

75% KOH w/v } different.
 450% KOH w/v } W

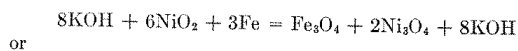
and a reference electrode such as zinc, sponge lead, or preferably cadmium. Cadmium curves are included in the diagram.

Vinal, Craig, and Snyder³ studied the addition of small amounts of cobalt, nickel, and iron sulfates to the electrolyte of commercial batteries which were then subjected to 150 cycles of charge and discharge. Cobalt decreased the charging potential of positive plates, and nickel decreased the charging potential of negative plates. Iron showed no significant effect on the potentials of either plate. Cobalt reduced the corrosion of some of the positive plates but had a harmful effect on the wood separators. Decreased positive plate potentials are of interest because they may permit the use of lead alloys free from antimony.

Lead storage batteries are used for stand-by electric-power services where the pasted-plate type is preferred; for electric vehicles; train lighting; gasoline engine and automobile starting, lighting, and ignition; signaling and control work; as well as many other applications.

ALKALINE SECONDARY CELLS

There are only two alkaline storage cells in commercial use in the United States. The first is the Hubbell consisting of the system Ni threads and Ni oxide|KOH|Fe, used in miners' lamps. The second is the more important Edison battery consisting of the system finely divided Ni + Ni peroxide|21 per cent KOH|finely divided Fe. The active materials of the Edison cell consist of nickel peroxide for the positive plate and finely divided iron for the negative. Typical cell construction is shown in Fig. 46. Small amounts of LiOH are added to the electrolyte, and certain amounts of mercury are incorporated with the iron of the negative plate to overcome the passivity of the iron, while layers of flake nickel are added to the positive plate nickel oxide to increase its conductivity. The reactions of the cell are



which, when read from left to right, are the reactions of discharge

³ VINAL, G. W., CRAIG, D. N., and SNYDER, C. L., *J. Research Natl. Bur. Standards*, 25, 417-420 (1940). (Research Paper 1335.)

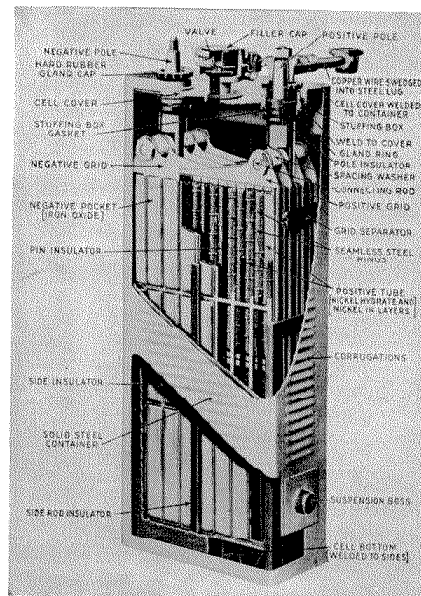


FIG. 46. General construction of the Edison cell. (Edison Storage Battery Company.)

and, inversely, those of charge. It is probable that the iron and nickel oxides are both hydrated. In charging the cell, the electrolyte density does not change as in the lead storage cell, but concentration changes of the electrolyte in the pores of the active materials do take place with perhaps the formation of higher oxides of nickel.

Positive Plates. The positive plates are filled with nickelous hydroxide, which is converted to a higher oxide of nickel by the formation process. Additions of flake nickel are made to increase the conductivity of the mass, as the nickelous hydroxide is a nonconductor. Alkaline cells, other than those of Edison, use graphite for this purpose. The positive plate consists of a

sheet steel. The two leads pass up through bushes of hard rubber in the lid of this container, which is also provided with a valve permitting the escape of gases during charge, but preventing entrance of atmospheric CO_2 , and with a suitable opening for filling. The electrolyte is 21 per cent. KOH solution (S.G. 1.21).

The electrolyte must be replaced about every twelve months. As there is a continual loss of water due to gassing during charging, and as the quantity of electrolyte in the cell is small in comparison with a lead cell of similar capacity, it is necessary regularly and frequently to add water during working.

Reversible Voltage Relations.—The E.M.F. of the Edison cell is 1.33–1.35 volts. It is only very slightly dependent on the concentration of the potash, as Foerster has shown between the limits of 0.2 N–6 N. The following are some of his figures for 25°C .

Electrolyte.	Voltage.
5.3 N. KOH	1.3349 volts
2.82 N. KOH	1.3377
1.0 N. KOH	1.351

The temperature coefficient of E.M.F. as measured by Thompson and Richardson,² is positive, and increases as the alkali concentration diminishes. They obtained the following values:

50 per cent. KOH	+ 0.00008 $\frac{\text{volt}}{\text{degree}}$
23.8 per cent. KOH	+ 0.00026–0.00022,
6.25 per cent. KOH	+ 0.00069.

The Edison cell will therefore cool slightly during reversible discharge. The resistance of a cell depends somewhat on its size and on the stage of discharge reached, but varies between 0.0015–0.006 ohm.

Charge and Discharge.—The above reversible values for E.M.F. hold good of course only for cells standing idle. When current passes irreversible effects come into play, and these are unfortunately of considerable magnitude in the present case. Fig. 63 contains typical charge and discharge curves, taken at a normal rate.³ If discharged immediately after charging, the initial voltage is about 1.45 volts. This rapidly falls to 1.3 volts, and then drops very slowly during the course of the discharge to 1.15 volts. At this point it begins to fall more rapidly, and drops to zero, showing a second short halt at about 0.7 volt. Under normal working conditions this stage is not reached, the discharge being interrupted when the voltage has fallen to 0.9 volt. On charging, the curve shows a small maximum shortly after the start, and a subsequent con-

¹ *Zeitsch. Elektrochem.* **14**, 285 (1908).

² *Trans. Amer. Electrochem. Soc.* **7**, 99 (1905).

³ For other data on the working of the Edison cell under different conditions, see Bennett and Gilbert, *Trans. Amer. Electrochem. Soc.* **23**, 359 (1913); Turnock, *ibid.* **30**, 273 (1916); Thompson and Byrne, *ibid.* **31**, 339 (1917).

tinuous rise from 1.65 to 1.8 volt. From the beginning, an evolution of hydrogen, which finally becomes considerable, is noticed at the negative plate. Oxygen evolution at the positive does not commence immediately, but is very brisk before the end of the charge.

Efficiency.—Owing to these facts, the ampere-hour efficiency of the iron accumulator is low—82 per cent. under normal conditions compared with the 95 per cent. of the lead accumulator. It depends largely, however, on the rate of discharge and charge. If these are low, or if a small fraction only of the possible capacity of the cell is utilised, then the ampere-hour efficiency can be much higher. The voltage efficiency is about 72 per cent. (roughly $\frac{1.2}{1.7}$), and consequently the watt-hour efficiency 59 per cent., whereas that of the lead accumulator averages 80 per cent. The voltage losses are not in this case due to concentration

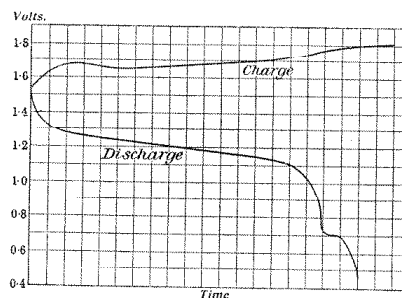


Fig. 63.—Charge and Discharge Curves of Edison Accumulator.

polarisation, but, as we shall see, are essentially connected with the current losses.

As at present manufactured, iron accumulators will furnish up to 450 amp.-hours or 540 watt-hours at normal rates of discharge. The energy capacity per unit weight— $13 \frac{\text{watt-hours}}{\text{pound}}$ ($28 \frac{\text{watt-hours}}{\text{kilo}}$)—is high, but nevertheless shows no overwhelming advantage in that respect over the portable forms of the lead accumulator. The advantage of the iron cell lies more particularly in its indifference to violent mechanical treatment, to overcharging, to discharging above the normal rate, and in its freedom from deterioration on standing or after long use. In fact, both capacity and efficiency appear gradually to increase during use. Holland records a case in which three cells, after helping to drive a wagon for some 17,000 miles, had improved with respect to overcharge capacity, watt-hour output under normal conditions (an increase of 16 per cent.), and efficiency.