

A method of cobalt addition to improve nickel plaque electrode performance

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Abstract

The addition of cobalt to the surface of aerospace-quality sintered nickel plaque was observed to improve plate performance. Initially, substitution of cobalt metal powder for 5% of the nickel powder in sintered nickel plaque improved electrode performance during cycling in a LEO regime at 80% DoD in a boilerplate cell. A soak/resinter method was developed to reduce the amount required and limit cobalt addition to the plaque surface. A boilerplate cell containing these cobalt-enhanced nickel plates had higher capacity utilization than a 50 A h NiH₂ cell containing electrodes made from standard sintered nickel plaque over the temperature range –10 to +20°C. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The addition of cobalt and other ions to the nickel electrode has been studied extensively. Several review articles have discussed the effects of ions on nickel electrode performance [1–4]. Information in the literature indicates that addition of cobalt to the active material by co-precipitation with nickel hydroxide active material has several positive effects on electrode performance [3]: (1) charge efficiency improves, especially at higher temperatures; (2) electrode swelling is reduced; (3) the number of formation cycles required is reduced; and (4) the oxygen overpotential is increased. The addition of cobalt also reduces the working potential of the electrode slightly [5], increases reversibility of the Ni(II)/Ni(III) redox potential [6], and decreases the effect of iron poisoning (capacity loss) to a level similar to that observed in lithiated electrolytes [5].

Cobalt is beneficial for plate performance when additions are made to the plaque, or plaque surface, and to the electrode surface. Cobalt addition to the nickel screen substrate showed improved bonding between the screen and the sintered nickel powder [7]. Addition of cobalt to

the nickel plaque as a nickel–cobalt alloy was suggested as a way to reduce corrosion of nickel plaque, thereby improving the nickel electrode performance and extending the life of nickel–cadmium batteries [8]. The beneficial effects of cobalt appear the same irrespective of whether cobalt is co-precipitated with nickel hydroxide or added by some treatment to the electrode surface. In one study [9], electrodes were prepared by the electrochemical impregnation (EI) method in a bath containing only nickel nitrate and subsequently treated by electrochemical deposition in a cobalt nitrate solution after the impregnation. Cycling test results indicated that the utilization behavior of these electrodes, with only the cobalt surface treatment, was comparable to results with electrodes previously impregnated by electrochemical co-precipitation of both nickel and cobalt hydroxides, followed by the cobalt surface treatment.

Nickel sinter corrosion occurs normally at the nickel sinter/active material interface of a nickel plaque electrode during life cycling in, e.g., a NiH₂ cell cycling under Low Earth Orbit (LEO) conditions. The occurrence of sinter corrosion results in an increase of H₂ pressure and gradual buildup of an additional layer of essentially pure active nickel hydroxide material at the interface. As a result, plate performance decreases due to an increase in resistance at the sinter/active material interface. However,

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if cobalt (or a cobalt–nickel alloy) is present at the interface, it will be incorporated into the corrosion layer as it develops and minimize the expected buildup of resistance at the interface [10]. As a result, the plate should maintain a high level of capacity utilization and minimize the buildup of residual capacity, recoverable only at low discharge rates.

In one study [11], the cobalt content in the active material was increased above the nominal level of cobalt close to the interface with the current collector, i.e., at the nickel sinter surface in contact with the active material. This distribution creates a positive cobalt gradient, in which the cobalt concentration at the interface is greater than it is at a distance from the interface. As a result, plate performance improved early in the nickel electrode life, up to 10% in comparison to an electrode containing a nominal level of cobalt throughout the active material. However, the positive cobalt gradient approach may not be adequate later in life when sinter corrosion is expected to occur, especially during high rate cycling applications.

This paper discusses the development of a new method for cobalt addition to improve nickel electrode performance. Cobalt-enhanced electrodes were fabricated by addition of cobalt powder to sintered nickel plaque, by the positive gradient method [11] and by a soak/resinter method [12]. The electrodes were compared with standard aerospace-quality nickel electrodes in boilerplate cells.

2. Experimental

2.1. Fabrication of nickel electrodes

All sintered nickel plaque fabrication and nickel electrode processing steps were carried out in Yardney's Nickel–Hydrogen Battery Production Facility. Initially, cobalt-enhanced nickel electrodes were fabricated from nickel plaque made with a slurry containing 5 wt.% cobalt metal powder.

Cobalt-enhanced plaque masterplates were prepared by soaking standard nickel plaque in 2.0 M $\text{Co}(\text{NO}_3)_2$ solution for a period of 30 to 60 s at a temperature of 80°C. The wet plaque was air-dried for 24 h, then oven dried at 70°C for 2 h and resintered at 700°C in a reducing environment [12]. Cobalt-enhanced and standard plaque masterplates were electrochemically impregnated with $\text{Ni}(\text{OH})_2$ active material using an aqueous nickel nitrate bath containing 4 to 5% of $\text{Co}(\text{II})$ ion, based on the nickel ion concentration. These were then converted in a 15% KOH electrolyte to a rechargeable crystalline structure and given several formation cycles in 31% KOH electrolyte.

Nickel electrodes with a positive cobalt gradient [11] were fabricated by modification of the EI procedure. Standard nickel plaque was electrochemically impregnated for 5 min in a 1:1 molar mixture of a cobalt–nickel nitrate

electrolyte and converted before continuing with the normal EI procedure in the standard bath electrolyte.

2.2. Assembly of boilerplate cells

Boilerplate cells were assembled from either standard or cobalt-enhanced nickel electrodes and standard aerospace quality hydrogen electrodes using cut-down cores, end plates and other hardware for standard aerospace-quality 50 A h cells. The dual separator was a combination of Zircar and reconstituted asbestos separator components. The anode and cathode tab bundles were bolted to 1/4" diameter nickel terminal feed-throughs in the cover. The 3/4" thick cover with terminals, pressure gauge and inlet valve for electrolyte activation and hydrogen gas addition was bolted to the boilerplate cell case (3/4" wall) with an O-ring seal. Boilerplate cell components were activated with 31% KOH electrolyte in a starved condition. The H_2 pressure of a fully charged cell was adjusted to 900 psi.

2.3. Voltammetry

Cyclic voltammetric evaluation of boiler plate cell nickel electrodes was performed using a PAR Model 173 potentiostat outfitted with a Model 175 universal programmer and a Hg/HgO reference electrode in a cell containing 31% KOH electrolyte.

3. Results and discussion

3.1. Comparison of cobalt-containing plaque with standard plaque electrodes

Boilerplate cells containing four working pairs of nickel and hydrogen electrodes were cycled at 80% DoD in a LEO regime, 60 min charge followed by a 30 min discharge, to compare standard production plates with plates made with 5% cobalt-containing plaque. As shown in Fig. 1, the standard plaque and cobalt plaque plates were cycled for 1275 and 2000 cycles, respectively, before the end of discharge voltage fell below 1.0 V. Scatter in the cell voltage vs. cycle number values was due to instrumental variations with the cycler, line voltage and temperature fluctuations. These results suggest that the presence of cobalt in the nickel sinter improves the high rate cycle life of aerospace quality nickel electrodes. Supporting evidence is further provided by a comparison of cyclic voltammograms for cycled and non-cycled plates of both the standard and cobalt-containing plaque types as seen in Figs. 2 and 3, respectively. A large increase was observed in the slope of the voltage vs. current curve, i.e., plate resistance, during both charge and discharge for a cycled standard plate, as seen in Fig. 2, thereby revealing the extent of degradation which occurred during high rate cycling. The

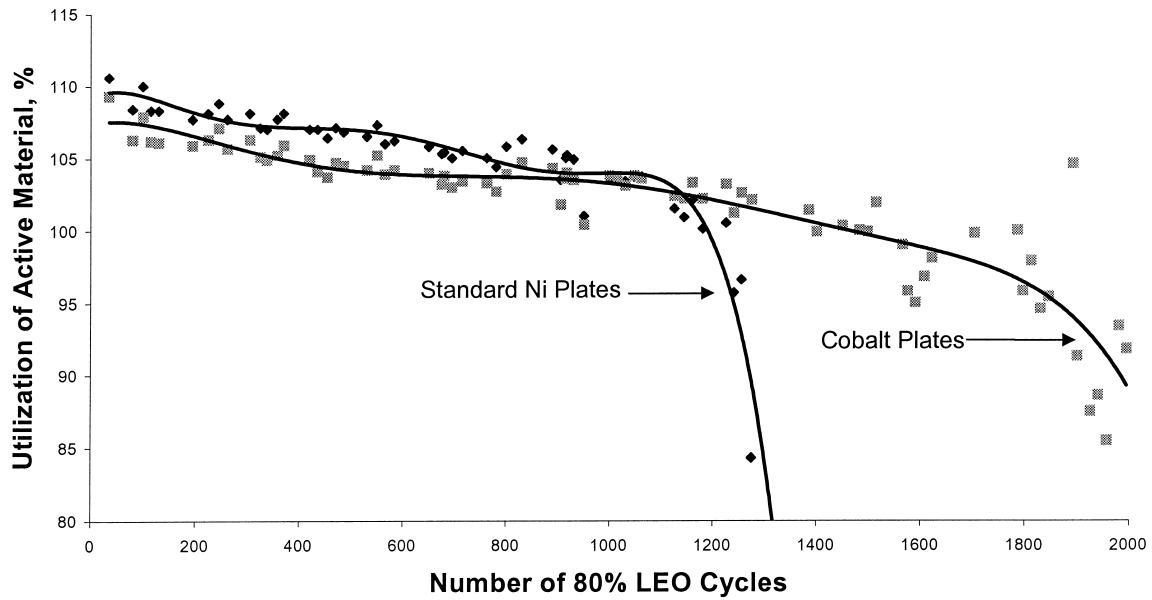


Fig. 1. Capacity vs. cycle number for boilerplate cells containing nickel electrodes made from standard plaque or plaque made with 5 wt.% cobalt metal powder.

increase in plate resistance also caused an increase in the separation of the charge and discharge peak voltages. By comparison, the cycled nickel plate made from cobalt-containing plaque in Fig. 3 looks similar to a non-cycled cobalt-containing plaque plate. Thus, the improved performance observed with plates made from cobalt-containing plaque may be attributed to the presence of cobalt at the sinter/active material interface where it helps maintain a

low interfacial impedance during extended periods of high rate cycling.

The improvement in high rate LEO cycling observed for nickel electrodes fabricated from cobalt-containing plaque is also supported by the results of a more recent study with lightweight nickel plaques for aerospace-quality electrodes. In that study [13], a special nickel Fibrex[®] with nickel and cobalt powders added to the fiber (50 parts

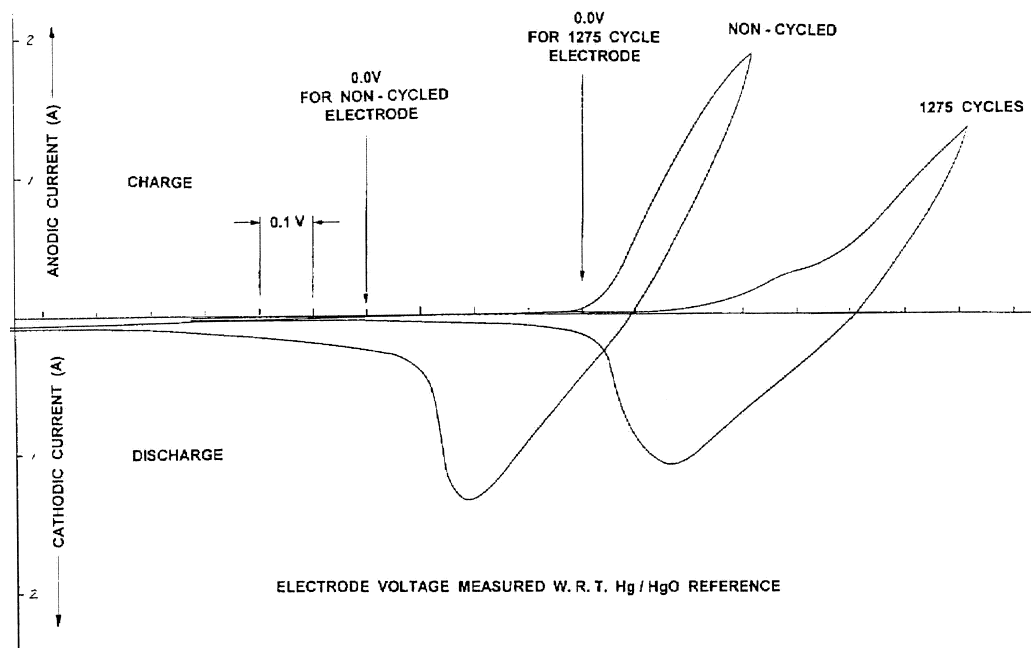


Fig. 2. Cyclic voltammograms for cycled and non-cycled standard nickel electrodes.

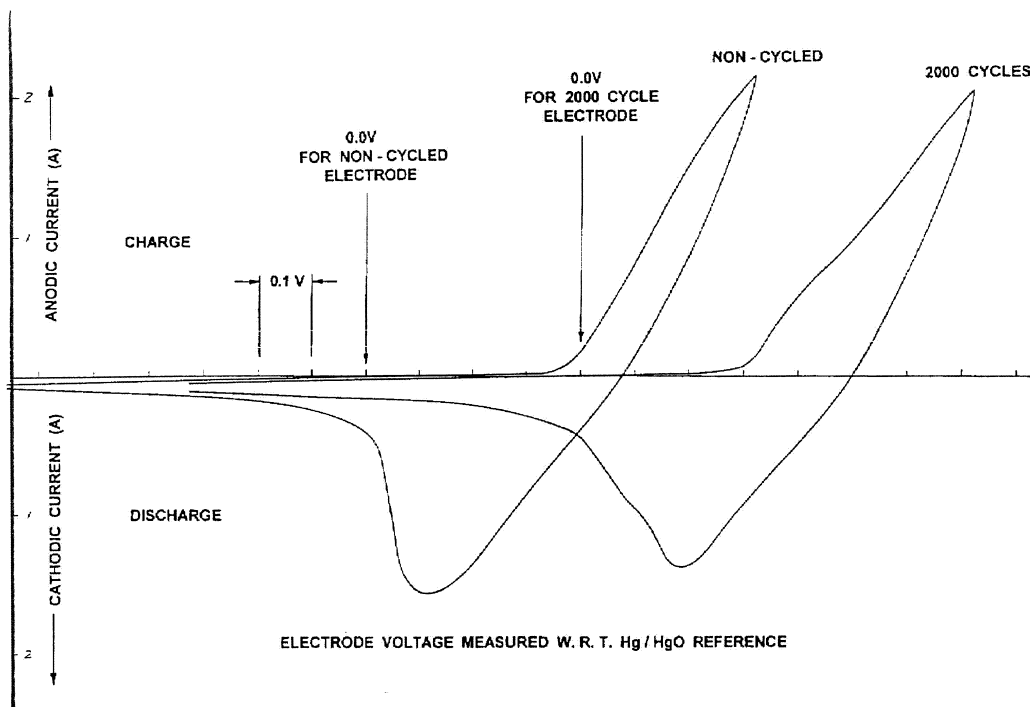


Fig. 3. Cyclic voltammograms for cycled and non-cycled nickel electrodes made from plaque containing 5 wt.% cobalt metal.

nickel fiber, 35 parts nickel powder and 15 parts cobalt powder) gave utilizations up to 121% (capacity measurement) during cycling in a flooded LEO regime at 80% DoD and extended cycle life when compared to a similar Fibrex[®] plaque without the cobalt powder addition.

Since cobalt powder added to the wet slurry during nickel plaque fabrication is distributed throughout the plaque, cobalt concentration is limited on the plaque surface at the sinter/active material interface. In the absence of adequate cobalt concentration, a high impedance barrier layer can develop due to both sinter degradation and the agglomeration of active material (active material masses that largely fill the pores of the sinter) which occur during extended periods of high rate cycling [10]. The soak/resinter method [12] was developed to minimize the quantity of cobalt required for enhancement and to maximize the surface concentration of cobalt on the plaque at the sinter/active material interface.

3.2. Comparison of positive gradient and soak/resinter type electrodes with standard production electrodes

3.2.1. Temperature dependence of capacity

Two boilerplate cells (A and B) were assembled with the positive gradient and soak/resinter type of cobalt-enhanced nickel electrodes, respectively. Each cell contained eight working electrode pairs. Both boilerplate cells were cycled over a wide temperature range at a $C/2$ discharge rate to 1.0 V to determine whether there was a difference in plate performance that could be attributed to the method

of cobalt enhancement. These boilerplate cells were compared with the performance of two 50 A h standard NiH₂ production cells over the same temperature range. The two 50 A h cells were discharged at the C rate to 1.0 V. The capacity and percent utilization values listed in Table 1 were obtained for each cell at selected temperatures in the temperature range from -10 to $+30^{\circ}\text{C}$. The percent utilization is equal to the actual capacity ($\times 100$) divided by the theoretical capacity, C_{th} . The value of C_{th} is based on plate weight gain during fabrication and a weight gain capacity of 0.289 A h g^{-1} of active material.

Cell B had the highest utilization of active material: 120% or better over the temperature range -10 to $+15^{\circ}\text{C}$. The early production cell, cell 1, had the poorest utilization over the range -5 to 30°C . Utilization increased somewhat with an improved version of this cell, cell 2. Cell A had better utilization (over 100%) which approached the value of cell B at -10°C . A direct comparison of utilization values for the production and boilerplate cells is difficult to make because of differences in the discharge rates, improvements made in the fabrication of nickel electrodes and loading levels. Cell B has the highest loading level, 1.80 g/cm^3 , in comparison to loading levels of 1.63 g/cm^3 for cell A and 1.65 g/cm^3 for the two production cells.

3.2.2. Arrhenius plot of utilization (U) for cobalt-enhanced and standard NiH₂ production cells

An Arrhenius plot of $\log U$ vs. $10^4/T$ is shown in Fig. 4 for each cell in Table 1. A single slope is possible only

Table 1
Temperature dependence of capacity for production and boilerplate cells

Temperature (°C)	Production				Boilerplate			
	Cell 1: standard plaque, $C_{th} = 55.30$ A h		Cell 2: standard plaque, $C_{th} = 55.67$ A h		Cell A: positive Co gradient $C_{th} = 12.41$ A h		Cell B: co-enhanced plaque $C_{th} = 13.54$ A h	
	C (A h)	U (%)	C (A h)	U (%)	C (A h)	U (%)	C (A h)	U (%)
30	43.84	79.3	52.13	93.60				
22					13.06	105.2		
20	50.02	90.5	55.88	100.4			15.88	117.3
15					13.53	109.0	16.25	120.0
10	52.93	95.7	60.42	108.5	13.66	110.1	16.28	120.2
5					14.06	113.3	16.48	121.7
0					14.47	116.6	16.52	122.0
–5	54.20	98.0	60.90	109.4	14.48	116.7	16.67	123.1
–10					15.12	121.8	16.62	122.7

Cell capacity (C) and utilization (U) to 1.0 V.

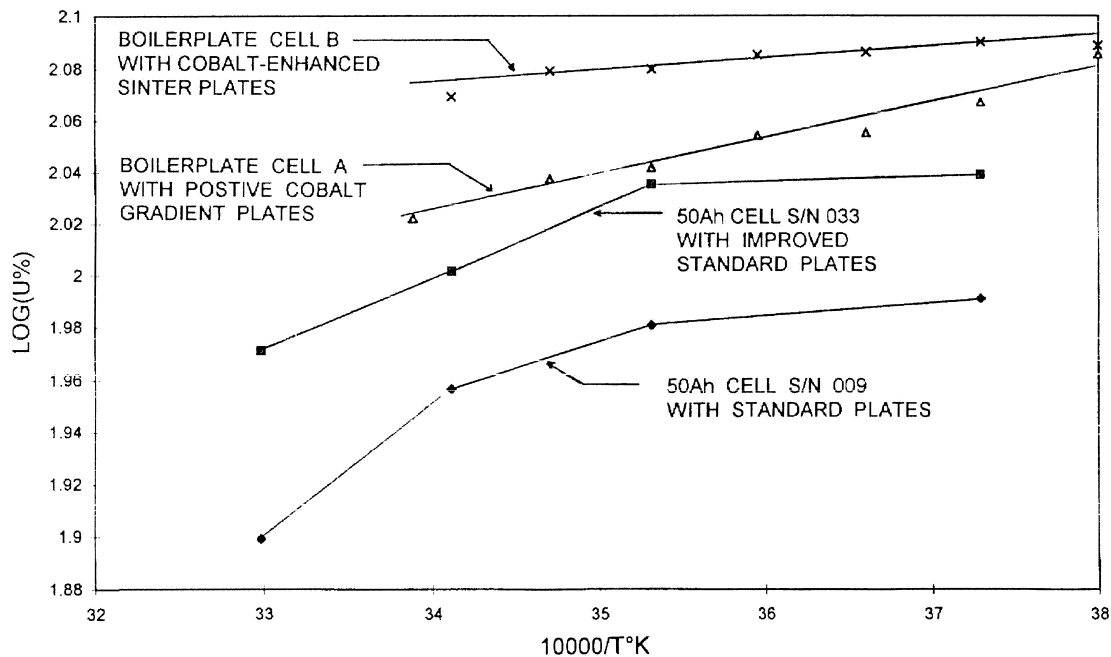


Fig. 4. Arrhenius plot of capacity utilization for boilerplate cells containing positive gradient plates, cobalt-enhanced plates and production NiH_2 cells containing standard nickel plates.

for the two boilerplate cells. The positive slope indicates that cell capacity increases when going to lower temperature for the range of temperatures examined here. The small slope value for cell B suggests that the electrochemical charge and discharge processes in soak/resinter cobalt-enhanced plates are dominant and essentially temperature independent. Activation energies for the two boilerplate cells, cell A and cell B, are -0.029 and -0.00944 eV, respectively. The decrease in capacity at higher tem-

peratures caused a break in the Arrhenius plot at 10°C for both production cells. A change in slope normally results from a change in mechanism.

3.2.3. Discharge voltage profile dependence on temperature

The discharge voltage profile dependence on temperature for cells A and B is shown in Figs. 5 and 6, respectively, for the temperature range -10 to 15°C . The end of

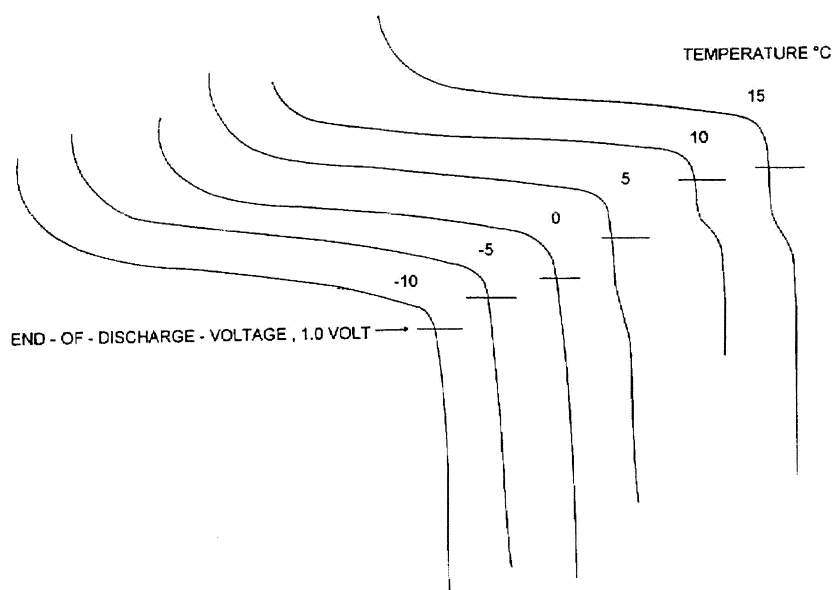


Fig. 5. Temperature dependence of the discharge voltage profile for boilerplate cell A. This cell contains nickel plates made with standard sintered plaque with a positive cobalt gradient in the active material.

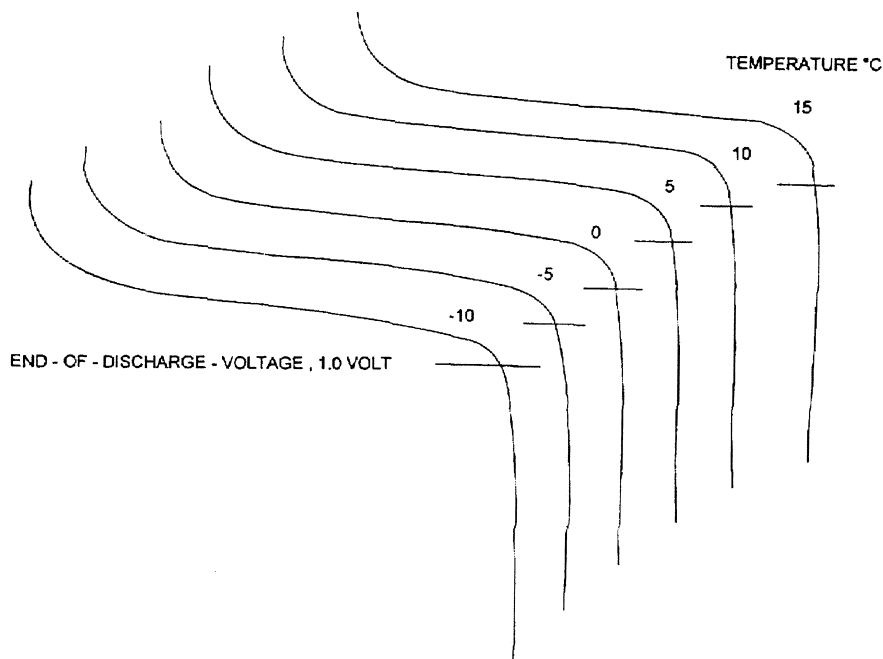


Fig. 6. Temperature dependence of the discharge voltage profile for boilerplate cell B. This cell contains nickel plates made with a cobalt-enhanced sintered nickel.

discharge voltage segment of the discharge voltage profiles at -10°C are almost identical. However, cell A develops a second plateau voltage component of capacity with increase in temperature which is very distinct at 5°C and above. By comparison, the end of discharge voltage segment for cell B seen at -10°C becomes slightly less rounded at higher temperatures with the steepest voltage drop-off and no evidence of residual capacity occurring at 15°C . Cell A results are in agreement with the utilization values given in Table 1 which decrease with increase in temperature. The corresponding values for cell B in Table 1 remain high because no residual capacity is developed above a temperature of -10°C at the $C/2$ discharge rate.

4. Conclusions

The addition of cobalt metal powder to sintered nickel plaque improved the cycle life of nickel electrodes during cycling in a LEO regime at 80% DoD compared with standard production electrodes. A soak/resinter method was developed to reduce the amount of cobalt required and to maximize cobalt addition at the plaque surface. This method improved plate utilization in the temperature range -5°C to $+20^{\circ}\text{C}$ compared with standard 50 A h production cells. The temperature dependent discharge voltage profile results demonstrate that the soak/resinter method of cobalt enhancement has a direct influence on the electrode discharge characteristics. This new method of cobalt addition to the nickel plaque surface improves the conduc-

tivity across the sinter/active material interface during extended periods of high rate cycling. The results of a stress test evaluation to compare cobalt-enhanced with standard plates are presented in a subsequent paper.

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