Notes from the Oesper Collections

The Dichromate Cell

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The previous issues of *Museum Notes* have described the Edison nickel-iron alkaline storage cell (1), the Daniel gravity cell (2), the Grove and Bunsen cells (3) and the Leclanché cell respectively (4). This issue will deal with yet a sixth cell 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 dichromate cell (often called, in violation of current rules of chemical nomenclature, the bichromate cell). First described in 1842 by both the English chemist, Robert Warington, and the German physicist, Johann Poggendorff (figure 1), this primary cell is based on the net cell reaction (5-8):

$$3Zn(s) + 7H_2(SO_4)(aq) + K_2(Cr_2O_7)(aq) \rightarrow$$

 $3Zn(SO_4)(aq) + K_2(SO_4)(aq) + Cr_2(SO_4)_3(aq)$
 $+ 7H_2O(1) + \Delta E_{el}$

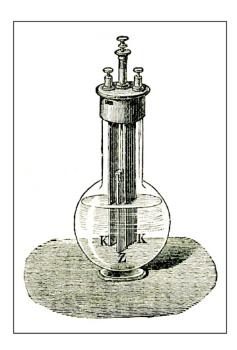


Figure 2. A 19th-century woodcut of the Grenet form of the dichromate cell. KK are the carbon cathode plates, Z is the zinc anode plate. The left electrical connection on the cap is for the cathode and the right is for the anode. What looks like a third electrical connection in the center is actually the device for raising and lowering the Zn anode plate.



Figure 1. Johann Christian Poggendorff (1796-1877).

in which Zn(0) is oxidized to Zn(II) at the anode, Cr(VI) is reduced to Cr(III) at the cathode, and the resulting net cell potential is roughly 2 V.

Warington simply substituted a mixture of sulfuric acid [H₂(SO₄)] and potassium dichromate [K₂(Cr₂O₇)] for the nitric acid in a standard Grove cell and thus retained both the expensive platinum cathode and the porous ceramic spacer, whereas Poggendorff made use of Bunsen's recent discovery that baked carbon electrodes could be used in place of platinum in Grove's cell (3). However, by the last quarter of the 19th-century the most popular form of the dichromate cell was the so-called "Grenet" or bottle form, first introduced in 1856, in which the ceramic spacer was eliminated and both electrodes directly immersed in the H₂(SO₄)/K₂(Cr₂O₇) mixture.

As may be seen from the examples shown in figures 2-5, this cell consisted of a thick amalgamated Zn anode plate arranged between two carbon cathode



Figure 3. A large two-liter Grenet cell and a smaller half-liter cell (Jensen-Thomas Apparatus Collection).

plates and mounted in a special round-bottom flask. They were sold in sizes ranging from a fourth liter up to two liters (9). The anode was connected by means of



Figure 4. Examples of surviving half-liter Grenet cells (Jensen-Thomas Apparatus Collection). The cell on the right has its Zn anode raised.

a rod to the top of the cell and could be raised out of the electrolyte when the cell wasn't in use.

Despite its large cell potential, the dichromate cell had the disadvantage that it gradually consumed its electrolyte as part of the net cell reaction and thus exhibited a progressively decreasing potential with continual use. It was most practical in situations requiring a short burst of high voltage, such as in detonating mines and other military applications, where detonation was achieved by rapidly plunging the Zn anode into the dichromate electrolyte. In addition, secondary reactions led to accumulation of dihydrogen bubbles on the cathode surface and to a subsequent drop in cell efficiency – a phenomenon known as polarization.



Figure 5. A famous photo of Thomas Edison posing in 1888 with his improved phonograph. Note the two-liter Grenet cell on the far left. Also note that its anode is in the raised position, thus indicating that it is not in operation.

In later models there was an attempt to eliminate this problem by blowing air over the cathode to disrupt bubble accumulation. In the end, however, it was the relatively high cost of dichromate salts that limited the cell's commercial applications and by the 1940s it had largely disappeared from most laboratory supply catalogs.

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. W. B. Jensen, "The Grove and Bunsen Cells," *Museum Notes*, November/December, 2013. Oesper Website.
- 4. W. B. Jensen, "The Leclanché Cell," *Museum Notes*, January/February, 2014. Oesper Website.
 - 5. For biographical background on Poggendorff see F.

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- Klemm, "Johann Christian Poggendorff" in C. C. Gillispie, Ed., *Dictionary of Scientific Biography*, Vol. 11, Schribners: New York, NY, 1970-1990, pp. 49-51.
- 6. For biographical background on Warington, see C. Hamlin, "Robert Warington (1807-1867)," *Oxford Dictionary of National Biography*, Oxford University Press: New York, NY, 2004.
- 7. R. Warrington, "On the Employment of Chromic Acid as an Agent in Voltaic Arrangements," *Phil. Mag.*, **1842**, *20* (*3rd series*), 393-395.
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- 9. Catalogue of Chemical & Scientific Apparatus, Townson & Mercer: London, 1901, p. 572.