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The Daniell cell: a historical case study[+*]

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Abstract

Daniell's cell didactic model has a key role in the teaching of electrochemistry, associated with fundamental concepts such as redox reactions. The original device created by John F. Daniell (1790-1845), however, presents notable differences if compared to the current didactic model. This paper conducts a historical case study about the battery developed by Daniell in the mid-nineteenth century. An analysis of Daniell's communications to the Royal Society on this subject reveals an important influence by Michael Faraday and William Snow Harris on his work. It took around ten years for Daniell reach the final version of his device, with an amalgamated zinc electrode in a diluted sulfuric acid electrolyte, and a copper electrode in contact with an acidic solution of copper sulfate. The separation between the electrolytes, initially made with an animal membrane, was later made by a porous earthenware container. Such battery, capable of supplying constant direct current for a considerable period of time, had a fundamental role in the expansion of telegraph networks. Understanding the process of development of scientific and technological knowledge and its implications for society, by means of a historical case study, may bring relevant contributions to science teaching.

Keywords: *Daniell Cell; Electrochemistry; History of Science.*

[+] A pilha de Daniell: um estudo de caso histórico

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I. Introduction

Laptops, tablets, smartphones, and other devices are part of the twenty-first century, allowing people to communicate, work, study, and socialize. None of that would be possible without batteries that charge these devices, which are increasingly efficient, compact, and durable. Industrial and technological development demands the efficient use of these devices and of others for different purposes, which led electrochemistry to become a relevant subject in basic education, as the understanding of the operation of these devices requires knowledge of electrochemistry (BOULABIAR *et al.*, 2004).

Electrochemistry began to be systematized as a field of knowledge around the nineteenth century and became part of university textbooks in the first decades of the twentieth century, with a growing amount and variety of contents. One of the purposes of introducing electrochemistry into curricula is to teach what are called oxidation-reduction (redox) reactions, or electron transfer reactions. These subjects are broad and exist in an area of intersection between physics and chemistry, involving specific learning difficulties.

Similar to other scientific subjects, the incorporation of didactic models to conceptual teaching happens here. The type of models involved is *representational*, that is, models that express something concretely (JUSTI, 2006). The addition of these models in teaching has a purely didactic purpose, that is, their purpose is to teach: they function as simplifiers and mediators of scientific theories towards reality; however, they *are not* reality (CUPANI, PIETROCOLA, 2002).

In the teaching of electrochemistry, the Daniell cell is a widely used didactic model, which is related to the teaching of the concepts of batteries, electrochemical cells, oxidation-reduction reactions, cathodes, anodes, oxidation number, among others (WALANDA *et al.*, 2017). A quick internet search with the keyword “Daniell cell” results in images of didactic models similar to those found both in high school and university textbooks (Image 1).

The didactic model in Image 1, which represents a battery prototype for the teaching of electrochemistry, is often called Daniell cell. However, its characteristics are significantly different from the original device developed by John F. Daniell (1790-1845) in the nineteenth century. The model that is present in didactic contexts shows the copper electrode and the zinc electrode in separate containers, connected to a device that shows the existence of electrical current (an analogic or digital meter, or even a lightbulb), and a salt bridge between the beakers to maintain the ionic balance between the electrolyte solutions. It is common to find the oxidation and reduction half-reactions written next to the respective electrodes. In the device originally created by Daniell, however, the arrangement of the containers for the electrolytes was quite different; there was no salt bridge, and the electrolytes were different from the way in which they appear in the didactic models.

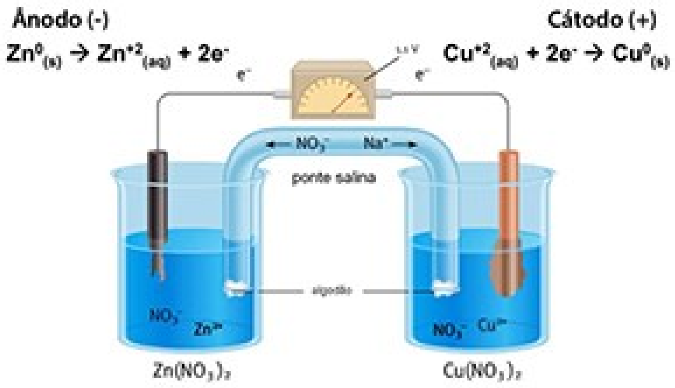

Image 1 – Typical result in online searches for Daniell cell. Source: <https://pilhadedaniellmodelo.blogspot.com/2010/06/pilhadedaniell.html>. Accessed on: June 14th, 2021.

The objective of this work is to emphasize the differences between the device created by Daniell in the nineteenth century and the didactic model that is currently associated to him through a historical case study based on original works. We intend to show the development of the aforementioned cell, the motivations and difficulties faced by Daniell and the device's importance in the social and historical context in which it was developed. Therefore, this paper aims to contextualize the Daniell cell by revealing some of the complexity that lies in that which is often just a name associated to a didactic model in textbooks.

II. John Frederic Daniell: a brief biography

John Frederic Daniell (Image 2) was born on March 12th, 1790, in Strand, a small district of London, where he received his formal schooling at home, following traditions of the time (GILLISPIE, 1990; SISTRUNK, 1952). Since his youth, he showed an affinity for investigating Nature and attended lectures that covered several subjects on natural philosophy.

In 1812, aged twenty-two, he joined the *Royal Institution*, and was accepted as an official member in 1819. From 1828 until his death in 1845, he was responsible for the chemistry section of official communications at the *Royal Institution*. He was a civil servant and also worked in a relative's sugar refinery (JAMES, 2004). His professional qualities made him become a government adviser on the issue of protecting British navy ships against corrosion, and also on the development of apparatus that could protect the ships from lightning (GILLISPIE, 1990).

Image 2 – John Frederic Daniell. Source: <https://www.worldofchemicals.com/205/ chemistry-articles/john-frederic-daniell-inventor-of-daniell-cell.html>. Accessed on: June 14th, 2021.

Daniell also worked intensely with meteorology. In 1823, he published over two dozen works on different atmospheric, geological, and climatic studies in a book that received three editions: *Meteorological Essays*. He also conducted studies on crystallography to understand the structure of different minerals, as well as to discuss the crystallization and density of salts.

In addition to his most famous enterprise, the cell that bears his name, other less known creations can be highlighted, such as the water barometer (used to measure atmospheric pressure), the pyrometer (used to measure temperature from a distance) and the dew point hygrometer (developed in 1820 to measure atmospheric humidity, still in use today). He also investigated heat and ideal temperatures for smelting furnaces. His work on ideal humidity for greenhouses led him to receive the *Rumford Medal*, offered by the *Royal Society* in 1832. He was also lauded for his contributions in climate records and measurings.

As well as being an administrator and experimenter, he was also a professor and an agent of scientific promotion. He sought the popularization and promotion of scientific knowledge among general audiences by publishing works and working in institutions that sought the same goal. In 1816, he and William Brande rereleased the *Quarterly Journal of Science and the Arts*, published by the *Royal Institution*. He was one of the mentors of the *Society for Promoting Useful Knowledge* (1827) and from 1836 until his death, he taught chemistry and geology in the military seminar of the *East India Company*. He was also connected to the founding of the *Chemical Society of London* (1836).

In 1831, he was invited to teach chemistry at the newly founded *King's College*, London, an institution where he initially worked at for the study of gas spectra in partnership with William Allen Miller (1817-1870) (GOLD, 1973). Concerned with teaching in the best possible way and also with the learning of beginner chemistry students, he wrote the book *An Introduction to the Study of Chemical Philosophy: being a preparatory view of the forces* *which concur to the production of chemical phenomena* (DANIELL, 1839a; DANIELL, 1843).

His work at the *Royal Institution* and his personal affinities led him to become close to Michael Faraday (1791-1867) (BURNS, 1993). Daniell reproduced Faraday's experiments in his laboratory, seeking to understand different phenomena connected to electrolysis and electricity in general, thus turning to electrochemistry. A resolute and curious man, he published many works in his professional life. His early and sudden death, on March 17, 1845, occurred after a stroke (apoplexy), moments after attending a work commitment at the *Royal Institution* (JAMES, 20014).

III. Daniell's works: primary sources for the case study

In this case study, we used six of Daniell's works (Table 1). The book called *An introduction to the study of chemical philosophy* is a great treaty on the chemical knowledge of the time. Its two editions, from 1839 and 1843, were obtained via Google Books®. We also used four communications issued by Daniell to the *Royal Society.*

Table 1 - Primary sources used in this case study.

Title	Year
An introduction to the study of chemical philosophy: being a preparatory view to the forces which concur to the production of chemical phenomena (1st ed.)	1839
An introduction to the study of chemical philosophy: being a preparatory view to the forces which concur to the production of chemical phenomena (2nd ed.)	1843
On voltaic combinations. In a letter addressed to Michael Faraday	1836
Additional observations on voltaic combinations	1836
Further observations on voltaic combinations	1837
Fifth letter on voltaic combinations	1839

The texts offer complementarity in approaches. The two editions of the book cover vast subjects, which made the approximation to chemical thinking at the time possible. The communications to the *Royal Society*, on the other hand, offer specific information on Daniell's studies on the cell. For this case study, we selected chapters of particular interest from the book, with subjects including electricity, electric circuits, electrochemistry, among others. In the investigation, we bestowed special attention on the comprehension of phenomena in context, as well as on the use of words that are currently in disuse or that have gained new meanings through time, yet are still present in the vocabulary of electrochemistry, such as electrode and electrolyte.

Other primary sources come from the digitalized collection of the *Philosophical Transactions of the Royal Society*, with the oldest publications being from 1665. We found several communications by Daniell, of which we selected fourteen of them, related to the Daniell cell, developed by him as a constant battery. Among them, four were deigned relevant to this work and were analyzed in more detail.

IV. Daniell, chemistry, and electricity

From the title of the book *An introduction to the study of chemical philosophy: being a preparatory view to the forces which concur to the production of chemical phenomena*, it is possible to see its introductory character to the study of chemistry as a philosophy of Nature. Daniell was concerned in writing a treaty that contained the whole scope of chemistry and some aspects of the natural philosophy of his time. Through different ways, he sought to have a relevant role in formalizing the teaching of chemistry of his time, and to make chemistry more accessible to general audiences.

Although he wanted his audience to come to know and interact with the chemical knowledge of his time, the author emphasizes that his book is not a guide or a mere manual, but a tool to better understand the chemical art (practical operations) and philosophy, which are distinct instances of knowledge (DANIELL, 1843). Thus, he was committed to enabling people to experience chemistry in a meaningful way. In addition, he wanted Faraday's studies to be known to the general public. Daniell claims that he reproduced all of Faraday's experiments on electrolysis and other phenomena related to electricity (DANIELL, 1839a, p. v).

The text was designed to culminate in the study of electrical phenomena along the devices that were being developed at the time. When organizing his book, Daniell understood that it was necessary to first present ideas relating to electricity and to phenomena related it, and then the invention of different devices. First, he dealt with static electricity, starting with the ideas attributed to the Greek philosopher Thales of Miletus and mentioning everything he believed to be relevant on the subject, from experimental evidence that intrigued people to empirical praxis related to phenomena. Through comments that guide the reading, there is a concern for the way a lay person would start to understand the covered topics.

Beyond the behavior of the then-called *electric fluids*[2], Daniell sought to show how the interaction of said fluids with bodies made of different materials occurred, that is, the question of conduction or non-conduction through materials. He showed particular interest in conduction in metallic materials. In this context, we highlight the works of William Snow Harris (1791-1867), which played a vital part in the development of the Daniell cell.

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[2] At the time, there were two major conceptions on the nature of electricity: The Du Fay hypothesis and the Franklin Hypothesis. Charles Du Fay (1698-1739) proposed the existence of two elastic and imponderable fluids, one of them *vitreous* and the other *resinous*, which would compose the *electric fluid* (DANIELL, 1943). For Benjamin Franklin (1706-1790), there was a single *electric fluid*; only when this *fluid* was in disbalance between bodies that the attraction or repulsion between them would occur. Explanations based on *electrons* as part of atoms would only be developed in the nineteenth century.

V. Snow Harris' influence

William Snow Harris was born on April 1st, 1791, in Plymouth, England. After finishing his medical studies in Edinburgh, he worked as a military surgeon in the British Army. He worked continuously for the *Royal British Navy*, developing, and improving lighting rods for ships (DANIELL, 1843). His studies on lighting rods for protection of English ships were extended; however, his ideas faced resistance, and around twelve years were needed for the Navy to recognize and pay for this work (ANONYMOUS, 1868, p. xx-xxi). After working with medicine and his studies on electricity for a few years, in 1824, Snow Harris started to dedicate his time solely to natural philosophy. For many years, he was a member of the *Edinburgh Royal Society*.

Snow Harris' first publication in the *Proceedings of the Edinburgh Royal Society* dates from 1829 and deals with "*Experimental Investigations into the Laws of Magnetic Forces*". The studies and devices invented by Snow Harris to investigate electricity caught the attention of the President of the *Royal Society*, Sir Humphry Davy, who invited him for a conference. The work presented was "*On the relative powers of various metallic substances as conductors of electricity*", which led him to become a member of the *Royal Society*.

Snow Harris studied the relationships between magnetism and electricity and created cylindrical and plate electrical machines that were extremely useful in studying electricity in England. His works had a great influence on Daniell's choices regarding the metallic materials for the cell. Using a device called air thermometer (which he built himself), Snow Harris studied how different metallic materials behave and produce heat when *electric fluids* pass through them. His experimental data were presented by Daniell in *An Introduction to the Study of Chemical Philosophy* (Image 3), and certainly influenced the final choice of the zinc and copper pair for the construction of the constant current battery. Before reaching that conclusion, Daniell had experimented with many different pairs of metals, and for a long time, he used zinc and platinum or zinc and silver.

Snow Harris' work was pioneering and brought with it important contributions to other studies in the area. The experimental data presented in Image 3 show the values of an intensive property that Snow Harris called *resistance* for different metals and an alloy (brass, a copper and zinc alloy). This property is now called *resistivity* – that is, the opposition that a material offers to the passage of electric current: the lower the resistivity value of a material, the better the conduction of electrical current through it[3]. In Image 3, we can observe that Snow Harris used arbitrary units for the resistivity[4], and that his measurements were precise,

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[3] It is important to distinguish resistivity and resistance (R). Resistance refers to the opposition to the passage of current in a circuit and may be described by Ohm's Law (V = R.i). These quantities are important to determine which is the most adequate material for distinct situations, such as in electronic circuits or electrical installations in buildings and industries.

[4] In the International System (IS) that is currently used, the unit for resistivity is Ω.m (ohm-meter).

as silver is the metallic material with the lowest known resistivity (1,6 . 10^{-8} Ω.m), followed by copper (1,7 . 10^{-8} Ω.m) and gold (2,4 . 10^{-8} Ω.m).

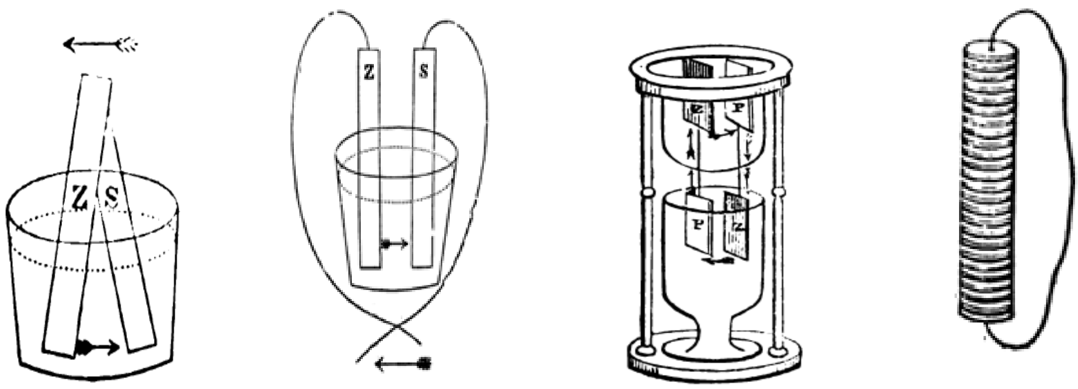
TABLE XXXVIII. *Electrical Conduction.*

	Heat evolved.	Resistance.
Silver	6	1
Copper	6	1
Gold	9	1½
Zinc	18	3
Platinum	30	5
Iron	30	5
Tin	36	6
Lead	72	12
Brass	18	3

Image 3 – Snow Harris' experimental data on the behavior of different metallic materials. The released heat ("heat evolved") represents how much the material in question would heat up when electricity passed through it; "resistance" represents a quantity that is analogous to what we understand today by resistivity. Source: Daniell (1843).

VI. Searching for a constant current battery

Daniell, who started his studies on electricity by reproducing Faraday's experiments, became independent when noticing a gap in relation to the existing devices made to produce and transmit electricity. In *An Introduction to the Study of Chemical Philosophy*, after conducting a historical review on the ideas regarding electricity, Daniell discusses the ideas of his time and reaches the then important issue of batteries. Similar to how he increased the complexity of his descriptions about the ideas of electricity, he also did so when talking about circuits. He introduced less complex circuitry and the Voltaic pile, which was called that because it literally is a pile of zinc and silver disks, interspersed with cloth or cardboard soaked in a mixture of strong acids. The action of acids corroded the zinc disks and led to the production of hydrogen gas bubbles, causing the Voltaic pile to produce electricity for no more than a few minutes.



(a) (b) (c) (d)

Image 4 – (a) A zinc plate (Z) and a silver plate (S) in contact inside a container with an electrolyte; the arrows indicate the direction of the electric current, called affinity force by the author; (b) zinc and silver plates in a container containing an electrolyte and connected with a wire; (c) a "cup circuit": two zinc plates (Z) and two platinum plates (P) in different containers with an electrolyte in each, in contact through conducting wires; (d) Voltaic pile. Source: Daniell (1843).

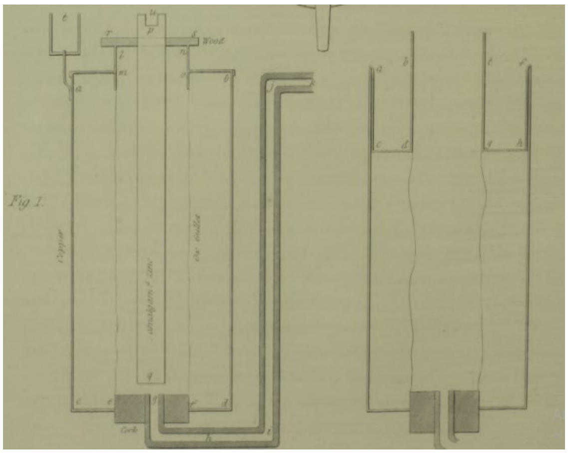
The essential elements to the production of an electric current by a battery were the metallic components in contact with a conducting environment (electrolyte)[5], and the wires or device (sometimes the galvanometer) that closes the circuit. The Voltaic pile was a pioneering device in the production of electric current.

In each of the four letters written by Daniell, processes related to variables involved in the creation of the constant battery are reported. In the first communication of 1836, *On voltaic combinations*, new voltaic combinations were tested, that is, different structural arrangements of battery electrodes and electrolytes due to technical needs. The electrodes previously used by Daniell were made of zinc and platinum. In this communication, he described how the use of the zinc and copper pair made it possible to solve several technical problems that, until then, had prevented the batteries from maintaining a constant current for a long time. The cell with zinc and copper and diluted sulfuric acid and copper sulfate solutions as electrolytes would become the final combination also described in the two editions of his book (DANIELL, 1839a; DANIELL, 1843).

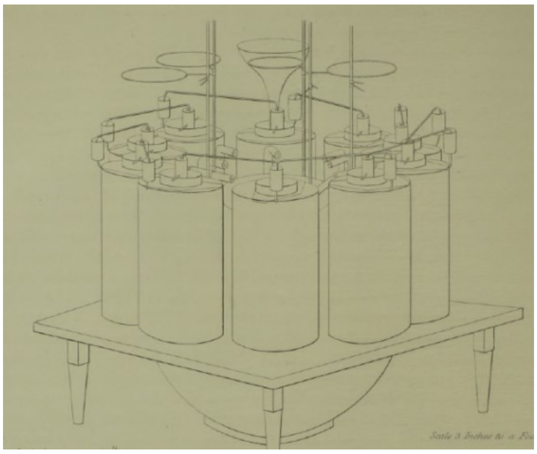
[5] The world *electrolyte* originally referred to what provoked electrolysis, that is, the chemical decomposition force that would provoke chemical separations. Faraday used the term for the first time, and Daniell refers to *electrolyte*s several times in his book. This word gained new meanings and currently, electrolytes are the means through which the passage of electric current in solutions or molten states occur, due to ionic dissociation. There are several quantities and physical-chemical forces that influence the action of electrolytes, such as the dissociation degree of the chemical species that is dissolved, the electrolytical force and the activity coefficient of the ionic species. In the current context of electrochemistry, the electrolyte itself does not provoke the conduction nor electrolysis.

In his initial studies on simple circuits, Daniell observed the rapid adhesion of hydrogen gas onto zinc plates that were submerged in strong acid electrolytes, which impeded the circulation of *current force* (or electric current). He avoided this problem by using an amalgam of zinc and mercury as the generating metal[6] – an alternative that proved to be economically viable. In addition, his acidic solutions were more diluted than those used by Volta.

The cell was assembled by placing the amalgamated zinc rod in the center, supported on its top by a wooden rod and surrounded by a membrane obtained from the tissue in oxen esophagus. The function of this membrane was to separate the electrolytes in which the two metal components of the cell were immersed. The Daniell cell did not have the operating inconsistencies that characterized the Voltaic pile, and that is why its inventor deigned it as a *constant*[7] *cell.* The 1836 communication included a drawing of the device (Image 5).



(a)



(b)

Image 5 – Drawing of the constant cell in Daniell's communication from 1863. We can observe the existence of a siphon in the inferior part and a compartment in the upper left corner (mercury cup) to contain mercury and through which the contact with other cells or with the object to be submitted to electricity was established. These components were excluded in later versions of the cell. (b) An association of ten cells on a wooden desk with a hole in the middle, with a bowl in the inferior part to hold the electrolyte, which was eliminated as more electrolyte was manually spilled into each cell with the help of funnels. Source: Daniell (1836a).

6 Daniell referred to the less noble (i.e., more reactive) metal of the pair as the *generating metal*, as he considered it responsible for *generating* the affinity force.

7 Generally, the term "battery" was used to refer to an association of several "cells" – what Daniell called each individual device. To simplify the understanding of this by the modern reader, in this article the terms "cell" and "battery" were used as synonyms, and "battery" was used in the sense used by Daniell, of battery association.

In Image 5a, we can observe that under the central zinc rod, there is a siphon (g,h,i,j) that connects the internal compartment with the exterior, and still a compartment t (on the upper left corner of the image), described as a mercury cup. Through this mercury cup, it was possible to connect this cell to others. The siphon allowed the flow of the liquid within the inner cylinder as more portions of liquid were poured through a funnel, in order to keep the concentration of the electrolyte constant. We can also observe that the device was mounted inside a copper cylinder, which served as a container for the second electrolyte and, at the same time, as the electrode itself. At the end of this communication, Daniell concluded that:

> *My principal object in these researches has been the attainment of this constancy [of the current]; but, in addition, this new combination will be found, I think, to possess advantages which will secure to it a more general application than I at first contemplated. First, the abolition of all local action by the facility of applying amalgamated zinc; Second, the trifling expense of replacing, the zinc rods when worn out (...); and the total absence of any wear of the copper; Third, the non-necessity of employing nitric acid, and the substitution of the cheaper materials, sulphate of copper and oil of vitriol [i.e., sulfuric acid]; to which I may add, the absence of any annoying fumes: And, fourth, the facility and perfection with which all metallic communications may be made (...)* (DANIELL, 1836a, p. 124).

The following year, 1837, Daniell wrote *Further observations on voltaic combinations*, in which his investigations on the influence of temperature on the voltaic action stand out. Daniell explained that, faced with an inconvenience, he had to interrupt an experiment, due to "the bursting of all the membranes which had been exposed for five weeks to the acid solution" (DANIELL, 1837, p. 124). He then began a series of attempts to replace the membranous material of animal origin intended to separate the two electrolytes with one that would withstand the experimental conditions. His final choice fell on a porous clay container (*porous earthenware*), a material that was thus always used, even at room temperature and regular conditions of the operation of the constant battery, as can be seen in the two later editions of the book *An Introduction to the Study of Chemical Philosophy*.

When seeking the aforementioned "constancy" of the produced electric current, Daniell noticed with his experiments that other factors could influence the obtainment of electricity. In his second communication from 1836, and again in 1837, Daniell stated that, after performing many experiments with different concentrations of acid in the inner cylinder of the cell (i.e., in contact with the zinc rod), he concluded that the most diluted solution (eight parts of water to one part of sulfuric acid) was the most adequate, which was thus adopted by him in all subsequent experiments (DANIELL, 1836b, p. 127; DANIELL, 1837, p. 141). In the external cylinder, Daniell experimented with different substances, such as ammonia, barite, ammonium sulphate, potash and muriatic (hydrochloric) acid, reaching the conclusion that the best results were indeed obtained with an acidic solution of copper sulphate as the electrolyte within the external cylinder (in direct contact with the metallic copper surface) (DANIELL, 1837).

His focus was on the variables that seemed to influence the period during which the battery would produce electricity without significant decreases in intensity. The goal was to obtain "an invariable current[8] of force sufficient to effect chemical decompositions" (DANIELL, 1836b, p. 125). In the second communication of 1836, Daniell includes reports of battery operation for fifteen, twenty and twenty-four uninterrupted hours, with a small decrease in its action, while in the previous communication he described the operation of the device for up to eight hours.

In order to compare the performance of different batteries, researchers at the time had to develop equipment that could somehow quantify the produced electricity. Among the devices they used were the galvanometer and the voltameter[9]. The galvanometer consisted of a magnetic needle surrounded by a coil with two terminals and was often the final element of a circuit. When placed between the electrodes of a circuit, as an example, the deflection of the needle (measured in degrees) made it possible to infer the intensity of the current: the greater the deflection of the needle, the more intense the current through the circuit. However, as effective as the galvanometer was, this was a measure of qualitative rather than quantitative nature. Therefore, the development of the voltmeter proved to be important, as it made it possible to measure the electric current in a more precise way, even if it was an indirect measure.

When a circuit was closed, with the voltameter terminals in contact with an electrolyte (aqueous solution of diluted sulfuric acid) within a container connected to a graduated and closed glass column, a water electrolysis reaction started immediately: the gases were collected, and their volume was measured in the graduated column. It was inferred that the greater the amount of collected gas, the greater the amount of electricity produced by the battery connected to it (SANTOS *et al.*, 2020, p. 333). Daniell himself conducted experiments seeking to optimize the operation of the voltameter created by Faraday, in order to compare the performance of different batteries (DANIELL, 1836b, p. 125-126).

In another experiment, instead of using a voltameter, Daniell connected a twenty-cell battery to a thin, eight-inch-long platinum wire, which was heated to red hot (glowing) and remained so for a long period of time (DANIELL, 1836b). Thus, in addition to making changes related to the development of the battery, there was also an interest in changing the

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[8] It is important to note that the modern concept of electric current (as motion of elementary electric charges) had not yet been developed at this time. What Daniell calls a *current* is related to what was called the *opposite affinity force* and the *current force* established by electrical fluids in the production of electricity. For electricity to flow, the current strength must be quantitatively greater than the opposite affinity strength.

[9] The device referred to here as a voltameter should not be confused with what we know today as a voltameter, used to measure the difference in electric potential. The name "*voltameter*", used by Daniell, can be understood as an abbreviation of "*volta-electrometer*", that is, the Volta electrometer. This device was created by Faraday to measure electric currents, collecting the gases that were produced in the electrolysis of an aqueous solution: the volume of gas produced is directly proportional to the electric current that passes through the circuit.

way in which experimental observations were made. In this case, the glow of the wire was qualitative evidence of the intensity of the electrical current that was produced.

The influence of the distance between the generating and conducting surfaces and the length of the wires that connected one cell to another was also studied. Daniell investigated the effect of bringing the generating metal closer to the conductive metal, reducing the diameter of the copper cylinder – which also implied reducing the surface of the conductive metal (DANIELL, 1839b). Thus, he observed that there was a decrease in battery action (measured by the volume of produced gas as measured by the voltameter), which was approximately equal to the respective reduction in the surface area of the conducting cylinder. As he increased the diameter of the copper cylinder, however, he noticed that the battery's action also decreased. Without having an explanation for this behavior, he declared that further investigations would be necessary and admitted that:

> *(...) the conclusion which we can at present draw from the experiments (...) is, that cylinders of 3.5 diameter form much more effective conducting plates in a voltaic arrangement than cylinders of either greater or less diameter. It must, however, be borne in mind that this has only been proved with a series of ten cells; for it is highly probable limits of efficiency may change with the number of the series* (DANIELL, 1839b, p. 90).

Careful observations regarding the development of the elements in the constant battery, with variations in and shapes of the components in search of the best arrangement, led Daniell to make some theoretical considerations about what the ideal battery would look like:

> *Considered in a theoretical point of view, these experiments seem to me to lead to the conclusion that the most perfect voltaic combination would consist of a solid sphere of a generating metal, surrounded by a hollow sphere of a conducting metal, with a stratum of intervening electrolyte perpetually renewed, and the metals communicating by a wire defended from the electrolyte by a glass tube covering that portion which it would be necessary should pass through it* (DANIELL, 1836b, p. 128).

Daniell recognized the impossibility of creating his idealized battery and concluded: "The rod of zinc within the cylinder of copper is probably the nearest practical approximation which can be made to such an arrangement" (DANIELL, 1836b, p. 128). The constant cell illustrated in the 1843 edition of his book presents the dimensions of the electrodes that resulted in the best performance: an amalgamated zinc rod of three-and-a-half inches in diameter, inside a copper cylinder of six inches in diameter.

In another series of experiments, Daniell investigated the effects of using different numbers of cells (with standardized diameters) connected in series in different arrangements, involving up to twenty cells. For other experiments, however, he used even more cells:

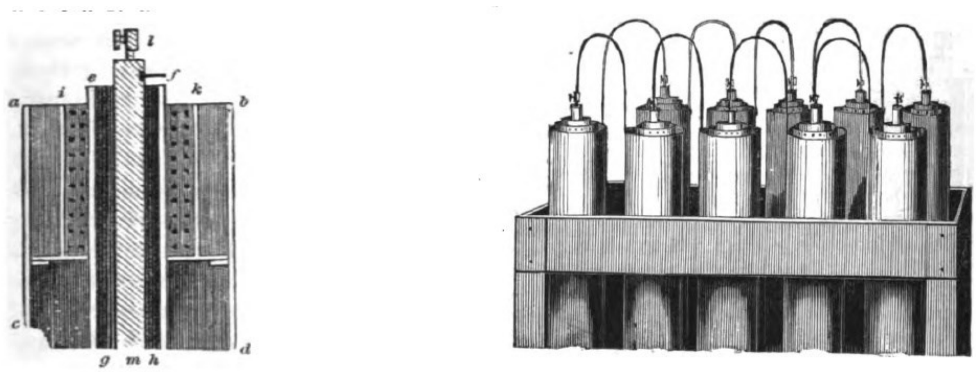
> *I now combined in a single series a battery of* ***seventy cells*** *of the same dimensions and charged in the same manner, for the purpose of observing chiefly the light and heat produced by the current in a state of high intensity and constant action* (DANIELL, 1839b, p. 92, highlights by the authors).

In addition to the large number of cells, the release of light and heat used as an indication of voltaic action is noteworthy. Daniell described several experiments in which he produced electrical discharges between two needles made of carbon, through the air and under vacuum, producing a glow so intense that it was harmful to the eyes, and the heat was capable of causing burns similar to those caused by the sun (DANIELL, 1839b, p. 92).

An interesting series of experiments refers to the use of voltaic batteries to decompose water, keeping the gases inside a closed container. Among Daniell's objectives was the observation of whether the growing pressure of the gaseous mixture would have any effect on the action of the battery, or even if the gases might recombine. Several experiments were conducted, including the electrolysis inside a hermetically sealed glass tube, until the internal pressure of the gases led to the explosion of the tube. In no case was any alteration in the battery observed, which led Daniell to conclude that the "electric force" in the battery was not affected, even when it was opposed to the "elastic force" from the accumulated gases. When calculating the internal pressure in the tubes, Daniell speculated whether this type of experiment could be used in the liquefaction of gases – a subject of interest for Faraday (DANIELL, 1839b, p. 94-95).

Daniell also sought to contribute to the nomenclature used in electrochemistry, following in the footsteps of Faraday – who created, in collaboration with William Whewell (1794-1866), a series of terms used in the field, such as electrode, anode, cathode, ion, anion, cation, electrolyte and electrolysis (ROSS, 1961). Daniell suggested the use of the name *zincode* for the electrode corresponding to the generating metal, and *platinode* for the electrode corresponding to the conducting metal – although, in his text, the use of these terms is confusing (DANIELL, 1839b, p. 92). Unlike the terms created by Faraday (which gained other meanings over time, but still in use today), this suggestion by Daniell was eventually forgotten.

After years of research, Daniell present in his book *An Introduction...* (1839a, 1843) the perfected version of his constant battery (Image 6).



(a) (b)

Image 6 – Daniell's constant cell. On the left, lm is a zinc rod amalgamated with mercury; abcd is a copper cylinder that contains the entire voltaic array; efgh is a porous clay cylinder. The outer cylinder is filled with a saturated copper sulphate solution, and the inner cylinder with a diluted sulfuric acid solution. Solid copper sulphate is placed in the container ik to keep the solution in the outer cylinder saturated; (b) Ten cell association. Source: Daniell (1843).

Neither the mercury cup nor the siphon appear in this version of the battery, which did not need these components. The drawing (Image 6b) shows that the connection between the cells was made only with metallic wires, eliminating the mercury compartment from Daniell's first batteries. In addition, to keep the electrolyte in the outer cylinder saturated, bags of muslin – a cotton-like fabric – were inserted, containing a solid copper salt, whose dissolution slowly released it into the electrolyte. Thus optimized, the associations of cells produced electrical currents for long periods of time. It is possible to observe how the cell built by Daniell was quite different from the didactic models in use today: there were no separate containers made of glass, but concentric containers of porous clay and copper; one of these containers (the outer cylinder) was the copper electrode itself; there was no salt bridge (the contact between the electrolytes was through the porous clay); one of the electrolytes was diluted sulfuric acid, and the metal immersed in it was amalgamated zinc, instead of pure zinc (i.e., an alloy of zinc and mercury).

After optimizing the working of his constant battery, Daniell used it in studies on electrolysis. This device became a laboratory tool for several British researchers interested in electricity, or one who needed a source of direct current for specific purposes (OWEN, 2001).

In his second communication of 1836, Daniell suggested that the action of his battery would make it an economical source of oxygen (by electrolysis of aqueous solutions) for use in laboratories, thus highlighting an example of its practical utility. Shortly thereafter, in a postscript to his 1837 communication, Daniell explicitly stated that the constant battery showed new possibilities for economic applications for voltaic electricity. It is clear, therefore, that his motivations for improving the device were not restricted to Nature Studies or voltaic electricity *per se*, but also included practical aspects. The battery developed was especially important for the implementation of a large-scale communication system for the time, initially in England and later between more distant locations: the telegraph.

VII. The Daniell cell and the electric telegraph

In mid-nineteenth-century England, there was great interest in enabling communication between geographically distant industrial or mineral exploration centers, as well as between areas that were progressively becoming more urbanized within the country. The economic and industrial development of Great Britain during that time was largely due to the textile industry, supplied with cotton coming from colonies, especially from India (LEONARDO *et al.,* 2009). In this context, the electric telegraph was a welcome invention.

The need to establish direct communication within English territory and with other countries for commercial purposes, especially with the United States and with European countries with active stock markets, was met with the advent of telegraph networks. Between the 1830s and the 1850s, telegraph networks[10] were consolidated, and British companies held a monopoly of knowledge and technique for their implementation (HUUDERMAN, 2003).

The telegraph started a new era of efficient communication, connecting the world in a way that had never been possible. An example of its consolidation was the creation of the World Observatory, to standardize international time zones (KOCHER, 2014a). Although telegraph networks developed relatively quickly in two decades, in the previous period, there were different obstacles to their implementation. One of them was the need for a direct current power supply for the networks, an obstacle which Daniell decisively contributed to.

The efficiency of telegraphs stemmed from a physical principle that was well-known and explored in the nineteenth century: the conduction of electricity by a metallic material. The words in a message were encoded in electrical impulses that had to travel through the network. The transmission networks consisted of metallic wires (initially made of iron and later replaced by copper wires) coated with insulating materials such as resins or natural rubbers, including gutta-percha, and suspended on wooden poles.

In this context, the battery as a source of electricity was an essential component to the development of the telegraph. The innovations introduced by Daniell concerning electrolytes and the device's internal arrangement made the battery more efficient and facilitated its use, which allowed the structuring of telegraph networks on a large scale.

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[10] Generally, the use of the word "*telegraph*" refers to electric telegraphs, that is, those that depended on electricity to send messages consisting of electrical pulses through conducting wires. The wires could be arranged through the air (aerial networks), the ground (underground networks) or water (underwater networks). However, the electric telegraph is not the only existing type: the visual telegraph (of the optical type, which was simpler and had light signals) emerged first as an alternative to marine signalers. In this work, the word "*telegraph*" refers to the electric type, but this was not the only type used in the eighteenth and nineteenth centuries.

Image 7 – Association of Daniell cells for telegraph networks. Source: <http://www.victorianweb.org/painting/reviews/decoded1.jpg>. Accessed on June 1st, 2021.

Singer (1958, p. 649) points to three moments in the evolution of telegraphs. The first was the creation of electrostatic telegraphs, such as the telegraph owned by the Spaniard Francisco Salvá y Campillo, in which electricity was stored in Leyden jars[11] connected to wires that had a corresponding letter (HIGHTON, 1852). The second was the development of electrochemical telegraphs, which used voltaic batteries to produce the current used to send messages. The third moment is characterized by electromagnetic telegraphs, such as the Wheatstone and Cooke telegraph, which was a commercial model. This model had five magnetized needles that were arranged on a wooden base; with the passage of electric current, the needles moved at specific angles and pointed to the corresponding letter (KOCHER, 2014b).

Among the different telegraph models, the one to achieve the highest popularity was Samuel Morse's (1791-1872) telegraph, due to its simplicity and efficiency in sending messages. Morse created a system of dots and dashes, in which each electric impulse with the duration of a second was a dot, while a three-second impulse was a dash. Each letter of the alphabet and each number was composed by a group of dots and dashes.

The impact of the Daniell cell in its time can be illustrated by the focus given to it in a book of scientific dissemination dedicated to the "*Triumphs and wonders of the nineteenth century, a volume of original, historic and descriptive writings showing the many and marvelous achievements which distinguish a hundred years of material, intellectual, social and moral progress*", as stated by its title. In this book, there was a section dedicated to the telegraph, in which the author highlights the importance of Daniell's contributions:

[11] The Leyden jar can currently be interpreted as a kind of capacitor, that is, a device capable of storing electric charged. Created in 1746 by Pieter van Musschenbroek (1692-1761) in Leyden, Netherlands, it consisted of a cylindrical flask coated with a conductive material inside and out, with an insulating material between them. According to Jardim and Guerra (2018), significant amounts of electric charge could be stored in the Leyden jar, which enabled and boosted studies in electricity.

> *(...) up til 1836, no battery had been produced that was sufficiently constant in its operation to supply the kind of current required [to power telegraphs]. For feasible telegraphy, two important steps were yet necessary. One was the discovery of the electromagnet, 1825-30. The other was the discovery of Daniell's battery or cell in 1836, by means of which a constant electric current could be sustained for a long time* (BOYD, 1901, p. 27).

For us to understand the rapid growth in demand for batteries to supply the telegraph networks, it is worth mentioning that in the headquarters of the London General Post Office alone, there were about 20,000 cells (PREECE; SIVEWRIGHT, 1876; PRESCOTT, 1860). In the telegraph center of the Western Union Telegraph Company in New York, the batteries were organized in cases with eight double shelves, each with twenty-four cells, adding up to one hundred ninety-two cells per shelf (Image 8) (PRESCOTT, 1879).

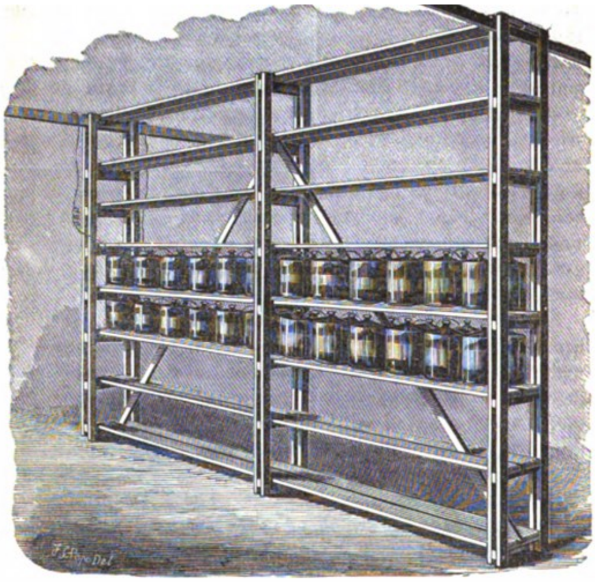

Image 8 – Battery cases in the telegraph center of the Western Union Telegraph Company in New York For a better understanding, in this image, only two of the eight shelves seem to hold batteries. Source: Prescott (1879).

VIII. Final thoughts

The case study in this work leads to a series of reflections that are useful to the initial and continuous training of science teachers on the topic of the connection between teaching and the history of science. Some aspects of Daniell's career, the focus of this work, offer counterpoints to commonly disseminated images in the media and even in certain teaching materials about the activities of scientists.

Daniell became known for his work in electrochemistry, but his scientific performance also expanded to other fields of knowledge and activities, such as scientific dissemination and teaching at *King's College*, London (DANIELL, 1843). We can thus see that the creation of an efficient cell was not an isolated and ingenious event, but part of a complex scientific career. This complexity also involves the influence of other intellectuals: the study of texts published by Daniell reveals mentions of about three dozen previous and contemporary authors, with Michael Faraday and William Snow Harris being the most frequently cited. Furthermore, the development of the Daniell cell did not happen overnight: for nearly a decade, Daniell worked on a series of attempts to improve the device capable of producing direct current stably. The choice of electrodes, for instance, involved trying different metals, alloys and mineral coal and for a long time Daniell used the metallic pair of platinum and zinc, as well as silver and zinc, before choosing copper and zinc.

This case study also provides a glimpse into the context in which the Daniell cell was developed, when several researchers were exploring the new field of electrochemistry. The constant battery was an important tool for studies in electrolysis and in several areas, developed by Daniell himself, by Faraday and by many others. It was also important in the establishment of one of the first modern communication systems on a global scale, the electric telegraphs, and it also found applications in electrometallurgy (MERTENS, 1998). In this case, there was a fruitful convergence between society and science. Thus, this episode can also contribute to the understanding of the importance of the Daniell cell for the history of communication.

When observing Images 6 and 7, the modern reader will notice that the development of the Daniell cell was quite different from the didactic model that is commonly presented to students today, in which the electrodes are in separate beakers and there is a salt bridge between them (Image 1). In fact, the cylindrical shape of the Daniell cell, with an outer metal container and an inner electrode in the shape of a rod, more closely resembles our "AA" batteries – although, of course, both conductive materials and electrolytes are quite different from these current devices.

The complexity of the peer-to-peer collaboration and communication process that resulted, over the years, in the development of the constant battery remains hidden from students who come across idealized models of the Daniell cell in textbooks. This historical case study exemplifies how didactic models are often dissociated from the events, devices, or scientific concepts that inspired them, which may bring consequences to science teaching. The historical perspective can be useful to recover forgotten knowledge and to bring scientific knowledge and school knowledge closer together, increasing the interest and involvement of students at different levels of education.

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