

Notes from the Oesper Collections

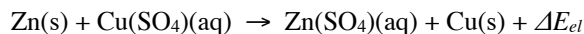
The Daniell Cell

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The secondary Edison nickel-iron alkaline storage battery was the subject of the previous issue of *Museum Notes* (1). However, it is not the only item of interest to be found in the collection of historical voltaic cells donated to the Oesper Collections some years ago by the Chemistry Department of Oberlin College. Yet other items of note are several variations of a primary cell known as a Daniell cell after its inventor – the British electrochemist, John Frederic Daniell (figure 1) – who first described it in 1836 (2, 3).

All of these variations are based on the net cell reaction:



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 about 1.1 V when the cell is fully charged. The system is unique in that it is the first ex-



Figure 1. John Frederic Daniell (1790-1845).

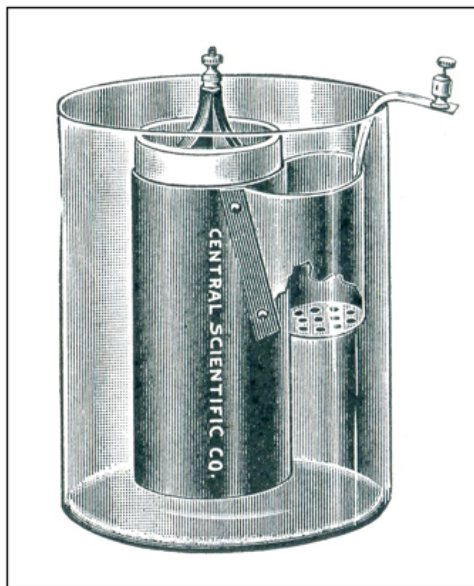


Figure 2. An early form of the Daniell cell with a ceramic spacer. The fluted Zn rod in the center compartment is the anode and the cylindrical wrap of sheet Cu on the outside of the spacer is the cathode. The bottom of the smaller Cu cylinder to the right is perforated and is intended to hold the solid Cu(SO₄) crystals necessary to maintain saturation.

ample of a commercially successful two-fluid cell (4). In other words, rather than sharing a common electrolyte, like the cells described in the previous issue of *Museum Notes*, each electrode has its own separate electrolyte: a saturated aqueous solution of Cu(SO₄)(aq) in the case of the Cu cathode and a solution of Zn(SO₄)(aq) and H₂(SO₄)(aq) in the case of the Zn anode.

In the original form of the cell the cathode and anode compartments were separated by means of a porous ceramic cup or spacer (figures 2 and 3) with the anode and its accompanying electrolyte located inside the cup and the cathode and its accompanying electrolyte outside the cup. Both the fluting on the Zn anode and the large sheet of Cu used for the cathode were designed to maximize the surface areas of the electrodes and thus both the rate of reaction and current generation.

Examination of the net cell reaction shows that not only is the Zn anode gradually consumed, so is the Cu(SO₄)(aq) electrolyte, thus requiring that it be con-

tinuously replenished. In the form of the cell shown in figures 2 and 3, this was accomplished by means of the small Cu cylinder attached to the Cu cathode. This was filled with $\text{Cu}(\text{SO}_4)(\text{s})$ crystals and these, in turn, were in direct contact with the cathode electrolyte via a series of holes punched in the bottom of the cylinder. Consequently, as the concentration of the $\text{Cu}(\text{SO}_4)(\text{aq})$ in the cathode electrolyte diminished, the crystals would gradually dissolve and so maintain saturation.

The presence of the ceramic spacer in this cell meant that the cell had a relatively high internal resistance and therefore that a portion of its energy was consumed internally rather than being available for external work. Starting in the 1850s numerous attempts



Figure 3. An actual surviving example of the Daniell cell shown in figure 2 (Jensen-Thomas Apparatus Collection).

were made to eliminate the ceramic spacer by exploiting the large density difference between the saturated $\text{Cu}(\text{SO}_4)(\text{aq})$ solution and the dilute $\text{Zn}(\text{SO}_4)(\text{aq})$ solution. Indeed, Benjamin in his 1893 treatise on the voltaic cell described no less than 37 variations of the Daniell cell proposed between 1849 and 1890 (5)

Of these, one of the most important was the globe or so-called Meidinger cell (figures 4-6) (6). This consisted of an inverted round-bottom flask or globe whose neck terminated in a narrow tube. This tube extended almost to the bottom of a short glass cup containing the Cu cathode. This cup was placed inside a larger glass cylinder with the inverted globe or flask resting on top. The upper half of the larger cylinder had

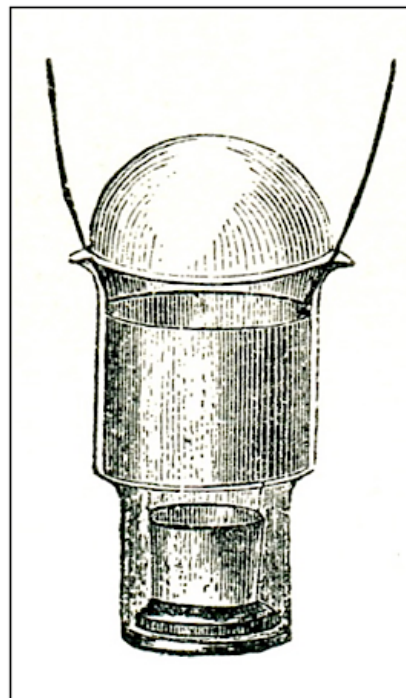


Figure 4. The globe or Meidinger form of the Daniell cell.

a diameter slightly bigger than the bottom half, thus creating a ledge which supported the Zn anode in the upper half. The inverted globe was filled with several



Figure 5. An actual surviving example of the globe or Meidinger form of the Daniell cell shown in figure 4 (Jensen-Thomas Apparatus Collection).

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pounds of $\text{Cu}(\text{SO}_4)(\text{s})$ crystals and the cell with slightly acidified water to the top of the Zn anode. This level corresponded to about half of the globe also being filled with water, which soon dissolved some of the $\text{Cu}(\text{SO}_4)(\text{s})$ crystals to create a dense saturated $\text{Cu}(\text{SO}_4)(\text{aq})$ solution which then displaced the clear water from the small cup and surrounded the Cu cathode, while the slightly acidified water in the upper part of the large cylinder remained free of $\text{Cu}(\text{SO}_4)(\text{aq})$ and now contained a very dilute $\text{Zn}(\text{SO}_4)(\text{aq})$ solution instead.



Figure 6. A disassembled Meidinger cell. From left to right: The outer cylinder and Zn anode, the globe or $\text{Cu}(\text{SO}_4)(\text{s})$ reservoir, the inner cup and Cu cathode.

But perhaps the most successful variation of the Daniel cell was the form shown in figures 7-8. Secondary sources are vague as to who deserves credit for this innovation (7), but by the 1880s it seems to have largely displaced the more powerful Grove cell in most telegraph offices, in large part because it did not release obnoxious $\text{NO}_2(\text{g})$ vapors when operating. An array of intersecting copper strips on the bottom of the cylindrical cell jar functioned as the cathode and a heavy cast Zn anode with radiating fingers hung on the the jar's upper lip. It was the supposed similarity between the shape of this anode and that of a crow's foot which gave the cell one of its characteristic names.

To activate the cell, about three pounds of $\text{Cu}(\text{SO}_4)(\text{s})$ crystals were placed on the bottom of the jar between the branches of the Cu cathode and slightly acidified water carefully added until it covered the Zn anode at the top. Once again, as the $\text{Cu}(\text{SO}_4)(\text{s})$ dissolved it would form a dense, saturated $\text{Cu}(\text{SO}_4)(\text{aq})$ solution at the bottom of the jar which only gradually merged into the less dense dilute $\text{Zn}(\text{SO}_4)(\text{aq})$ solution at the top and thus eliminated the need for a ceramic

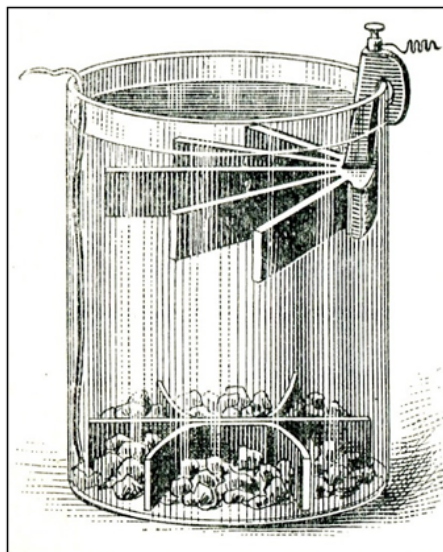


Figure 7. The crowfoot form of the Daniell gravity cell (Jensen-Thomas Apparatus Collection). The multiple branching of both the upper Zn anode and lower Cu cathode is intended to increase the area of active contact with the electrolyte. Not clearly shown is the concentration gradient between the lower layer of $\text{Cu}(\text{SO}_4)(\text{aq})$ solution and the upper layer of $\text{Zn}(\text{SO}_4)(\text{aq})$ solution.

spacer. As the $\text{Cu}(\text{SO}_4)(\text{aq})$ solution became depleted, more of the excess crystals in the bottom of the jar would dissolve and thus maintain saturation. Since the



Figure 8. An actual surviving example of the crowfoot form of the Daniell gravity cell shown in figure 7 (Jensen-Thomas Apparatus Collection).

cell's construction depended on the difference in the densities or specific gravities of the $\text{Cu}(\text{SO}_4)(\text{aq})$ versus the $\text{Zn}(\text{SO}_4)(\text{aq})$ solutions, such cells were also called gravity cells.

If these cells were used for long periods of time, it was customary to float a thin layer of oil on top of the electrolyte to inhibit evaporation. However, starting around 1916, a sharp rise in the cost of $\text{Cu}(\text{SO}_4)(\text{s})$ caused the cell to fall out of commercial favor and resulted in its displacement by the alkaline Edison-Lalande cell described in the previous issue, which was not only less expensive but required far less maintenance (8). At present the Daniel cell is essentially an artifact of the freshman chemistry course, where its continued popularity is largely a function of the simplicity of its underlying redox reaction.

References and Notes

1. W. B. Jensen, "The Edison Nickel-Iron Alkaline Storage Cell," *Museum Notes*, July/August 2013. Oesper Collections Website.

2. For biographical background on Daniell, see A. Thackray, "John Frederic Daniell," in C. C. Gillispie, Ed., *Dictionary of Scientific Biography*, Vol. 3, Scribners: New York, NY, 1970-1990, pp. 556-558.

3. J. F. Daniell, "On Voltaic Combinations," *Phil. Trans. Roy. Soc.*, **1836**, 126, 107-124.

4. An earlier two-fluid cell was described by Becquerel but was not commercially viable. Interestingly this cell was described by Jules Verne in his 1874 novel, *The Mysterious Island*. See "Captain Nemo's Battery and the Science Fiction of Jules Verne," in W. B. Jensen, *Captain Nemo's Battery: Assorted Chemical Annotations on Science Fiction and Literature*, The Epicurean Press, Cincinnati, OH, 2013, pp. 10-19.

5. P. Benjamin, *The Voltaic Cell: Its Construction and Capacity*, Wiley: New York, NY, 1893, pp. 195-226.

6. H. Meidinger, "Ueber eine völlig constante galvanische Batterie," *Pogg. Ann. Physik*, **1859**, 184, 602-610.

7. Thus the historical account in G. W. Vinal, *Primary Batteries*, Wiley: New York, NY, 1950 mentions the names of Varley, Callaud, and Meidinger in this regard but with insufficient information to evaluate the accuracy of the claims.

8. Reference 7, p. 235.