Batteries
ACME Faculty, EHVE course
B.Sc. Studies, III year, V semester

Leszek Niedzicki, PhD, DSc, Eng.

Nickel-Cadmium batteries

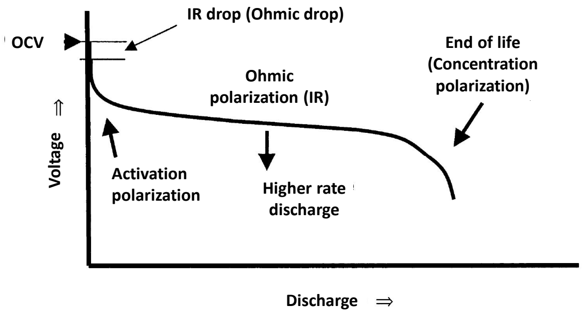
Voltage change vs state of charge

Cells (and batteries) have their nominal voltage. This voltage is a mean value of minimum and maximum usable voltage that is obtained by a cell. Cells have higher (maximum) voltage when they are fully charged and lower (minimum) when fully discharged. Different materials have different potentials. One can say, that during “filling” or “emptying” of electrodes, they change their composition (and their potential).

Voltage change vs state of charge

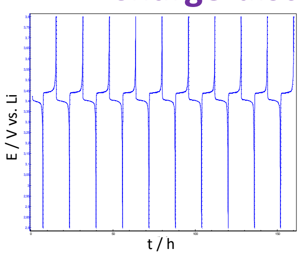
Thus, voltage of a cell changes with the progress of charging. From the measurement of state of charge (SoC) point of view it would be the best if that change was always linear. However, it almost never is. Also, with ageing of a cell, maximum and minimum voltage of every cell change as well (as a voltage slope). That is why in phones and notebooks state of charge bar is often wrong. More importantly, cell voltage change not with linear slope but with the characteristic charge-discharge curve.

Charge-discharge curve



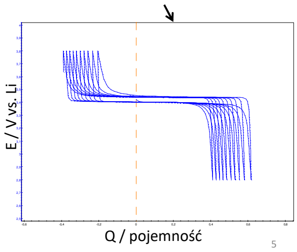
M. Winter, R.J. Brodd, Chem. Rev. 104 (2004) 4245

Charge-discharge curve



← discharge with the constant current

cell capacity fade and “input” current drop with cycles



Curves from real cells

Memory effect and formatting

If cell was discharged only partially (and far for being fully discharged) and subsequently was fully charged then cells of some chemistries will lose some capacity (although they will be fully charged). Such effect is called **memory effect**. Depending on exact chemistry of a cell, original capacity can be restored or not through a very slow (C/20 or slower) full charge-deep discharge cycling procedure.

Nickel-Cadmium batteries

The first non-acidic rechargeable cell was Nickel-Cadmium battery. It was invented by a Swedish inventor, Waldemar Jungner in 1899. Jungner invented also Nickel-Iron and Silver-Cadmium cells. The cell manufacturing company established by Jungner at the time was bought out by a competition as recently as in 1991. However, it still exists.

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Nickel-Cadmium batteries

$Cd \mid KOH_{(aq)}$ 30% $\mid NiOOH$

Reactions at electrodes (discharge to the right):

$Cd + 2OH^- \rightleftarrows Cd(OH)_2 + 2e^-$

$NiOOH + H_2O + e^- \rightleftarrows Ni(OH)_2 + OH^-$

Overall reaction is:

$2NiOOH + Cd + 2H_2O \rightleftarrows 2Ni(OH)_2 + Cd(OH)_2$

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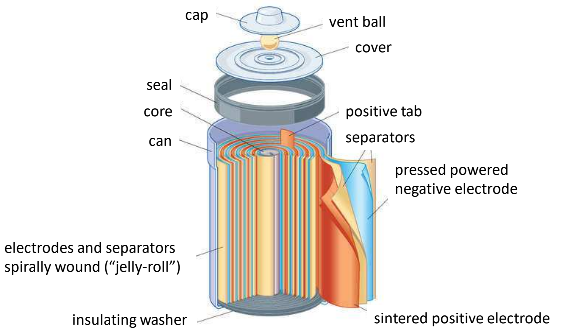
Nickel-Cadmium: jelly-roll (spiral) design



whole can filled with electrolyte – $KOH_{(aq)}$

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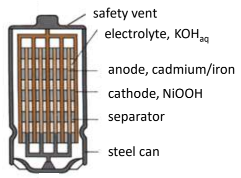
Nickel-Cadmium: manufacturing

Positive electrode is made of nickel oxyhydroxide. Negative electrode is made of the cadmium, iron (20%) and graphite mixture (nickel additive is used sometimes). Electrolyte is a 6 mol dm^{-3} KOH_{aq}.



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Nickel-Cadmium: manufacturing

Most of the modern NiCd cells are based on the jelly-roll design, as it provides lower specific resistance of the cell. That secures higher energy and current densities. Both electrodes can be base on porous nickel matrix. It is made of pressed and sintered nickel carbonyl ($Ni(CO)_5$). Ammonium carbonate can be added to the substrate. At the high temperature $Ni(CO)_5$ decompose to nickel and gaseous products forming nickel sinter with pores (due to the lack of escape route and being under pressure). Porosity of the sinter can be as high as 85%. Sinter pores can be filled with cadmium or NiOOH by electrochemical or thermal decomposition of suitable solutions that nickel sinter is soaked with first.

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Nickel-Cadmium: manufacturing

An alternative for sintered electrodes are the pasted ones. Nickel foam that is a matrix for active mass is formed through deposition of nickel on the polymeric unwoven fabric (PE, PP), and subsequently pyrolytically removing the polymer (residues of graphite after pyrolysis form the conductivity enhancing foam additive). Foam is then filled with cadmium or NiOOH paste.

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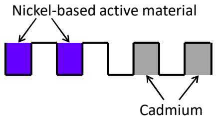
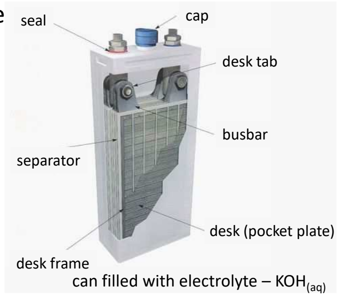
Nickel-Cadmium: pocket design

Plates are alternating pockets made of perforated nickel-plated steel. Electrode material here has very low porosity here. Those cells due to numerous disadvantages are rarely used. Their only important advantage is low manufacturing cost.





Nickel-Cadmium: pros and cons

Advantages:

- Maintenance-free (compared to basic Pb-acid);
- Leak-proof and lighter (compared to Pb-acid);
- Scalable – cells up to couple tens Ah;
- Able to provide impulses with high current, endure high currents during continuous charge or discharge up to 10C (capacity drop can take place during this cycle, but no long-term consequences of high rate cycling);

Nickel-Cadmium: pros and cons

Advantages – cont'd:

- No significant voltage changes during discharge (although for battery management system this can be a disadvantage);
- Endure overcharging;
- Slow self-discharge (compared to NiMH/Pb-acid);
- Endures low temperatures (no issues up to -30°C).

Nickel-Cadmium: pros and cons

Disadvantages:

- Expensive manufacturing (few-fold higher than Pb-acid);
- Heavy (compared to Li-ion);
- Low cell voltage – lower energy density;
- Slow voltage drop during discharge (although for powered devices this can be a disadvantage);
- Contains toxic cadmium (affects health of manufacturing, maintenance and service workers, issues with recycling; NiCd is now prohibited in numerous countries to use in big scale applications);
- Poorly behaves when partially charged/discharged.

Nickel-Cadmium: operation conditions

- OCV is 1.3 V;
- Slow voltage change with state of charge, steeper change only close to the full charge. This effects in issues with state of charge indication (no concentration changes like in Pb-acid);
- Subtle potential changes throughout the cell life (makes state of charge measurements harder);
- Round-trip (charge-discharge cycle) efficiency of 50-70% (charging losses on oxygen, hydrogen and Ni^{4+} generation, the last one reduces spontaneously to Ni^{3+});
- No electrolyte concentration changes, as the reaction advance does not change its concentration (as well as it does not change its conductivity).

Nickel-Cadmium: operation conditions

- Memory effect results from formation of insoluble cadmium compounds at the anode (*e.g.* $CdOOH^-$ or $Cd(OH)_3$) or (less frequently) nickel compounds at the cathode (*e.g.* NiOOH in other, less soluble crystalline form). As they are insoluble, they clog electrode pores making further cell operation in this area impossible. Thus, capacity of such cell drops;
- Excess of gases forming during cell operation is removed by the safety vent.

Nickel-Cadmium: operation conditions

- Cells with safety vent (typical ones) have a life span up to 1000 charge-discharge cycles;
- Hermetic cells (without the vent) have a life span of 3000-5000 cycles;
- Voltage range during operation from 1.4 to 0.9 V (between 1.2 and 0.9 V fits only ca. 10% of the overall capacity).

Nickel-Cadmium: modifications

- Ni-Cd batteries may contain water excess for enlengthening their life.;
- Leak-proof batteries (no safety vent) may have higher cathode mass, so at the end of the charge there won't be any hydrogen evolution taking place. Oxygen at the cathode still forms, but it dissolves in water and oxidize cadmium to cadmium hydroxide. Disadvantage of such solution is that the cell has lower energy density (excess mass of one of the electrodes is unused) and that slow self-discharge takes place due to oxygen reaction with cadmium;
- Few mass percent of $Co(OH)_2$ and $Ba(OH)_2$ is added to cathodes in pocket design to enlarge capacity and lifespan of the cell.

Nickel-Cadmium: modifications

- For cells operating at moderate temperatures (-10°C to 50°C) electrolyte is ca. 6M KOH with the 2% LiOH addition enhancing mechanical stability of electrodes;
- In cells operating at low temperatures (down to -30°C) LiOH is not added due to its poor conductivity parameters at low temperatures;
- In cells operating at high temperatures KOH is used at higher concentrations or NaOH is added. At higher concentrations KOH causes swelling of electrodes to a higher extent than usual.

Environmental hazards

Cadmium as a hazard for:

- Organisms in general – blocks nerve signals, changes rate of micronutrients absorption, blocks certain cell components and/or blocks alkali metals balance at the cellular level.
- Human – damages kidneys, liver and testes (due to accumulation), causes osteoporosis, is teratogenic and carcinogenic. High toxicity (inhalation LD50 < 40 mg/m3/h or oral ~500 mg);

Nickel-Cadmium: applications

UPSes and emergency supply, circuit breakers and switches at power stations, starting batteries in aviation/marine propulsion/diesel engines (especially custom-made), starting gas turbines.

Applications in which battery operates tilted and leak-proof. As being tolerant to low temperatures still used on a mass scale in aviation, space industry and by military. Predecessor of Li-ion cells in handheld/mobile devices; in all applications where they are still used, they are subject to exchange to nickel-hydride batteries.