## Notes from the Oesper Collections

## The Grove and Bunsen Cells

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The previous two issues of *Museum Notes* have described the secondary Edison nickel-iron alkaline storage cell (1) and the primary Daniel gravity cell (2) respectively. This issue will deal with two more closely related primary cells of historical importance found among the collection of voltaic cells donated to the Oesper Collections some years ago by the Chemistry Department of Oberlin College – the Grove nitric acid cell and the Bunsen carbon cell. First described by the British scientist and jurist, William Robert Grove (figure 1), in 1839 (3) both of these cells are based on the net cell reaction (4):

 $Zn(s) + H_2(SO_4)(aq) + 2H(NO_3)(aq) \rightarrow Zn(SO_4)(aq) + 2NO_2(g) + 2H_2O(1) + \Delta E_{el}$ 

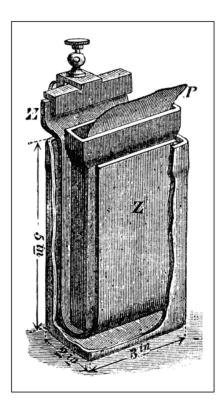


Figure 2. A period etching of a cutaway of a Grove nitric acid cell. Each rectangular 2"x 3"x 5" cell consisted of a sheet of zinc (Z) wrapped around a narrow ceramic separator with a flared lip, which contained, in turn, a sheet of platinum (P) as the cathode.

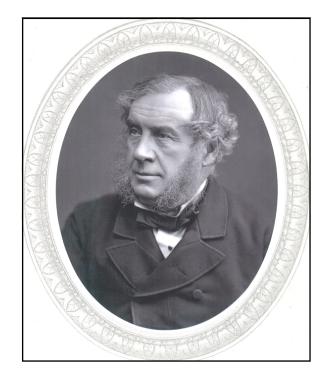


Figure 1. William Robert Grove (1811-1896).

in which Zn(0) is oxidized to Zn(II) at the anode, N(V) is reduced to N(IV) at the cathode, and the resulting net cell potential is roughly 1.9 V.

Like the Daniel cell described in the previous issue, the Grove nitric acid cell was a two-fluid system that employed separate electrolytes for the cathode and anode and a ceramic spacer. In his prototype Grove had employed the bowls from broken clay pipes as his spacers, with an inert platinum (Pt) cathode and nitric acid [H(NO<sub>3</sub>)] electrolyte inside the pipe bowl, and a Zn anode and dilute sulfuric acid [H<sub>2</sub>(SO<sub>4</sub>)] electrolyte outside the pipe bowl (5).

In the final commercial version of the cell (figures 2-3), the pipe bowl was replaced by a narrow ceramic separator with a flared lip and the original rod-like electrodes with sheets of Zn and Pt in order to maximize electrode surface areas. Presumably, because of the expense of the Pt cathode, the first commercial cells were relatively small and usually corresponded to a 2"x 3"x 5" rectangular glazed ceramic or glass box.

Because of their high net cell potential, these cells soon became a favorite of telegraph operators, electroplaters, and experimental electrochemists. However, both the expensive Pt cathode and the obnoxious  $NO_2(g)$  fumes produced during cell operation continued to be serious drawbacks. The first of these problems was finally eliminated in 1841 when the German



Figure 3. An actual surviving example of the Grove cell shown in figure 2 (Jensen-Thomas Apparatus Collection) and a spare ceramic spacer.

chemist, Robert Bunsen (figure 4) – of both burner and spectroscope fame – proposed replacing the inert Pt cathode with an equally inert, but substantially cheaper, version made of baked coke or carbon (6, 7). Precisely the same suggestion was made by the American chemist, Benjamin Silliman Jr, a year later (8). Though Silliman's proposal was apparently made independently of Bunsen, as is usually the case in science, the winner takes all, and any claim to fame Silliman may have had for this innovation soon disappeared from the historical record.

In Bunsen's original modification of the Grove cell – usually referred to as a Bunsen carbon cell – he employed a cylindrical carbon cathode. This was placed in a cylindrical, rather than a rectangular, glazed ceramic cell container. Inside the cathode was a cylindrical ceramic spacer and the Zn anode. However, because of the expense of nitric acid, most later modifications of the cell reversed this design (figures 5-6). The inert



Figure 4. Robert Wilhelm Bunsen (1811-1899).

carbon cathode (usually in the form of a rectangular block) and the nitric acid electrolyte were placed inside the ceramic spacer and the Zn anode and H<sub>2</sub>(SO<sub>4</sub>) electrolyte on the outside. In early versions of this cell the anode was merely a large sheet of Zn, but in some later modifications it corresponded to a thick, heavy Zn casting (figures 7-8). The Jensen-Thomas Apparatus

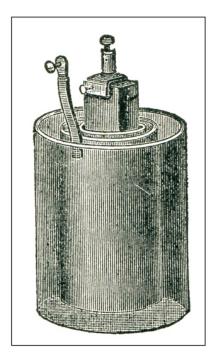


Figure 5. The original Bunsen cell with a rectangular carbon cathode inside the ceramic cup and a sheet of zinc for the anode wrapped around the outside.

Collections contains surviving examples of both varieties.

With the introduction of the less expensive Bunsen cell, the original form of the Grove cell soon disappeared from both commerce and the chemical laboratory. Unfortunately, the Bunsen cell failed to eliminate the second of the above problems – the obnoxious NO<sub>2</sub>(g) fumes, and it was this problem which eventually led to the cell's commercial demise and its replacement, first by the crowfoot form of the Daniell



Figure 6. A example of a Bunsen carbon cell like that that shown in figure 5 (Jensen-Thomas Apparatus Collection).

gravity cell in the 1880s, and then by the Edison-Lalande alkaline cell in the 1920s (9).

## **References and Notes**

- 1. W. B. Jensen, "The Edison Nickel-Iron Alkaline Storage Cell," *Museum Notes*, July/August, 2013. Oesper Website.
- 2. W. B. Jensen, "The Daniell Cell," *Museum Notes*, September/October, 2013. Oesper Website.
- 3. For biographical background on Grove see J. G. Crowther, *Statesmen of Science*, Cresset Press: London, 1965, pp. 77-101, and E. L. Scott, "William Robert Grove," in C. C. Gillispie, Ed., *Dictionary of Scientific Biography*, Vol. 5, Schribners: New York, NY, 1970-1990, pp. 559-561.

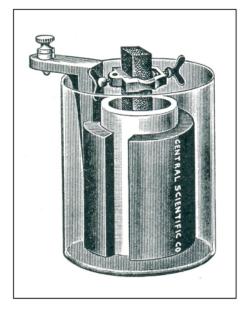


Figure 7. A modified Bunsen carbon cell but with a thick, heavy, casted Zn anode rather than a sheet of Zn on the outside of the ceramic spacer and a clear glass rather than a glazed ceramic container.

- 4. W. R. Grove, "On a New Voltaic Combination," *Phil. Mag.*, **1839**, *14 (3rd series)*, 388-390; "On a Small Voltaic Battery of Great Energy," *Ibid.*, **1839**, *15 (3rd series)*, 287-293.
- 5. W. B. Jensen, "The Chemical Uses of Clay Tobacco Pipes," *Museum Notes*, September/October 2011. Oesper Website.



Figure 8. An actual surviving example of the Bunsen carbon cell shown in figure 7 (Jensen-Thomas Apparatus Collection).

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- 6. For biographical background on Bunsen, see G. Lockemann, *Robert Wilhelm Bunsen*, Wissenschaftliche Verlagsgesellschaft: Stuttgart, 1949.
- 7. R. W. Bunsen, "Ueber die Anwendung der Kohle zu Volta'schen Batterien," *Pogg. Ann. Physik*, **1841**, *54 (2nd series)*, 417-430; "Ueber Bereitung einer das Platin in der Grove'schen Kette ersetzenden Kohle," *Ibid.*, **1842**, *55 (2nd series)*, 265-276.
- 8. B. Silliman, Jr., "On the Use of Carbon in Grove's Battery," *Am. J. Sci.*, **1842**, *43*, 393; "Description of a Carbon Voltaic Battery," *Ibid.*, **1843**, *44*, 180-186.
- 9. J. Stock, "Bunsen's Batteries and the Electric Arc," *J. Chem. Educ.*, **1995**, 72, 99-102.