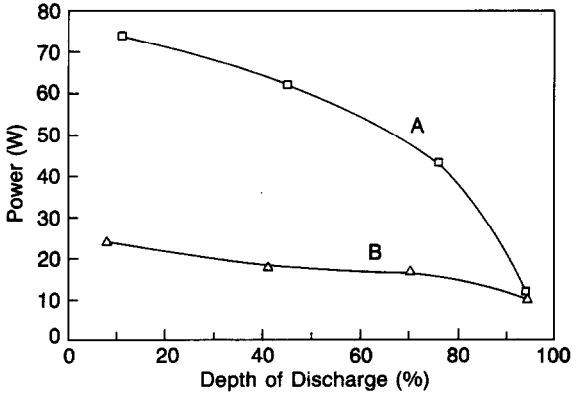

Fig. 12. Peak power output as a function of depth of discharge for pentaelectrode Ni–Zn cells with pasted–rolled nickel oxide electrodes: after 17 cycles, A, after 82 cycles, B.

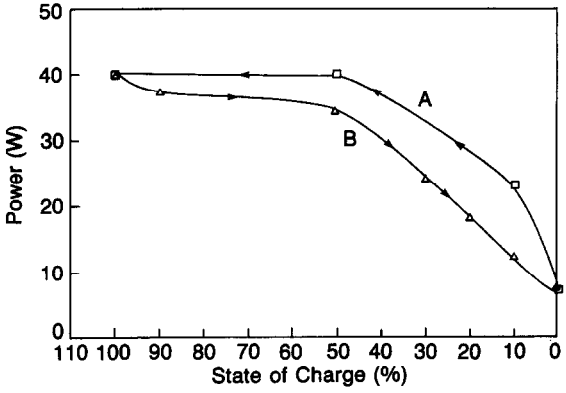

Fig. 13. Peak power output as a function of state of charge of a pasted–rolled nickel oxide electrode in a trielectrode Ni–Zn cell during charge, A, and during discharge, B.

because it is representative of the power available during discharge and the power output is less dependent on state of charge in this region.

Power fade

Sintered nickel oxide electrodes of the type developed by the Delco-Remy Division of General Motors generally show no degradation in power capability during the cycle life of Ni–Zn batteries (typically 300 - 500 deep discharge cycles). However, the power capability of non-sintered nickel oxide electrodes typically degrades to levels not useful for automotive purposes in a fraction of this lifetime. This deterioration in power capability, termed "power fade", is evident in the results of Fig. 4. A major thrust of work at General Motors Research Laboratories has been towards solving the power fade problem. Future publications will deal with the significant progress made in this area [8].

Conclusions

Several general results here applied to a variety of Ni–Zn and Ni–Cd cells with sintered and pasted–rolled nickel oxide electrodes being developed for Ni–Zn EV batteries:

(i) the power output was limited by the nickel oxide electrodes in the cells studied;

(ii) the cell impedance displayed during the pulse power test was not a simple resistance, but the effective resistance at the end of each pulse showed ohmic behavior;

(iii) as a result, the power performance of these cells could be completely characterized by a peak power output obtained from one pulse power test;

(iv) the power output was dependent on the state of charge of the nickel oxide electrode. There was also a hysteresis in this dependence during each charge/discharge cycle. The peak power output at 50% depth of discharge was a good measure of the power that could be withdrawn during discharge;

(v) results obtained in Ni–Cd cells were related to Ni–Zn pulse power results. Thus, Ni–Cd results could be adjusted to project the power output in comparable Ni–Zn cells. In this way the nickel oxide electrode power capability in Ni–Zn cells could be monitored without complications due to degradation of the zinc electrodes.

The results here were especially useful in the development of non-sintered nickel oxide electrodes for Ni–Zn EV batteries. The pulse power tests were a useful tool in efforts to improve the power performance in these cells.

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