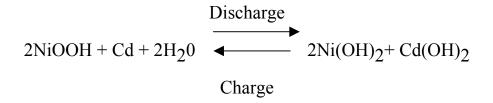# CHAPTER 4

NICKEL-CADMIUM BATTERIES

Nickel-cadmium alkaline batteries have gained respect as a very reliable, long life electrochemical system from their performance in (4-1) industrial starter and standby service and in the space program. Space batteries were sintered plate type cells, hermetically sealed, requiring precision workmanship and very high quality control on the manufacturing line. Their chief disadvantage for use in terrestrial solar photovoltaic systems is their very high cost. Industrial nickel-cadmium batteries with lower cost are commercially available for starter, standby and cycling service. These are normally pocket plate types which are vented to the atmosphere through resealable vents in each cell to relieve abnormally high internal pressures without spontaneous oxidation of their cadmium negative plates by atmospheric air. Industrial pocket plate cells are suitable for solar photovoltaic systems and can be considered by the system designer.

CHEMISTRY AND CONSTRUCTION

Active materials in nickel-cadmium cells are nickel hydrate (NiOOH) in the charged positive plate and sponge cadmium (Cd) in the charged negative plate. The electrolyte is an aqueous potassium hydroxide (KOH) solution in concentration of 20-34 percent by weight pure KOH. The basic electrochemical reaction is (4-2):

$$2NiOOH + Cd + 2H_2O \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} 2Ni(OH)_2 + Cd(OH)_2$$

The reversible potential E_r of cells can be expressed in terms of the chemical activity of water (aH_2O) in the electrolyte and the standard cell potential (EO) when all activities of reactants and products are at unit activity:

$$E_r = E° - 0.059 \log aH_2O \text{ at } 25°C.$$

E° is 1.299 volts at 25°C. Thus the voltage of the cycling cell can be influenced by changes in activity (proportional to concentration) of the water in the electrolyte. In hermetically sealed cells oxygen gas is evolved during overcharge from the positive plates of positive limiting cells and recombines chemically with the excess cadmium in the negative plates. Overcharge can occur continuously in well designed cells with no damage to the cell. In vented cells atmospheric oxygen can react with the negative plate active material (Cd) and discharge it chemically. Vents must be designed spring loaded to reseal tightly In addition, carbon dioxide in the air can react with KOH in the electrolyte to form K_2CO_3 , and $CdCO_3$ can be formed on the negative plates. Both of these compounds interfere with normal cell operation. Thus, even in vented cells the integrity of the seal is important.

Sintered nickel-cadmium cells have relatively thin sintered nickel matrices as the plate grid structure. These matrices are highly porous and are impregnated with the active positive or negative material in the solution state. The plates are then formed electrochemically, washed and dried. In other variations of the process the active material in the sintered matrix is converted chemically, or thermally, to an active state

and then formed. In general, there are many steps to these cycles of impregnation and formation and the production lines must be automated to reduce cost (4-3). Thin sintered plate cells are ideally suited for very high rate charge and discharge service.

Pocket plate nickel-cadmium cells have the positive, or negative active material, pressed into pockets of perforated nickel plated steel plates or into tubes (4-4). The active material is thus trapped securely in contact with a metal current collector and active material shedding is largely eliminated. Plate designs vary in thickness depending upon cycling service requirements. Lower rate charge-discharge service calls for cells with fewer thicker plates to reduce cost and increase output energy density.

Pocket plate cells may have either a plastic or metal cell case Metal cell cases must be insulated from each other in a battery cell pack since the cell case is normally the negative cell terminal. Metal cases are preferred for applications requiring high shock and vibration resistance. Plastic cases, normally polypropylene, are preferred for typical solar PV applications to help eliminate leakage paths to ground.
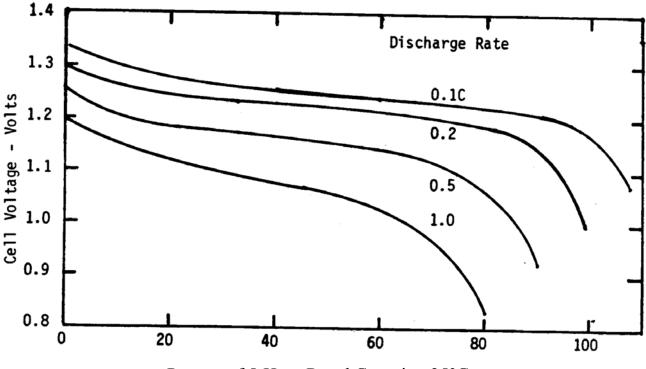
In long life cells a large excess of electrolyte is contained in cell cases over the plates reducing maintenance for water addition to once in each two years, depending upon the amount of overcharge and the operating temperature. Flooded cells of this type have low internal gas recombination rates. Their covers therefore contain spring loaded

pressure relief vents to relieve excess hydrogen and oxygen formed during overcharge. Their venting range is from 2 to 10 psi.

Resealable, vented nickel-cadmium cells are recommended over hermetically sealed cells for solar PV installations because of their much lower cost, although still more expensive than lead acid cells. Also, in series string arrays, unbalanced cells can be brought to the same state of charge more readily by overcharging when vented

DISCHARGE CHARACTERISTICS OF Ni Cd CELLS

Discharge curves are similar in shape to lead acid except that cell voltages are lower and range from 1.35 volts initially to a minimum cut-off voltage of 0.85 volts per cell at discharge rates from 10 to 3 hours. Figure 4-1 gives a family of discharge curves
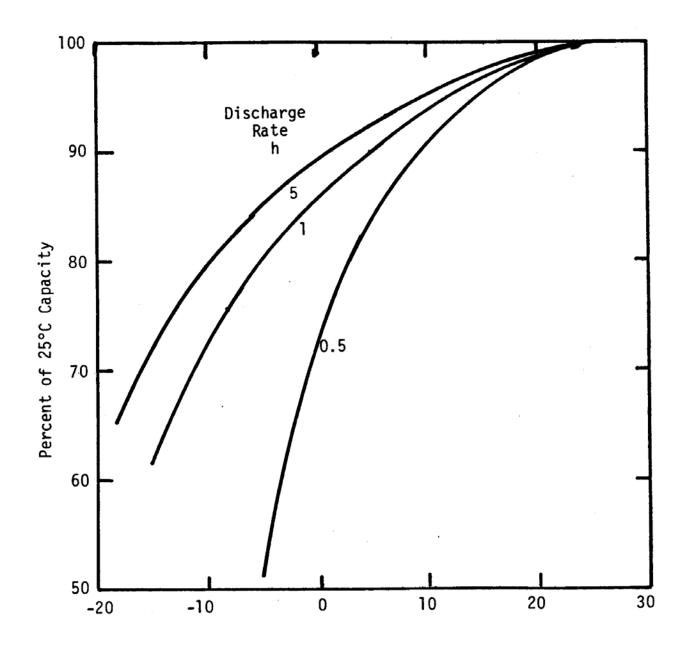
Figure 4-1 Effect of Discharge Rate on Capacity and Voltage Regulation

for an intermediate rate pocket plate cell at the 0.1,0.2,0.5 and lC rates at 25°C. The rated capacity (100% point on the "X" axis) is the 5-h rated capacity to 1.0 volt at 25°C. Figure 4-1 shows that increasing the rate of discharge from the 5-h to the 1-h rate decreases capacity from 100 to 68% of the 5-h rated capacity and the average cell voltage falls from 1.23 to 1.13 volts per cell. This change is relatively small and is an advantage of the NiCd system.

Figure 4-2 shows the effect of operating temperature on rated discharge capacity in the temperature range -20 to 25°C at the 5, 1 and 0.5-h discharge rate. Thinner pocket plate cells with greater plate surface area for the same rated capacity would have higher cell voltages and higher percentages of 2SoC rated capacity at the lower temperatures. To obtain the best cell design for each application the system design engineer should collaborate with the battery manufacturer's application engineer in arriving at the optimum cell construction.

Discharge Temperature - °C

Figure 4-2 - Effect of Operating Temperature on Discharge Capacity

Nickel-cadmium cells operate well at low temperature provided the electrolyte does not freeze. Table 4-1 gives the freezing temperatures for aqueous KOH solutions of 20-34 percent KOH

TABLE 4-1

Electrolyte Freezing Temperature

KOH Concentration	Density	Freezing Point	
wt%	g/ml	°C	°F
20	1.184	-25	-13
22	1.203	-30	-22
24	1.223	-35	-31
26	1.244	-42	-44
28	1.265	-48	-54
30	1.285	-59	-74
32	1.306	-65	-84
34	1.328	-53	-63

Particular care has to be taken to assure that cells with lower KOH concentration electrolyte are not directly exposed to operating temperatures below these freezing points.

Discharge voltages and capacities of sintered plate cells, sealed and vented, can be temporarily lowered by the "memory effect", This lower capacity reduces the time of discharge at a given rate to a predetermined voltage. The effect is brought about by repeated cycles of less than full capacity. When full capacity is demanded, the cell cannot produce the rated capacity. Generally, the memory effect can be erased and full capacity obtained by a small number of complete charge-discharge cycles at 100% depth of discharge (4-5).

When batteries of both sintered and pocket type are floated at a constant voltage, such as in utility and telephone applications, the negative plate becomes "passive" and less than full capacity is available. Generally, this capacity loss can be restored by a gassing
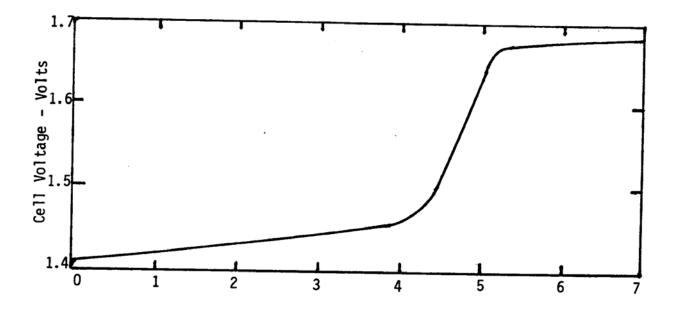
overcharge which is given at a rate of 5-10 A per 100 Ah of the 5-hour rated ampere-hour capacity for 6-12 hours.

CHARGING CHARACTERISTICS

Nickel-cadmium cells may be charged by constant current. constant potential, or combinations of these methods. Higher charge rates can be tolerated by NiCd cells than by lead-acid cells designed for the same discharge rate, and rates of 25 A per 100 Ah of the 5-hour rated capacity are commonly used without harmful effects. One method for

cycle application is to recharge at a constant current of 20 A per 100 Ah to an input 20-40 percent greater than the previous discharge output.

During a typical constant current charge at 20 A per 100 Ah, cell voltage rises from near 1.40 volts to the gassing voltage (1.45 volts per cell at 25°C) and then very quickly to 1.68 volts, remaining near this voltage during overcharge. See Figure 4-3.

Charge Time - Hours

Figure 4-3   Constant Current Charge of Pocket Plate Nickel-Cadmium Cell at
20A/100 Ah, 25°C

The gassing voltage is temperature dependent. In the temperature range 15°C to 40°C the gassing voltage increases 0.0025 volts for each degree Centigrade increase in electrolyte temperature.

The modified constant potential method of charge is more often recommended for long life cycling regimes in photovoltaic systems. A typical charge starts at constant current (20A per 100 Ah 5-hrou rated capacity) and continues at the current until the cell voltage rises to a predetermined voltage limit (1.55 volts per cell at 25°C). The voltage during charge then becomes constant and the current tapers quickly to a final float current. Table 4-2 gives typical charge times and recharge capacity available for the next discharge and assumes a 20% overcharge (4-6) .

TABLE 4-2

Modified Constant Potential Charge Input vs. Rate of Charge
Intermediate Rate Pocket Plate Cells

Depth of Previous Discharge %	Charging Time h	% Capacity Available 1.55v/c		1.65v/c	
		10A/100AH	20A/100Ah	10A/100Ah	20A/100Ah
50	6	89	94	92	98
	10	92	97	100	100
	20	95	98	100	100
100	6	57	89	57	93
	10	86	95	86	100
	20	94	98	100	100

Highest rate, thin plate pocket cells show lower voltages during charge at the same charge state, charge rate, and temperature, and can be <u>charged fully</u> in a shorter time period. Charging at temperatures above 45°C is harmful to the active material of the cells.

Modified constant potential charging of pocket plate cells is normally at pre-set voltages of 1.60-1.65 volts per cell to obtain maximum input in the shortest time. After a deep discharge the charge current is constant for the first 4-5 hours, then decays rapidly to less than l0A/l00Ah in the first hour and more gradually during the next 4-5 hours to final float currents. These float currents vary typically (4-6) with the pre-set voltage limit as follows at 25°C:

Voltage Limit volts/cell	End-of-Charge Current A/100Ah
1.50	0.5
1.55	1
1.60	3
1.65	10

Charge acceptance and charge time are considerably influenced by charge temperature.

Lower temperature increases charge time and decreases charge acceptance. At 0°C, for example, the end-of-charge current will be approximately one-fifth of the 25°C value. The solar PV system voltage regulator must be designed with temperature compensated charge voltages to obtain highest charging efficiency.

At 25°C ampere-hour charge efficiency is 71 percent for an over-charge of 40%, and turn around energy efficiency would be 60 percent, or lower, at either lower or higher charge temperatures. These inefficiencies are a relative disadvantage fo the NiCd system, and the overcharge required to maintain capacity increases water loss over that required for lead-acid cells.

OPERATING AND CHARGED STAND LIFE

Life measurements are not available to compare cycle life at various depths of discharge and operating temperatures. Life must be obtained in actual tests on the regime and under the environment of the application. Cycle life increases with decreasing discharge depth. Typical life data for pocket plate NiCd cells is shown on the following page (4-7).

Depth of Discharge at 25°C % of 5h Rated Capacity	Cycles to Failure (Capacity Below 80% 5h Rated Ah)
20	2500
40	1700
60	1100
80	750
100	500

These projections assume continuous 5h discharges and controlled charging to restore discharge capacity plus optimum overcharge at 25°C. At 50°C average cycling temperature, life can be 50% of the above estimates. Under proper maintenance conditions, wet lives of 10-25 years and cycle lives of 1000-4000 at 60-80 percent depth of discharge have been reported (4-8).

Charged stand loss in capacity at -20°C is essentially zero but increases with increasing stand temperature and cell plate area per unit capacity. At 25°C the loss is 0.1 to 1.0% per day averaged over 4-6 months, but loss rates during the first 10-20 days will be 1-2% per day and much lower thereafter. At 45°C the loss rate is about 3 times that at 25°C (4-9). Charged stand loss rates of space type thin plate hermetically sealed NiCd cells were observed to be 0.1% per day at 0°C, 0.7% per day at 20°C, and 2% per day at 30°C (4-10). Conditions which lead to higher charged stand losses are excessive overcharge, high operating and stand temperature, and the contamination of the electrolyte by nitrates and tin.

Increased concentrations of potassium carbonate in the electrolyte will lower discharge voltages, increase charge voltages, decrease charge acceptance and reduce life (4-11).

MAINTENANCE AND SAFETY PRECAUTIONS

Each battery manufacturer can provide the system designer detailed service and operating instructions for the battery. This document will include recommendations for periodic maintenance and safety precautions to be followed by the user.

For vented nickel-cadmium cells. the maintenance requirements will be:

1. Watering the cells to supply water lost during overcharge;
2. Maintaining intercell connectors at proper torque; and,
3. Keeping cell tops and exposed sides clean and dry.

In a standby float operation a nickel-cadmium battery will require water additions no more often than every two years. In reqimes with considerable overcharge more water will be necessary. In full over-charge maximum water consumption can rise to 0.336 cc/Ah. First, estimate the accumulative overcharge per year, then, calculate the theoretical water consumption and add 5-10% for evaporative losses. Add this amount each year but do not overfill beyond the manufacturer's recommended upper water line in each cell.

Torque intercell connectors with a torque wrench just up to the torque value recommended by the battery manufacturer. Do not allow metal wrenches to short cell tenninals.

Electrolyte spillage can form grounding paths. White moss around vent cap seal is potassium carbonate (K_2CO_3). Clean up these surfaces wi th pure water and dry. In handling the caustic potassium hydroxide electrolyte safety goggles should be worn to protect the eyes and plastic gloves and an apron to protect skin and clothes. In case of spillage on hands or clothes neutralize the alkali immediately with vinegar 3% acetic acid) or dilute boric acid solution (one pound per gallon of water}; then rinse with clear water.

During overcharge explosive mixtures of hydrogen and oxygen are formed in nickel-cadmium cells. When the cell relief valves vent these gases to the atmosphere, a potential explosive hazard can exist if sparks or cigarette or lighted matches are nearby. "No Smoking" signs should be posted in battery rooms. As a further safety measure room ventilation can be designed to prevent hydrogen concentration in closed spaces from exceeding one percent by volume. Destructive explosions can occur at concentrations above four percent by volume in air.

REFERENCES

4-1   Paul Bauer, "Batteries for Space Power Systems", NASA SP-172, 1968.

4-2   IBID, page 70.

4-3   5. Uno Falk and A. J. Salkind, '[1]Alkaline Storage Batteries", John Wiley & Sons, Inc., 1969, page 125.

4-4   IBID, page 59.

4-5   Paul Bauer, "Batteries for Space Power Systems", NASA SP-172, 1968, page 98.

4-6   VARTA, Prospectus 30 - 322e, NiCd Batteries, VARTA Batteries, Inc., Elmsford, N.Y. 10523.

4-7   NIFE, Incorporated, P.O. Box 100, George Washington Highway, Lincoln, R. I., 02865.

4-8   Reference 4-3, page 304.

4-9   IBID, pa•ge 303.

4-10 IBID, page 404.

4-11 D. T. Barney, A. J. Catotti and S. F. Pensabene, Power Sources 1970, Preprint Paper 8.