Notes from the Oesper Collections

The Edison Nickel-Iron Alkaline Storage Cell

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The Oesper Collections not only preserve historically important chemical apparatus used in teaching and research laboratories, but also an occasional commercial product of chemical and historical interest. Among the latter are several artifacts related to Thomas Edison's development of his famous nickel-iron storage battery acquired as part of a collection of historic voltaic cells donated to the Oesper Collections some years ago by the Chemistry Department of Oberlin College.

Before summarizing the history and chemistry of this cell, it is important to say something about the terminology of electrochemistry. A combination of two electrodes (called the cathode and anode) and a suitable ionically conducting electrolyte designed to chemically generate electrical energy is technically known as a voltaic or galvanic cell. Two or more cells wired in series is technically known as a battery. This use of the word battery to describe a collection or array of objects actually has broader application in everyday life. Thus, for example, a collection of cannons is called a battery. Unhappily, in everyday usage the terms cell and battery have become hopelessly confused. Thus the size D, AA, and AAA cells used in such everyday devices as flashlights, portable radios, and TV remotes are often incorrectly called batteries, when in fact they are single cells. On the other hand, the larger rectangular 9 V snap cells actually contain six smaller 1.5 V disk cells wired in series and are therefore technically batteries.

A second pertinent distinction is the difference between a primary voltaic cell and a secondary voltaic cell. A primary cell is irreversible. Once it has consumed its chemical "fuel" and "burned out," it cannot be recharged and must be disposed of. In contrast, a secondary cell is reversible. Once it depletes its chemical fuel, it can be reversed or recharged again by pumping electricity into the cell so as to regenerate the initial starting chemicals once more. Thus in a sense, it acts as a storage tank for electrical energy which can be repeatedly refilled when empty. For this reason such cells, when connected in series, are also called "storage batteries." However, the recharging is never perfect and becomes less so with repeated recharging until

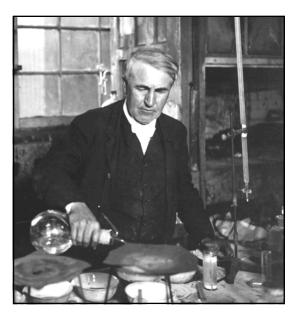


Figure 1. Publicity photo of a middle-age Thomas Edison (1847-1931) posing at the chemical bench.

eventually these cells also burn out.

Published biographies of Edison (figure 1) are literally legion and differ widely in their emphasis and sophistication. However, a little-known 1971 study by Byron Vanderbilt, which focuses exclusively on the chemical aspects of Edison's work, is of particular value when it comes to understanding the basics of Edison's alkaline storage cell (1). According to this author, the first commercial electric car, known as the "Electobat" was produced in 1894 by Henry Morris and Pedro Salom of Philadelphia, and by 1899 ninety percent of the motorized cabs operating in New York City were electrical.

The power source for these early vehicles was a storage battery composed of an electrochemical cell (figure 2) first described by Gaston Planté in 1859 and improved by Camille Faure in 1881. It was based on the net cell reaction (2):

 $Pb(s) + PbO_2(s) + 2H_2(SO_4)(aq) \Leftrightarrow 2Pb(SO_4)(s) + 2H_2O(1)(s) + \Delta E_{el}$



Figure 2. A Planté lead cell (Jensen-Thomas Apparatus Collection). This setup was for demonstration purposes only and the commercial version in your car battery has a far more complex electrode configuration. The number of such cells in older car batteries could be determined by simply counting the number of openings for replenishing the $H_2(SO_4)$ electrolyte in each cell compartment.

in which Pb(0) is oxidized to Pb(II) at the anode, Pb(IV) is reduced to Pb(II) at the cathode, and the net cell potential is 2.2 V at full charge. For obvious reasons, such batteries are most commonly referred to as lead storage batteries rather than as Planté cells and they are still used in modern automobiles, but for purposes of powering the electric starter and running the lights and radio when the motor is turned off, rather than as the vehicle's primary source of motive power.

By 1900 the trend in electric vehicles had caught Edison's attention and he was determined to cash in on this growing market by developing a superior storage battery for electric vehicles. Lead storage batteries had several disadvantages. The dense lead electrodes meant that the battery was quite heavy and thus had a low energy to mass ratio. This is a critical parameter for an electric car. Since part of a battery's output must be consumed in transporting the battery itself rather than the vehicle and its passengers, the lighter the battery the better. This disadvantage alone restricted the average driving range to about 25 miles before recharging was required (3). Likewise the sulfuric acid [H₂(SO₄)] electrolyte was not only highly corrosive and dangerous to work with, it had to be continually monitored, since it was consumed in the course of the battery's cell reaction and thus caused the cell voltage to gradually decrease with use.

In response to these limitations, Edison decided to develop a cell employing electrodes made from materials much less dense than lead and an alkaline rather than an acidic electrolyte. These choices were almost certainly prompted by the fact that for more than a decade Edison had been successfully manufacturing a primary alkaline cell (figure 3) first described by Felix de Lalande and Georges Chaperon in 1883 (4). This was based on the net cell reaction (4):

$$Zn(s) + CuO(s) + 2Na(OH)(aq) \rightarrow$$

 $Na_2ZnO_2(aq) + Cu(s) + H_2O(1) + \Delta E_{el}$

in which Zn(0) is oxidized to Zn(II) at the anode, Cu(II) is reduced to Cu(0) at the cathode, and the net cell potential is roughly 0.7 V when fully charged.

As usual, Edison proceeded empirically. Inspired by the low-density CuO cathode in the Lalande cell, he first prepared a series of test-tube sized cathode half-cells using K(OH)(aq) as the electrolyte and various oxides deposited on porous carbon strips as the electrodes. These were coupled to a standard anode half-cell to determine which cathode best optimized the net cell potential. The winner proved to be nickel oxide hydroxide, NiO(OH). Using this cathode half-cell, he then varied the anode half-cell in the same manner and discovered that the optimal electrode choice was cad-



Figure 2. An Edison-Lalande cell (Jensen-Thomas Apparatus Collection). The embossed printing on the ceramic lid reads "Edison Lalande Battery, Patented June 17, 1890. Other Patents Applied For." The central plate is the Cu/CuO cathode and those on either side are the Zn anodes.

mium metal, thus giving the net cell reaction:

$$\begin{aligned} \text{Cd}(s) + 2\text{NiO}(\text{OH})(s) + 2\text{H}_2\text{O}(1) &\Leftrightarrow \\ \text{Cd}(\text{OH})_2(s) + 2\text{Ni}(\text{OH})_2(s) + \Delta E_{el} \end{aligned}$$

in which Cd(0) is oxidized to Cd(II) at the anode, Ni(III) is reduced to Ni(II) at the cathode, and the net cell potential is 1.5 V. However, at the time, Cd metal was too expensive for the market Edison had in mind. In addition – apparently unknown to Edison – this cell had already been patented in 1899 by the Swedish chemist, Waldemar Jungner, who began commercial production in Sweden in 1904, though the cell would not impact on the American market until the 1940s.

Searching for a more practical and less expensive replacement for Cd, Edison eventually settled upon iron as the best alternative, giving the net cell reaction:

$$3\text{Fe}(s) + 8\text{NiO(OH)}(s) + 4\text{H}_2\text{O}(1) \Leftrightarrow$$

 $\text{Fe}_3\text{O}_4(s) + 8\text{Ni(OH)}_2(s) + \Delta E_{el}$

in which Fe(0) is oxidized to a 1:1 mixture of Fe(II) and Fe(III) at the anode, Ni (III) is reduced to Ni(II) at the cathode, and the net cell potential is 1.6 V.

On the chemical side, commercial production of



Figure 3. A cutaway of the final commercial version of Edison's nickel-iron alkaline storage battery (Jensen-Thomas Apparatus Collection). The nine interleaved plates are not separate cells but are rather a way of increasing electrode surface area.



Figure 4. An almost pristine three-cell battery pack of nickeliron storage cells ready for installation in an electric car (Jensen-Thomas Apparatus Collection).

the cell required the development of entirely new industrial processes for the preparation and purification of the necessary chemicals, and for this purpose Edison built a chemical plant at Silver Lake, New Jersey. On the mechanical side, the production problems proved to be even more challenging. The end product (figure 3) was encased in a nickel-plated steel container and was composed of an elaborate array of between 9 and 17 interleaved nickel-plated steel electrode plates in order to optimize the active surface area of each electrode. Each plate, in turn, contained an array of either punched pockets or perforated metal tubes containing the appropriate chemically active oxide.

Unfortunately, pure NiO(OH) proved to be a poor electrical conductor and to correct this problem Edison initially tried intermixing it with graphite. The resulting cell was put on the market in 1904 but proved to be unreliable and had to be recalled. Edison eventually tried intermixing the NiO(OH) with feather-light flakes of Ni metal (for which he also had to develop an elaborate manufacturing process) and enhancing the K(OH)(aq) electrolyte by adding some Li(OH). This revised cell, unlike the original, proved reliable and was put on the market in 1909. The cells were wired in groups of three or five in steel cases with carrying handles (figures 4-5) and up to a dozen or more of these batteries, depending on vehicle size, were then installed under the hoods (figure 6) of such popular electric cars of the period as the Studebaker, Anderson, and Baker Runabout.

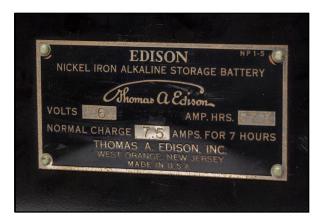


Figure 5. A closeup of the label on the battery pack in figure 4 (Jensen-Thomas Apparatus Collection).

Though its net cell potential was less than that of the lead storage battery, and it was far more expensive, the Edison nickel-iron cell also had numerous advantages. It had a higher energy to mass ratio, could be recharged almost indefinitely without deterioration, and allowed vehicles to travel 50-75 miles between rechargings rather than the 25 miles obtainable from early models of the lead storage battery. In addition, the lead storage battery was sensitive to mechanical shocks – a serious problem in this era of cobblestone city streets and unpaved country roads. Edison cells, on the other hand, with their steel-clad cases, were quite resilient, as Edison flamboyantly demonstrated by having his assistants throw them from the second- and third-floor windows of his West Orange laboratory.

But even before Edison began marketing his revised battery, several events occurred that would spell the eventual demise of the original electric car (5). These include the introduction of Henry Ford's popular and inexpensive gasoline-powered Model T in 1908 and the introduction of the electric starter by Charles Kettering in 1911, which eliminated the most objectionable and dangerous aspect of gasoline engines – hand cranking – and which would also ensure the future of the lead storage battery in automobile design.

Edison tried to carve out an alternative market for his creation through advocacy of battery-powered electric street cars, but without notable success. Eventually it found use as a power source for the small trucks used to handle baggage and freight at airports, shipyards, railway stations, and bus depots, as well as to move materials in factories. It was also used to power forklift trucks, mine and switch locomotives, and for railway signaling and communications equipment. One further advantage of the cell, not mentioned earlier, is its long shelf life (30-50 years) which has also made it a favorite for emergency electrical backup systems.

References and Notes

- 1. B. Vanderbilt, *Thomas Edison, Chemist*, American Chemical Society: Washington, DC, 1971, Chapter 7.
- 2. G. Planté, "Nouvelle pile secondaire d'une grande puissance," *Compt. rend.*, **1860**, *50*, 640-642.
- 3. In the case of commercial electric vehicles, the battery array did not remain in the vehicle itself while it was being recharged. Rather the array was exchanged for a fully charged array so the vehicle could be quickly put back into service and the depleted array set on the shelf for overnight recharging.
- 4. F. de Lalande, G. Chaperon, "Nouvelle pile à oxyde de cuivre," *Compt. rend.*, **1883**, *97*, 164-166; F. de Lalande, "Nouveaux modèles de pile à oxyde de cuivre," *Ibid.*, **1891**, *112*, 1253-1256.
- 5. For an excellent study of the economic and social factors contributing to the demise of the original electric car, see M. B. Schiffer, C. T. Butts, K. K. Grimm, *Taking Charge: The Electric Automobile in America*, Smithsonian Institution Press: Washington, DC, 1994.



Figure 6. Edison posing with an electric car. The hood has been opened in order to display the array of nickel-iron storage batteries inside.