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Strange Case of Signor Volta and Mister Nicholson: How Electrochemistry Developed as a Consequence of an Editorial Misconduct

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electrolysis of water · galvanic cell · Nicholson, William · pile · Volta, Alessandro

Abstract: *This Essay tells the colourful history of the invention of the pile by Alessandro Volta and of the subsequent discovery by William Nicholson of the electrolysis of water, carried out with the Voltaic pile (1800). Indeed, as a result of the dissemination of Volta's paper among London scientists, favoured by an incorrect behaviour of the President of the Royal Society, the article by Nicholson was published months before the publication of Volta's letter. The outstanding news that electricity could be generated by a simple and easy to build instrument (the pile) was printed also by daily newspapers, which favoured its spreading all over Europe and stimulated a multitude of enthusiast practitioners and amateurs to construct their own pile and to carry out the electrical decomposition of a variety of aqueous electrolytes. The correct chemical interpretation of the pile and of electrolysis had to wait for nearly one century, but in 1800 electrochemistry was born.*

1. Introduction

Let us consider the hypothetical case of a researcher A, who submits a paper, reporting on a novel and revolutionary technique, to a very prestigious scientific journal (e.g. the official journal of the scientific society of a leading country). The editor B is strongly impressed by the innovative nature and by the potential of the discovery and hands the article to a colleague and friend C for reviewing. The comment by C is highly positive, but publication of the paper takes several months. In the meanwhile, C, by using the technique learned from the refereed paper, performs experiments producing outstanding results. These findings are then described in an article, which is promptly published in a commercial scientific journal, whose editor is D (who, incidentally, cooperated with C in the researches). The paper authored by C and D appears months before the publication of the inspiring article by A.

Such a state of affairs, rather than hypothetical, seems today totally intolerable, in view of the severe ethical and editorial constraints of scientific literature and of the code of conduct universally accepted by researchers. However, something like that happened during the last year of the 18th century (1800), involving some renowned scientists: Alessandro Volta, professor of Experimental Physics at the University of Pavia (A); Sir Joseph Banks, a prominent botanist, President of the Royal Society (London) and Editor of Journal of the Society, *Philosophical Transactions* (B); Anthony Carlisle, a brilliant surgeon at Westminster Hospital, London (C), and William Nicholson, a chemist and founder/editor of *The Journal of Philosophy, Chemistry, and the Arts*, the first commercial monthly scientific journal in Great Britain (D), see Figure 1.

The paper by Alessandro Volta, describing the invention of the pile, as a source of electrical current, was sent to Sir Joseph Banks, dated March 20, 1800. The letter was read at the Royal Society on 26 June, 1800, and published in the September issue of the *Philosophical Transactions.* However, just after receiving Volta's letter, Joseph Banks, highly impressed by the novelty of Volta's machine and by its potential for immediate applications in physics, chemistry, and medicine, even if formally obliged to keep the author's discovery confidential, could not resist showing the document to some friends and colleagues, including Carlisle. The skilful surgeon showed in turn the letter to his friend Nicholson and, following the detailed instructions reported there, constructed a pile. Then, Carlisle and Nicholson performed experiments with the new apparatus and, in particular, they carried out the electrolysis of water. Eventually, Nicholson published a paper in *The Journal of Natural Philosophy, Chemistry and the Arts* (of which he was the Editor), announcing the discovery of electrolysis of water by Anthony Carlisle and himself, by using the Voltaic pile. Only two months later (September), Volta's paper was published in French in the *Philosophical Transactions of the Royal Society*, and in English in *The Philosophical Magazine* (another commercial scientific periodical) and made available for comments and as a source of inspiration for future experiments to the rest of the European scientific community.

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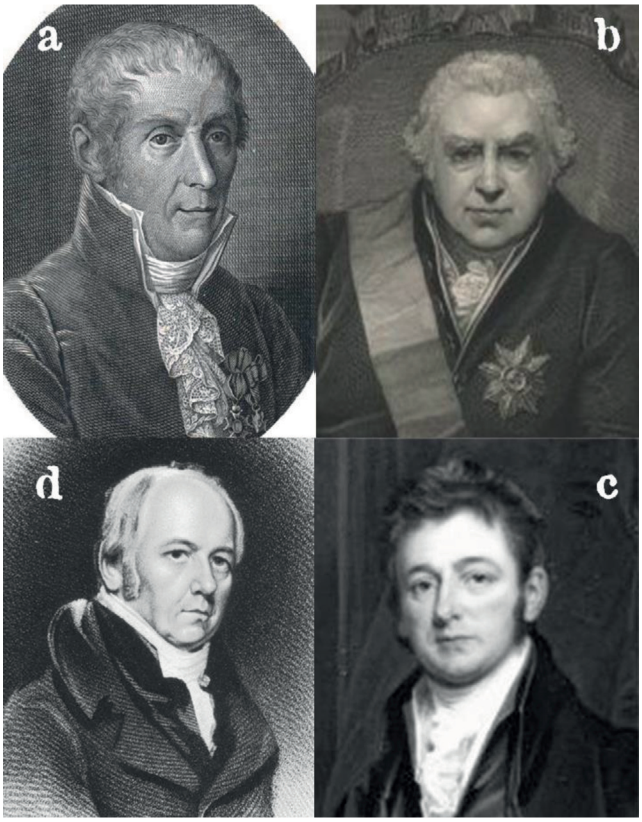


Figure 1. a) Alessandro Volta (1745–1827), engraving by Nicolò Bettoni, 1825; b) Joseph Banks (1743–1820), print from the portrait by Thomas Phillips, painted 1810; original held at the National Portrait Gallery London, 1815; c) Anthony Carlisle (1768–1840), print of a miniature portrait in enamel on copper by Henry Bone, 1827; d) William Nicholson (1753–1815), wood engraving by Thomas Blood, ca. 1810.

The affair, from a today's point of view, seems absolutely execrable and brings the way of making and communicating science in the period between 18th and 19th centuries into disrepute. However, before passing a drastically negative verdict, one should consider in more detail the course of the events and the boundary conditions, in their political, social and technical aspects.

__Luigi Fabbrizzi__ received all his education in Florence, where he obtained his degree in Chemistry in 1969. From 1972 to 1980, he was a Lecturer at the University of Florence. In 1980 he was appointed Professor of Chemistry at the University of Pavia, where he is currently Professor Emeritus. Since 2009, he has been an Honorary Professor at the East China University of Science and Technology of Shanghai. In 2010, he received the Izatt-Christensen Award in Macrocyclic and Supramolecular Chemistry. His research interests have covered coordination chemistry and supramolecular chemistry involving transition metals. In Pavia, Luigi Fabbrizzi held the Chair of General Chemistry (from 1980 to 2014), whose first holder was Professor Luigi Valentino Brugnatelli (from 1796 to 1818), colleague and close friend of Alessandro Volta.

2. Alessandro Volta, Professor and Natural Philosopher

Alessandro Volta was born in 1745 in Como, a pleasant small town on the shores of Lake Como, 40 km North of Milan. He belonged to an aristocratic, but not rich family, which addressed him to the study of law. However, the young Volta was strongly attracted by science, physics in particular, which he studied essentially as an autodidact. At the age of 18, he developed a specific interest in electricity and began to correspond with many of the leading scientists of the day, in Italy and abroad. In 1769, he published his first paper entitled *De Vi Attractiva Ignis Electrici* (On the Attracting Force of the Electrical Fire).[1] In 1775, he invented the electrophorus, an early form of electrostatic generator.[2] These studies caught some attention and helped him gain his first appointment in 1774, when he became a Lecturer, and one year later a Professor of Experimental Physics, at the Como's high-school, a position which allowed him to start systematic experimental research. Leaving for a while the electrical matter, in 1776 Volta isolated and characterized a new gas, methane,[3] which he used to operate a flammable air pistol that he fired using an electric spark (Volta's pistol). These discoveries made him considerably renown and as a result he received a travel grant from the Austrian government. This enabled him to travel around Europe and to meet and exchange ideas with the most important scientists, an aptitude he maintained during all his career. In this way, Volta acquired an international fame and entered the European community of natural philosophers.

In 1779 Volta was appointed to the post of professor of *Experimental Physics* at the University of Pavia. After a long period of decline when Lombardy was ruled by the Spanish, the University of Pavia experienced a fast and impressive rebirth with the incoming Austrian administration, in the second half of 18th century. In particular, Empress Maria Theresa (1717–1780) and her son Joseph II (1741–1790) chose Pavia to create a great Italian University, which could compete with the best in Europe. Thus, most important Italian scientists were invited and appointed as professors in Pavia, including the biologist Lazzaro Spallanzani (1729–1799), the mathematician Lorenzo Mascheroni (1750–1800), and the anatomist Antonio Scarpa (1752–1832).

The teaching of physics was typically divided into two distinct and separated branches. Professor Carlo Barletti (1735–1800) became responsible for *Classical or General Physics* (covering statics, dynamics, hydrostatics, hydraulics and astronomical physics, according to a sound mathematical approach), while Volta had to teach *Experimental or Particular Physics* (which treated electricity, magnetism, heat, pneumatics, acoustics, meteorology and optics and was more phenomenological and experimental).

Settled in Pavia, Volta was instrumental in the building of a new lecture theatre (today called „Aula Volta", see Figure 2), of the seating capacity of 120, to host the increasing number of students of physics, which was also used for public demonstrations of his electrical machines, open to citizenry. A public interest in natural philosophy (physics, chemistry, biology, medicine) had grown in Europe during the 18th

Figure 2. The Physical lecture Theatre of the University of Pavia (now Aula Volta), built over the period 1785–1787, under the direction of architect Leopoldo Pollack. The amphitheatre has been inspired from the Olympic Theatre in Vicenza by Andrea Palladio, completed in 1585.

century, as a natural consequence of the Enlightenment principle that wanted to make information available to the greatest number of people. Such a tendency generated an unprecedented interest in science and, more importantly, brought science into the public domain for the first time.[4]

3. The Controversy with Galvani and the Invention of the Pile

In Pavia, Volta continued his studies on static electricity, building increasingly sensitive electroscopes to detect and measure the effects of electric charge. In 1791, on recognition of his achievements in the electrical matter, Volta was elected to be a *Fellow of the Royal Society* of London. Then, the appearance of a paper on animal electricity by Luigi Galvani (1737–1798), professor of Anatomy and Obstetrics at the University of Bologna, induced a dramatic turn of Volta's interests and investigations. Since the mid 1780′s Galvani had investigated the effects of electricity on muscles and nerves of properly prepared frogs, and in 1791 he published the *summa* of his studies.[5] In a revealing experiment, Galvani fastened some prepared frogs by „brass hooks in their spinal cord to an iron railing which surrounded a certain hanging garden of my house" and he noticed that these frogs went into contractions. In a subsequent series of experiments, he found that whenever the nerves of a frog's leg were touched by one metal and the muscles by another metal, convulsions took place when the two different metals were brought to contact.

These findings centred the key phenomenon of galvanism: *electric current is produced from the contact of two different metals in a moist environment.* Really, Galvani did not think so, but he stated that animals possess in their nerves and muscles a subtle fluid quite analogous to ordinary electricity, which he defined „animal electricity".

Galvani sent a copy of his *opus magnum* (52 pages plus 4 figures with captions) to Volta, who replicated and extended Galvani's experiments (thus immolating a variety of reptiles, birds, and mammals). However, Volta proposed a totally different interpretation of the phenomena: electricity has not an organic, but rather an inorganic nature and derives from the contact of two different metals; nerves and muscles play a passive role and simply help to close the circle, making electricity flow from one metal to the other.[6] We are thus in presence of a new type of electricity: *metallic* or *contact electricity.* Then, Volta wrote a quite long report in which Galvani's and his own experiments were described and interpretations discussed.[7] The paper was submitted to the *Philosophical Transactions of the Royal Society* on October 25, 1792, then read in the Society meeting of January 31, 1793, and published. The article was written in French, because Volta mastered French better than English and because at that time French was probably the language most used by European philosophers. The article was well accepted and in 1794 Volta was awarded with the prestigious Copley Medal „for his several Communications explanatory of certain Experiments published by Professor Galvani". Copley Medal was and still is an award annually given by the Royal Society to outstanding scientists, alternating between physical and biological sciences, and could be reasonably considered an equivalent of Nobel Prize in that time period. After the appearance of Galvani's *Commentarius*, a lively, but never harsh Galvani/Volta debate on the nature of electricity, whether animal or metallic, began, which divided the community of natural philosophers in two sides (biologists and physiologists with Galvani, physicists and chemists with Volta).[8–10] Victory was assured to Volta with his announcement of the first generator of continuous electricity in 1800 in a paper submitted to *The Royal Society.*[11]

In an *a posteriori* analysis, one could hypothesize that Volta, on building his novel electrical machine, moved from two considerations: 1) in Galvani's circuit (or cell), constituted by the dimetallic arc and the frog's muscle/nerve, the animal tissue could be replaced by a fluid, for example, water, better if containing muriate of soda (NaCl), the salt present in the highest concentration in animal liquids; 2) to amplify the flow of electricity, a relevant number of galvanic cells should be set in series, in analogy with the *battery* of Leyden jars, introduced by Franklin, which provides a much more intense electric discharge than a single bottle (even if Franklin's battery works better when set in parallel than in series).[12]

Volta built his electrical machine in two versions. In one, the galvanic cell consisted of a glass container filled with salt water, in which two pieces of laminated metal (one of zinc, the other of silver) were dipped (idealized version in Figure 3a). Then, several cells were linked in a linear sequence (Figure 3b). Figure 3c shows the original drawing of the *couronne de tasses* (crown of cups) reported in the letter by Volta to the Royal Society.[11] If someone puts their hands in the two extreme containers, they will experience a slight shock due the passage of electric current from one hand to the other, along their body. The intensity of the shock will increase on increasing the number of cells (cups) in the series. Stronger shocks will be experienced when touching directly with one finger of each hand the first (silver) and the last (zinc) metal pieces. The linear arrangement of cups (or glasses) filled with salt water and connected each other with dimetallic arcs, as

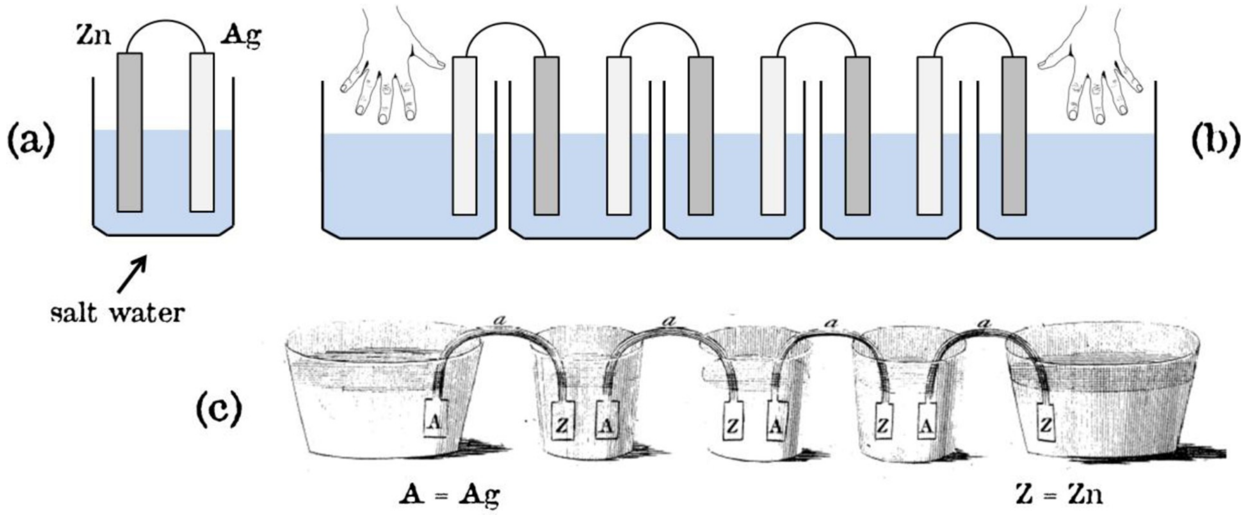


Figure 3. Volta's battery in the crown of cups version (*couronne de tasses*) a) the ideal galvanic cell 'zinc/salt water/silver„; b) a series of cells; c) the same series as in (b) in the original drawing from Volta's paper.[11] Notice that the series in (b) and (c) consists of 3 galvanic cells; the two outer vessels operate as simple conductors of electricity and do not contribute to generate the electromotive force of the whole system.

illustrated in Figure 3 b,c was a logical and smart conversion in a practical device of the principle that electricity is generated by the contact of two metals. We know now that the electromotive force is not generated by pairs of different metals in contact, but by the chemical processes occurring inside the Zn/electrolyte/Ag galvanic cells, thus the two external vessels are redundant. They act as simple conductors and do not contribute to generate the electromotive force. Thus, the electrical machine in Figure 3 b,c should be considered as made by 3 galvanic cells (Zn/electrolyte/Ag), rather than by 4 metallic arcs (Zn/Ag).

The other version is the real and typical Volta's Pile, whose arrangement is illustrated by the drawings in Figure 4. It consists of a varying number of triads, each made by a disc

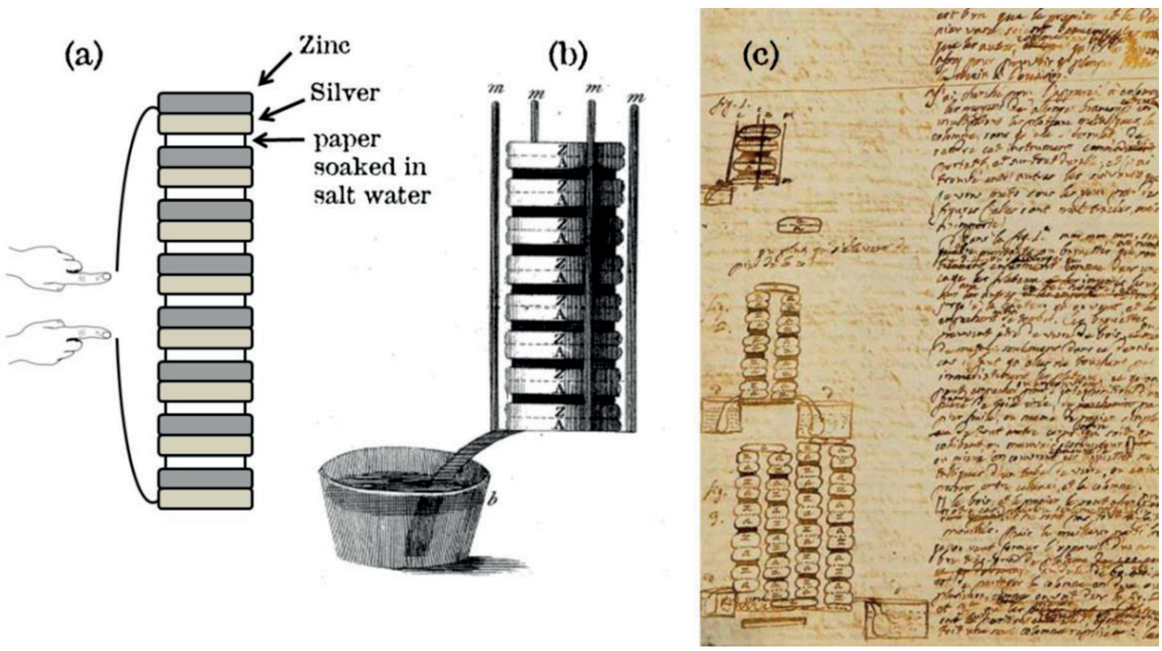


Figure 4. Volta's pile: a) a vertical arrangement of sequences of a disc of zinc, a disc of silver and a piece of cardboard soaked in salt water; if the extreme plates of zinc and silver of the column are touched by the fingers of an individual, the individual will behave as a conductor and will experience a shock, whose intensity will increase with the increasing number of discs; b) an original drawing taken from Volta's letter to the Royal Society.[11] In this version, in order to be *galvanized*, one should immerge one hand in the basin of salt water and touch with a finger of the other hand the upper zinc plate; c) a page of the rough draft of the French written manuscript, showing different arrangements of the pile: in order to increase the tension, rather than building a very high and unstable tower of discs, Volta safely decided to link several medium height columns with metallic wires. Again, in the arrangements illustrated in (a) and (b) the highest (Zn) and lowest (Ag) discs are unnecessary and operate as simple conductors of electricity.

of zinc, by a disc of silver (corresponding to the dimetallic arc of the crown of cups in Figure 3c) and by a disc of cardboard soaked in salt water (the equivalent of the brine containing cup), all arranged in a column. Such an unusual design is the product of an authentic genius. Due to its unique features (simplicity, ease of building, cheapness and availability of materials, minimum encumbrance, portability), the pile enjoyed immediate fame and popularity and, over the first years of the 19th century, inspired hundreds of scientists and amateurs. Volta named his apparatus *appareil à colonne* and *appareil électro-moteur.* He did not use the term *pile*, which was introduced by Nicholson and immediately adopted by English and French scientists, and later by Volta himself.

The article consists of 29 pages, including one with accurate drawings (two are reported in Figure 3c and 4c). The assembly of the apparatus is described in its fine details (silver better than copper, zinc better than tin, salty water better than pure water, how to prevent the fall of the column and the drying of the wet cardboard). Most of the text describes the effect of the electricity produced by the pile on the five human senses (experienced by Volta himself): actions were observed, with an intensity increasing with the number of discs, on touch, taste, sight, and hearing. Only olfaction was unaffected.

Volta deliberately did not attempt to provide a full explanation of the phenomenon. He stated: „*This endless circulation of the electric fluid (this perpetual motion) may appear paradoxical and even inexplicable, but it is no less true and real; and you feel it, as I may say, with your hands*“. And, a few lines below, he added: „*… this proposition, which I advanced in my first researches and discoveries on the subject of galvanism, and always maintained by supporting them with new facts and experiments, will, I hope, meet with no opponents*“. Volta was perfectly aware of the importance of his invention and of its astounding consequences in any discipline of Natural Philosophy (you can bring continuous electricity to a chemical bench, to an apparatus in physics, to the bedside of a patient). But he was also conscious that the state of contemporary scientific knowledge could not afford a disclosure of the operative mechanism of the pile. In any case, he was ultimately sure that electricity had a metallic nature and any other hypothesis (that of Galvani, in particular) had to be rejected. After a decade of gentle battles, the war had been finally won!

It may be surprising that Volta's letter was dated „*A Côme, en Milanois, ce 20^{me} Mars, 1800*“. Why should a Professor of the University of Pavia mention as a location of his scientific activity Como, where he owned a country house (to be precise, in Lazzate, a village 17 km north from Como), and not Pavia, where he had at his disposal a well-equipped laboratory and a skilful and devoted technician, and was supposed to teach and to do research?

To answer this question, one should consider the political situation that Northern Italy, Lombardy in particular, was going through during the last years of the 18th century. In the spring of 1796, General Napoleon, on command of the French revolutionary army, defeated the Piedmontese and Austrian coalition and occupied Lombardy. On May 16th, Bonaparte triumphantly entered Milan, where, among the others, a deputation from Como, including Alessandro Volta, paid homage to him. On the approach of the French troops, Austrians had closed the University of Pavia. Then, in April 1798, the University was reinstated as an institution of the freshly established Cisalpine Republic, supported by the French. However, in April 1799, on the return to Lombardy of the temporarily victorious Austrian and Russian coalition, the University was suppressed and its Professors fired. Volta lost his chair and salary. Not that bad, if one considers that his colleague and friend Carlo Barletti, professor of the parallel course of General Physics, who had openly expressed his favour to French, was accused of „Democracy and Jacobinism“ and incarcerated. The following year, after the definitive defeat of Austrians (battle of Marengo, 14 June, 1800), the First Consul decreed the opening of the University and guaranteed all the necessary support to teachers and students. In particular, Volta was reinstated as a Professor and confirmed as Director of the Cabinet of Physics.[13]

Volta developed the pile during 1799 and early 1800, when he was without chair and students and so without salary and without funds to afford the expenses for his researches. Thus, he had to carry out experiments in the private rudimentary laboratory he had set up in his country house in Lazzate. Despite the uncomfortable circumstances, Volta was able to complete a monumental work and to establish a milestone in the history of science. This testifies of a strong and tenacious character, of a firm self-confidence and of a proud consciousness of his value.

Scientists are often accused of social egoism, being determined to live in their ivory tower, pursuing their ambitions and disregarding tangible social and political problems. Scientists could argue that, in an universal order of values, a great scientific discovery (e.g. the invention of the pile) may match or precede a momentous political upheaval (e.g. the French Revolution). Do not ask Mr. Antoine Lavoisier for a comment.

4. Volta's Pile Explained by Chemistry

According to Volta, the electrical current was generated by the *mere contact* of two different metals and the wet material interfacing the pairs of metals simply played the passive role of conducting the electrical fluid from one metal pair to the next. The *contact* theory by Volta on the operating mechanism of the pile was immediately challenged by a new model of interpretation, the *chemical* theory, which argued that pile could be better explained in terms of chemical processes taking place in the solution interfacing the two metals inside each galvanic cell. It was a complex and long controversy, which lasted for nearly a century and involved some prominent physical chemists (no longer philosophers) of the 19th century.[14,15] The debate was concluded in 1889 with the work of Walther Nernst,[16] and chemistry won.

In particular, in the galvanic cell sketched in Figure 5, electric current (electrons) flows from the zinc electrode to the silver electrode, as a result of the occurrence of the two half-reactions illustrated. The zinc electrode dissolves, while H_2 develops at the silver electrode.

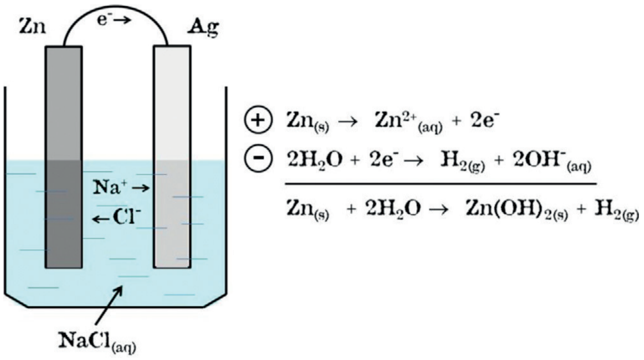


Figure 5. Schematic representation of a cell of Volta's pile with the half-reactions taking place at the electrodes: ⊕, anode: oxidation of Zn to Zn^{2+}; ⊖, cathode: reduction of water to hydrogen. On diffusion of OH^- ions, a white insoluble precipitate of $Zn(OH)_2$ forms on the Zn electrode surface. The electric circuit is closed through the migration of the ions of the background electrolyte (Cl^- toward the Zn electrode, Na^+ toward the Ag electrode).

Silver electrode serves only as a source of electrons and does not play a chemical role in the electrode reaction. Nothing changes if silver is replaced by copper, both metals behaving as „inert electrodes". OH^- ions diffuse to the zinc electrode and form with Zn^{2+} a white precipitate of $Zn(OH)_2$.

Since Nernst, we know that any homogeneous oxidation and reduction process can be converted into a galvanic cell. Figure 6 exemplifies the case of the redox process involving the reducing agent Sn^{2+} and the oxidising agent Fe^{3+}. The two platinum electrodes do not take part in the half-reactions and are there only to conduct electrons. The reducing agent and the oxidising agent have to be kept separated, to prevent the occurrence of a direct electron transfer from Sn^{2+} to Fe^{3+}, following collision (a short circuit). Charge circulation is ensured by a salt bridge containing a solution of the background electrolyte KNO_3: K^+ ions migrate to the cathode, NO_3^- ions to the anode.

The electrical cell illustrated in Figure 5, the elementary unit of pile, is based on a redox process in which one of the reactants, the reducing agent, is a reactive metal (Zn), which, being a solid and conducting material, can be used as an electrode. The electromotive force (emf, ΔE) of the cell is given by the difference of the electrode potentials of the oxidising half-cell minus that of the reducing half-cell [Eq. (1)]:

$$\Delta E = E_{H_2O/H_2} - E_{Zn^{2+}/Zn} \qquad (1)$$

The concentrations of the redox active species are far from standard conditions and, therefore, the values of E_{H_2O/H_2} and $E_{Zn^{2+}/Zn}$ are quite different from $E°$ values. However, inspection of $E°$ values allows the emf of a given galvanic cell to be predicted and modulated, and consequently, that of the voltaic pile derived from it. For instance, replacement of zinc ($E°_{Zn^{2+}/Zn} = -0.76$ V vs. NHE) with a more electropositive metal, for example, magnesium ($E°_{Mg^{2+}/Mg} = -2.38$ V vs. NHE) would make ΔE much higher. On the other hand, the value of E_{H_2O/H_2} ($E_{(pH\,7)} = -0.414$ V vs. NHE) could be made less negative, and ΔE more positive, on acidifying the solution. However, the acid should be not too concentrated, to avoid or to slow down the direct oxidation of the zinc electrode by H^+. It is not a coincidence that many practitioners replicating Volta's pile used pieces of cardboard or cloth moistened with diluted sulfuric acid to interface the discs of zinc and silver.

In many textbooks of General Chemistry, the Chapter of Electrochemistry begins with a short description of Volta's pile, including an illustration of the old-fashioned apparatus, but rarely provides an explanation of its mechanism on a chemical basis. Instead, in many textbooks, immediately after the short paragraph on Volta's pile, the Daniell cell is illustrated and described, while its operating mechanism is clearly explained in its chemical details. John Frederic Daniell (1790–1845), professor of Chemistry at King's College in London, wanted to eliminate the detrimental bubbling of hydrogen in Volta's pile and solved the problem by building a zinc/copper cell, consisting of two-half-cells based on the Zn/Zn^{2+} and Cu/Cu^{2+} redox changes.[17] The form of the Daniell cell typically used for classroom demonstrations is shown in Figure 7.

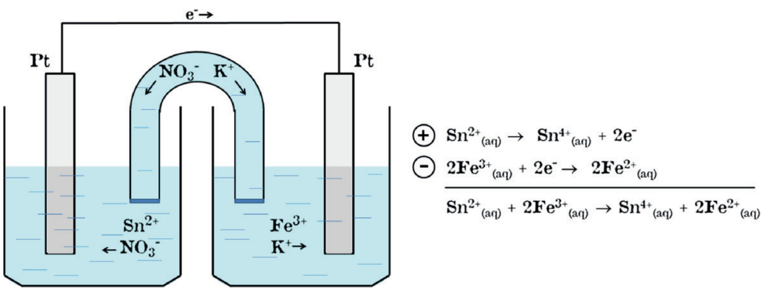


Figure 6. An electric cell based on the redox process involving Sn^{2+} and Fe^{3+}. The reducing agent Sn^{2+} and the oxidising agent Fe^{3+} are kept separated in different vessels (half-cells) to avoid the direct electron transfer following Sn^{2+}/Fe^{3+} collision. Electrical communication and ion migration is ensured by the „salt bridge" containing a solution of the background electrolyte KNO_3. Platinum „inert" electrodes provide a support for electron transport from one half-cell to the other. Porous plugs at the ends of the salt bridge slow down the diffusion of each redox agent to the opposite half-cell.

Each half-cell contains a solution of a salt of the metal of which the electrode is made: $ZnSO_4$ in the Zinc half-cell, $CuSO_4$ in the copper half-cell. Under standard conditions, the open circuit voltage is 1.10 V, which corresponds to the algebraic difference of the two standard electrode potentials: $E°(Cu^{2+}/Cu) = 0.34$ V; $E°(Zn^{2+}/Zn) = -0.76$ V. Over the course of the electrochemical process, the zinc electrode is corroded, while copper metal accumulates on the copper electrode. Neither gas is evolved on the copper electrode, nor precipitate is formed on the surface of the zinc electrode. As a consequence, no increase of the cell resistance is observed and the current remains constant over long periods (what Daniell was looking for). For this reason, Daniell's batteries were used for powering early telegraphy.

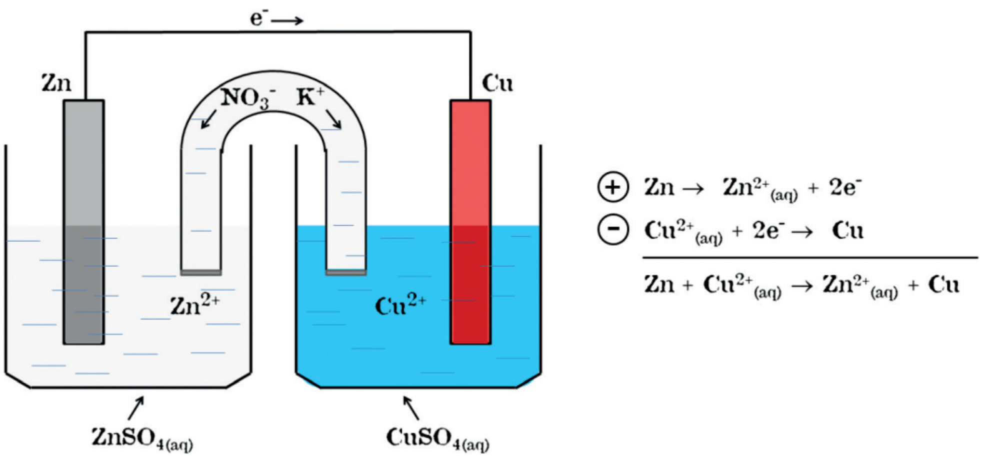


Figure 7. A Daniell cell of the type used in classroom demonstrations. Under standard conditions ($[Zn^{2+}]=[Cu^{2+}]=1$ M, $T=25\,°C$), the electromotive force of the cell, $\Delta E°$, is 1.10 V.

Confusion and misunderstanding can be generated in the students of a basic course of chemistry because of the apparent similarity of Volta's cell (which, in its cheaper version, is equipped with zinc and copper plates) and of Daniell's cell (which operates with electrodes of zinc and copper). Full similarity had been attained (and higher efficiency and durability of the apparatus achieved) if Professor Volta had used instead of brine to moisten the cardboards of the pile, a solution of blue vitriol ($CuSO_4{\cdot}5\,H_2O$). Blue vitriol was a well-known chemical because, added to caustic lime ($Ca(OH)_2$), it gave the *Bordeaux mixture*, used as a fungicide for grapes. Such a remedy could be in use at the time in the vineyards in the sunny hills in the part of the province of Pavia beyond the Po river (Oltrepò Pavese), which were, and still are, well known for the production of a variety of red and white wines.

5. Volta's Letters Arrive in London and the Pile Gains Immediate and Enthusiastic Popularity

In March 1800, Volta completed the writing of his manuscript on the pile, which he decided to submit to the Royal Society for discussion and publication in the authoritative *Philosophical Transactions.* Volta was a Fellow of the Royal Society (one of the few non-British members), had been awarded with the Copley Medal six years before, and probably considered the empirically oriented British scientific community especially prepared for appreciating his work. In view of the political and military troubles Europe was experiencing, Volta considered it safer to submit the paper in two parts: the first, an extended abstract of 4 pages, dated March 20th, 1800, was sent by mail and arrived in London around mid-April; the second part, the complete manuscript, dated April 1st, was handed to a local merchant leaving to London and arrived in early June. The first letter contained a detailed account of the instrument and a summary of the effects generated by the electric current on the human body. The recipient of the letter, Sir Joseph Banks, President of the Royal Society and an expert scientist, immediately realised the revolutionary nature of Volta's invention. Electricity, which since then could be generated and kept on an insulating material (e.g. glass or amber) by rubbing it with silk or wool, and which could be only instantaneously discharged with impressive light and sound effects, could now be produced as a constant and continuous current by a simple and inexpensive machine, and its intensity controlled at will, with a perpetual duration (at least according to the optimistic vision of Alessandro Volta). It is possible that Sir Joseph Banks got genuinely excited by the invention and felt the overwhelming need to share the news with colleagues and friends. These very human feelings were so powerful to overcome the canons of editorial policy, which recommend that the manuscript (or its existence) should be treated as confidential and should not be shown to, disclosed to, or discussed with others.

One of the friends that benefitted from this confidence was Anthony Carlisle (1768–1840), surgeon at the Westminster Hospital, who shared in turn the information with William Nicholson, a versatile chemist. Nicholson reports in the paper which was published on July 1st, 1800,[18] that, by April 30th, 1800 (Monday), Carlisle had completed the construction of *„a pile consisting of 17 half crowns, with a like number of pieces of zinc, and of pasteboard, soaked in salt water“.* The half-crown (made of solid silver, diameter of 3.2 cm, weight 14.1 g, $^1/_2$ oz) had the ideal size for replicating Volta's apparatus, while the cost of total silver (240 g, at the today price of $0.40\,€\,g^{-1}=96\,€$) could be sustained with *nonchalance* by a brilliant and fashionable London surgeon. The pile was arranged in such a way that the silver was at the bottom of the column and zinc at the top. To test the pile, the operator touched with the finger of one hand the highest disc (zinc) and with the finger of the other hand the lowest disc (silver) and he was happy to experience the typical shock. It was then observed that the action of the instrument was transmitted through the usual conductors of electricity, for example, brass wires. Serendipity got involved when Mr. Carlisle, in order to make the contact of the brass wire with the upper zinc disc safer, placed on the zinc a drop of water: to his big surprise, Mr. Carlisle observed the disengagement of gas round the touching wire. On May 2nd (Wednesday), the two practitioners put two brass wires, one connected to the silver disc at the bottom („silver wire“), the other to the zinc disc at the top („zinc wire“), in a glass tube filled with the water of the nearby New River: a fine stream of minute bubbles began to flow from the „silver wire“, while the „zinc wire“ tarnished. The chemistry occurring inside the tube is illustrated in Figure 8.

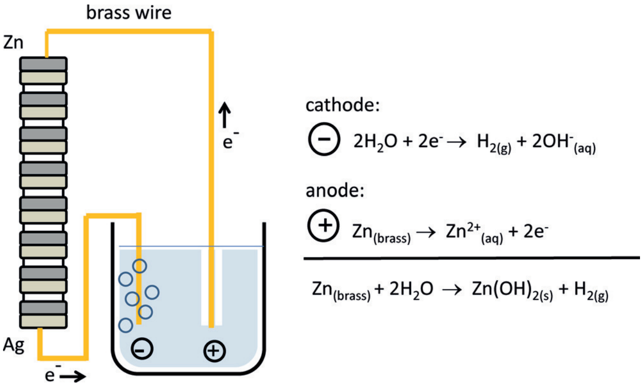


Figure 8. Electrolysis of water using brass electrodes. At the cathode H_2 develops; at the anode Zn (from brass) undergoes oxidation to Zn^{2+}, which forms $Zn(OH)_2$ on the electrode surface. The pile used by Carlisle and Nicholson consisted of 17 Ag/Zn/salt-water moistened cardboard triads. Notice that, in the typical arrangement of Volta's pile, the highest and lowest discs behave as simple conductors of electrons. In particular, the pile is made by 16 galvanic cells Zn/electrolyte/Ag.

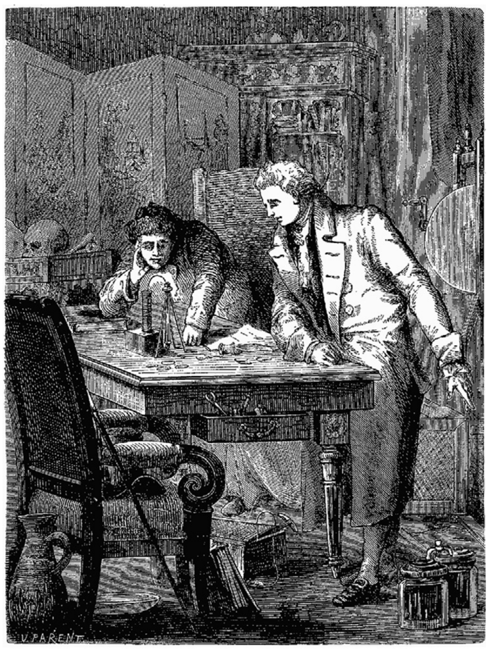


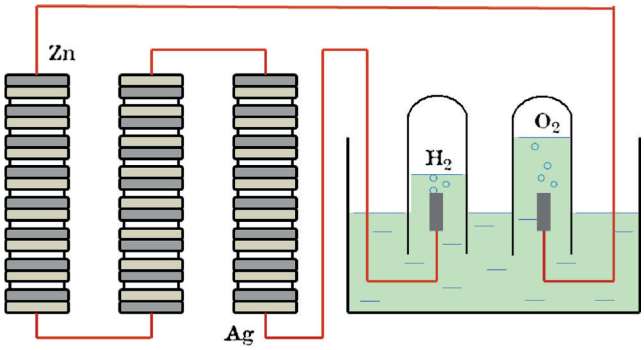
Figure 9. Louis Figuier, *Les Merveilles de la Science*, *Tome I*, Jouvet et C.ie Editeurs, Paris, 1867. „Nicholson et Carlisle, à Londres, décomposent l'eau par la pile de Volta, le 2 mai 1800." Conversely to what is illustrated in the caption, Carlisle (left) and Nicholson (right) are not carrying out the electrolysis of water, but are measuring the charge of the Volta pile with a gold-leaf electrometer.

The brass wire connected to the lowest silver plate behaves as a cathode and releases electrons to the most powerful oxidising agent in solution, in this case, water, which is reduced to hydrogen; at the anode, the zinc of the brass is oxidised to Zn^{2+}, which reacts with the OH^- ions migrating from the cathode, to form $Zn(OH)_2$. The insoluble hydroxide in part accumulates on the electrode surface and in part precipitates. It has to be recalled that the lowest silver plate of the pile is redundant and behaves as simple conductor of the electrons released on oxidation of the adjacent zinc plate. In the same way, also the zinc disc at the top of the column is superfluous, as it transfers to the silver disc the electrons coming from the oxidation of the brass anode. This „wrong" arrangement devised by Professor Volta was a corollary of the design of the pile as a sequence of pairs of silver and zinc plates *in contact*, interfaced by a liquid medium, permeable to the electric fluid. Considering (correctly) that the pile consists of a sequence of galvanic cells, the metal plates at the extremities of the column can be (today) eliminated.

Going back to May 2nd, 1800, Carlisle and Nicholson, after 2.5 h of electrolysis, collected a volume of gas of 2/3 of a cubic inch (corresponding to 4.3 cm^3). *„…[the gas] was then mixed with an equal quantity of common air, and exploded by the application of a lighted waxed thread"* (the equivalent of a match). It was hydrogen! (Figure 9).

Nicholson, as a chemist, was very excited and eager to extend studies on the electrolysis of water, in particular by testing a variety of metals as electrodes. The physician Carlisle did not share such a chemical enthusiasm, being more interested in the application of the pile to the physiological field. Thus, the couple split. Mr. Carlisle kept the pile for himself and Mr. Nicholson had to construct his own apparatus. However, being a chemist and an editor, and not an affluent surgeon, he did not use half crowns, but discs of pure silver of 1.8–2.0 inches diameter, laminated to 1/1000 of an inch, *„as flat as our flatting mills can bring it"*. Nicholson first build a pile consisting of 15 repetitions of the „zinc/silver/wet-cloth" triad and, after a number of experiments with different metals, he carried out electrolysis by using two electrodes of platinum: this time, everything went clean: *„the silver side gave a plentiful stream of fine bubbles, and the zinc side also a stream less plentiful. No turbidity, nor oxidation, no tarnish appeared during the course of four hours continuation of this operation. It was natural to conjecture that the larger stream from the silver side was hydrogen, and the smaller oxygen"*. Interested to produce the gases in measurable amounts, Nicholson reinforced the generator of electricity by putting in series two piles made by himself, each consisting of 15 triads, and the pile of Carlisle (36 triads), for a total of 66. Then, he arranged a system whose form is schematically illustrated in Figure 10.

In particular, Nicholson devised an arrangement in which the electrodes were placed beneath two reverse vessels full of water. During the electrolysis, each developing gas displaced water in order to find room at the top of the vessel. Asked how to determine the molar ratio of the two gaseous substances, even the less brilliant student of chemistry of the first year would proudly answer: *from the quotient of the corresponding volumes!* However, in 1800 ideas on the molar volume of gases might be under elaboration in the mind of Amedeo Avogadro (1776–1856), but they did not become of public domain before 1811.[19] In any case, Nicholson suspended electrolysis after 13 hours and was able to determine the weight of the water displaced from the reverse vessel: 142 grains at the electrode connected to the silver plate and 72 grains at the electrode connected to zinc, which makes 9.42 g and 4.68 g, respectively. Mr. Nicholson found it



$$\ominus \quad \text{cathode:} \quad 2 \times [2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}]$$
$$\oplus \quad \text{anode:} \quad 2H_2O \rightarrow O_{2(g)} + 4H^+_{(aq)} + 2e^-$$
$$2H_2O \rightarrow O_{2(g)} + 2H_{2(g)}$$

Figure 10. A schematic representation of the system arranged by Nicholson to carry out the decomposition of water through electrolysis by using platinum electrodes. Each electrode, connected to one extremity of a system of three Voltaic piles, is placed in a reverse tube full of water. The gases developing during electrolysis displace water from the reverse tubes, where they remain imprisoned. Copper wires connecting platinum electrodes to the pile were appropriately insulated from the solution.

comfortable that the quotient in respect of hydrogen and oxygen ($142/72 = 9.42/4.68 = 1.97$) was very close to the stoichiometric ratio of hydrogen and oxygen when the two gases react to give water.

6. The Subtle Game of Making Scientific Information Public

Nicholson, who completed his studies on electrolysis around mid-May, was aware of the importance of his discovery and felt the legitimate ambition of communicating with an article his achievements to the scientific community. However, while he did not consider the submission of any paper on this subject until Volta's paper had been read in the next session of the Royal Society, he could not resist the urge to talk colleagues and friends about Volta's pile (a word already spread with liberality by Sir Joseph Banks) and about the experiments on electrolysis carried out by himself and by Mr. Carlisle. Among these individuals there was Thomas Garnett (1776–1802), who just a few months before had been appointed as a Professor and Public Lecturer in Experimental Philosophy, Mechanics and Chemistry at the newly founded Royal Institution of Great Britain, based in London. The Royal Institution had been created for diffusing the application of science to the common purposes of life, by courses of philosophical lectures and experiments. Garnett had lent from a friend Volta's apparatus (seemingly, the construction of electrical piles had become the most fashionable hobby in London during May 1800), had experienced by himself the electrolysis of water and decided to present to the public Volta's pile and the water decomposition in the occasion of *The Wednesday Evening Lecture* at the Royal Institution. The lecture-demonstration was given on May 28th and enjoyed a tremendous success. On Friday May 30th, a London based newspaper, *The Morning Chronicle*, reported a detailed account of the lecture, in which the names of Volta, Carlisle and Nicholson were duly mentioned. However, the report had been written in such a way that the reader got the impression that Volta had invented *both* the pile and the electrolysis of water and that Carlisle and Nicholson had only repeated the experiments. Nicholson wrote to *The Morning Chronicle* a resentful note of comment, published on Tuesday June 3rd, in which he first clarified the correct attribution of the discoveries, then, with a bitter irony, contemplated the chance that „*the Royal Institution is to become an office for collecting the conversations of philosophers, and immediately publishing them in the Daily Papers*“.[4,20] In any case, since the invention of Volta had been made public and described in its material details, Nicholson felt himself free from any ethical constraint and wrote a manuscript,[18] which was submitted to the Editor of the *Journal of Natural Philosophy, Chemistry and the Arts* (i.e. to himself). The article was published in the next monthly issue, on July 1st, 1800. Noticeably, in the same July issue, another paper appeared by William Cruickshank, Chemist to the Ordnance and Lecturer in Chemistry at the Royal Military Academy at Woolwich, London, in which experiments of electrolysis on a variety of solutions, were described.[21] Cruickshank, to moisten the paper discs interfacing the Zn/Ag arcs, used a solution of muriate of ammonia (NH_4Cl), which, being slightly acidic (pH 5 at a 0.1 M concentration), may have prevented precipitation of $Zn(OH)_2$ and increased the electromotive force of the pile. Noticeably, in the four pages of the article the name of Volta was never mentioned. In the following monthly issues of 1800, another eight articles based on experiments with the pile appeared (by William Henry, Henry Haldane, Humphry Davy). Again, in the papers by the distinguished Philosopher William Henry (1775–1836), Professor of Chemistry at the Mechanics Institute in Manchester, and the father of Henry's Law, Volta was not quoted. Apparently, the pile had become a public good and, like for the wheel, the mill, and the lever, its inventor did not deserve any recognition. In the meanwhile, the second letter by Volta, in its extended version, arrived in London in the first days of June, and was read to the Royal Society in the session of June 26th, 1800. Finally, in September 1800, the paper was published in the *Philosophical Transactions* (in the language it has been submitted, French),[11] and in *The Philosophical Magazine*, a commercial scientific journal competing with Nicholson's journal, in its English translation.[22]

Professor Volta, totally unaware of the story tumultuously developing in London, was moving from Como to the reopened University of Pavia, where he had been confirmed as a Professor of Experimental Physics by decree of Napoleon, in June 1800. He was informed of the amazing reception in London of the pile through daily papers around mid-August. In fact, the article of *The Morning Chronicle* of May 30th, reporting on the lecture of Dr. Garnett on the pile of Volta and on the electrolysis of Nicholson and Carlisle, had been reprinted in *Le Moniteur Universel*, the main French newspaper, which had a large circulation in Europe during the

French Revolution and under the Napoleon regime and which reached all the countries under the French rule, including Italy. The article mentioned also that the electrolysis experiment was replicated in a public lecture in Paris. Volta judged the description of the pile „acceptable“. Thus, it appears that around the turn of 18th century, in a period of poorly efficient postal service in Europe, due to political and military troubles, the more widely disseminated daily newspapers and generalist magazines supplemented or replaced specialized periodicals in the diffusion of science. In any case, the news of the invention of the pile reached through direct or indirect ways most of the European countries, creating a great deal of enthusiasm and stimulating the ingenuity of scientists. Experiments of electrolysis were carried out by skilful practitioners in Great Britain, France, Germany, Austria, The Netherlands, Switzerland, Denmark. The most active country was Great Britain, historically noted to empiricism and to the practical aspects of science, where a number of philosophers and amateurs constructed their Volta's pile and carried out experiments inspired from the work of Carlisle and Nicholson. From this multitude emerged the figure of Humphry Davy (1778–1829), the first to consider the electrodes connected to a pile as real reactants to perform chemical processes and isolate new substances. Davy joined the *Pneumatic Institution* in 1798 as a laboratory operator. The Pneumatic Institution was a medical research facility in Bristol, committed to study the medical effects of the gases that had recently been discovered. When he read the article by Nicholson on electrolysis, published in July 1800, he immediately replicated experiments using piles never consisting of less than 110 pairs of metallic plates, but he introduced some smart variations. For instance, he dipped two gold wires, one connected to the silver plate of the pile, the other to zinc, into two separated glasses linked a fresh muscular fibre (an animal „salt bridge“): hydrogen developed at the gold electrode connected to the silver plate and oxygen at the gold electrode connected to the zinc plate and the masses of displaced water were equal to 65 grain measures and 33 grain measures. Davy used a variety of „salt bridges“, including a vegetable fibre, a moistened thread and, of course, the fingers of his hands. These findings were described in a paper published in the Nicholson's journal.[23] In the following years, Davy carried out the electrolysis of molten caustic soda and caustic potash and isolated sodium and potassium.[24] Then, using a mercury cathode, he isolated magnesium, calcium, barium, and strontium.[25]

Quite paradoxically, Italy, Volta's homeland, was one of the less fertile and productive grounds for the use of electricity in chemistry. For two main reasons: first, Italian culture was traditionally literary and humanistic, primarily due to the counter-reformation attitude of the Church, which considered scientific progress an attack to the well-established interpretation of nature based on the Christian revealed truth and on Aristotelian philosophy. Any experimental discovery in contrast with the Catholic beliefs was judged blasphemous and the discoverer prosecuted, as Galileo Galilei had to experience. This slowed down the development and the diffusion of the scientific culture in the society. Second, the division of Italy into small states made the scientific communication difficult and precluded the creation of a national scientific association, like the *Royal Society* in Great Britain (founded in 1660) or the *Académie des Sciences* in France (1666). However, chemists of the University of Pavia had the unique advantage of profiting from first-hand information from the close Cabinet (period term equivalent of the modern departement) of Physics and take their own way in the chemical applications of the Voltaic electricity. This happened, but not to the extent one could ever hope.

The first Chair of Chemistry in Pavia was established in 1776 when Giovanni Antonio Scopoli (1723–1788) was appointed as Professor of Chemistry and Botany. In 1784, Scopoli opened the first Cabinet of Chemistry inside the Botanical Garden, still in the centre of Pavia, but several hundred meters far from the central University building where the Cabinet of Physics was located. Scopoli was more interested in Botany than in Chemistry, his discoveries were highly appreciated by Carl Linnaeus, who named a solanaceous genus *Scopolia* (the source of *scopolamine*) in honour of his Italian colleague. In the years of the pile invention, the holder of the Chair of General Chemistry was Luigi Valentino Brugnatelli (1761–1818), former student of Scopoli and professor since 1796. Brugnatelli graduated in Medicine, but he was encouraged by his mentor Scopoli to study chemistry and to pursue the academic career. Brugnatelli was the founder of a variety of scientific periodicals on medicine, physics, chemistry and natural history. In these journals Brugnatelli described, in Italian, researches and discoveries he had read in scientific publications from all Europe, and added personal comments and pertinent results of his own investigations. This editorial activity was very useful and prevented Italian researchers from being estranged from the enormous progresses of the science in that period. Brugnatelli was a true follower of the modern ideas of chemistry by Lavoisier, but he was also self-righteous enough to propose emendations to the chemical nomenclature introduced by the French school,[26] a circumstance which made him unpopular among French scholars. In any case, Brugnatelli was an imaginative chemist, whose interests encompassed themes of medicinal, pharmaceutical, organic and inorganic chemistry.

In a letter dated September 22nd, 1800 to his colleague Marsilio Landriani,[27] formerly Regius Professor of Physics at the Brera College in Milan, then Embassy Counsellor at the Augsburg Court in Vienna, Volta wrote that in early April 1800, in a short visit to Pavia, he had shown to his colleague and close friend Brugnatelli the pile and that he had carried out a demonstration of its operation for him. Then, Volta went back to Como with his pile and Brugnatelli immediately constructed another. Thus, Professor Brugnatelli was one of the first chemists in Europe, if not the first, having a pile at his disposal. Brugnatelli, on replicating the experiments of Nicholson on the electrolysis of water, conceived that not only the solvent, but also the species dissolved in the electrolytic solution could be decomposed.[28] At that time, he was studying „ammoniures“, that is, compounds obtained by reacting salts of gold with ammonia, and decided to investigate their electrolytic decomposition. He first dissolved gold with *aqua regia* (to give $[Au^{III}Cl_4]^-$), then he neutralized the strongly acidic solution by addition of a large excess of concentrated ammonia: a precipitated formed, which was separated by filtration.[29] The resulting solution, which presumably contained $[Au^{III}(NH_3)_4]^{3+}$ and/or mixed chloro-amine complexes of formula $[Au^{III}(NH_3)_xCl_y]^{(3-y)+}$ $(x+y=4)$, was electrolysed: over the course of the electrolysis a thin layer of gold uniformly deposited on the silver cathode. Brugnatelli had invented gold electroplating!

Brugnatelli published these results in an article which appeared in a journal edited by himself.[31] Then, he sent a letter to his friend Jean-Baptiste Van Mons, a Belgian chemist, Professor of Chemistry and Experimental Physics at the *École Centrale du Département de la Dyle* (Brussels), providing detailed information on his studies. Van Mons published an abstract of a few lines (in French) in the scientific journal edited by himself (*Journal de Chimie et de Physique*).[32] The same abstract, translated in English, appeared in *The Philosophical Magazine*:[33] „*I have lately gilt in a perfect manner two large silver medals, by bringing them into communication, by means of a steel wire, with the negative pole of a Voltaic pile, and keeping them, one after the other, immersed in ammoniuret of gold newly made and well saturated*". The abstract was very concise, but clear enough to stimulate the ingenuity of European practitioners. However, nobody was interested in extending and deepening the studies of Brugnatelli on gold electroplating, probably because the process was too expensive (most of the precious metal being lost on precipitation of „fulminating gold") and also for the poor reproducibility of composition and concentration of the solution for electrolysis.

The theme of gold electroplating was revived in 1840,[34] when John Wright (1808–1844), a surgeon of Birmingham, repeated the experiment of Brugnatelli, using as an electrolytic bath a solution containing a well-defined gold(I) complex, $[Au^{I}(CN)_2]^-$, which could be easily obtained on reaction of gold with oxygen in aqueous potassium cyanide, a clean and quantitative process. Wright sold the recipe of the process to George and Henry Elkington, Birmingham based manufacturers of military badges and buttons, for £300. Since then, electroplating of noble metals has become matter of technology and industrial use. In any case, gold electroplating remains a minor, still distinguished, application of Volta's pile to chemistry made in Pavia. A little is better than nothing.

7. End Credits

Before 1800 Alessandro Volta was a fixed star of the firmament of the European Physics. After the publication of his letter to the Royal Society and of the papers by a large number of European scientists based on the pile, the fame of Volta raised to a level rarely achieved in science. He did not get indignant about the fact that his letter to the Royal Society had been incorrectly spread in London and its publication had been preceded by the appearance of a number of papers by other authors based on the pile. Quite the opposite! In a letter to Abbot Antonio Maria Vassalli Eandi, Adjunct Professor of Physics at the University of Turin, dated on March 26th, 1801, he stated: „*I am very pleased to see that everywhere in Europe Physicists and Chemists deal intensely on this subject*".[35] Moreover, also Napoleon contributed to enhance Volta's success and popularity. In particular, Napoleon, a son of the Enlightenment, believed in the power of reason, and thought science and technology could improve the quality of life and increase the economic status of the nations (France, in particular). He was therefore pleased to recognize the value of science and to encourage the leading scientists of France and of the countries associated to France, including Italy. Volta was special: an Austrian subject for 51 years, during the Austrian/French war he did not take definitely the Austrian side, but he remained grateful to the Augsburgs and to their administrators, who had favoured his career and had generously supported his researches. The First Consul was well aware of the good inclination of Volta towards the Austrian regime. Nevertheless, he demonstrated his limitless and unselfish respect for the science, independent of any political opinion, by inviting citizen Volta to visit him in Paris. Volta went in Paris accompanied by Brugnatelli, illustrated his researches on electricity and in particular those which led to the invention of the pile, in three distinct lectures to the *Classe des Sciences* of the *Institut de France* (November 7, 12 and 22, 1801 of the Gregorian Calendar; 16 et 21 Brumaire, 1 Frimaire of the Republican Calendar). Napoleon took part in all the three meetings of the Class, as well as the diplomatic corps, and a great number of French scientists. So impressive and exciting were Volta's presentations that the Italian scientist was made one of the eight foreign members of the *Institut de France*. On Napoleon's suggestion he was given a golden medal, and later he was appointed *Chevalier de la Légion d'Honneur* (1805), Senator (1809) and then Count (1810) of the Italian Kingdom. It is indicative of his fair and generous nature that, also in the moments of triumph, Volta kept referring to the new electrical phenomena generated by his pile as „galvanism" (a term coined by Volta himself) and always acknowledged his debt to his scientific enemy, Galvani, with deep respect and admiration.

Back to Pavia, Volta, ageing and eager to spend more time with his family in Como (he had married in 1794 and had three very young sons to raise and educate) asked to reduce his teaching duties. In 1804, Pietro Configliachi (1777–1844) officially succeeded Volta to the chair of physics. However, Volta still worked in the University, delivering his courses and doing research in the Cabinet of Physics, but his stays in Pavia became shorter and less frequent. After the Austrian Restoration (1814), he maintained his post and was appointed as Dean of the Faculty of Physics and Mathematics. In 1819, Volta, aged 74, finally left the scene and retired in Como, where, after a brief illness, he died on March 5, 1827, 82 years old.

Luigi Galvani could not see the triumph of his competitor, as he died in 1798. During his last years, Galvani had continued his studies on animal electricity, but his public and private life were disrupted by the dramatic political events that upset Italy during the last years of the 18th century. In 1797, after the French occupation of Northern Italy, the Cisalpine Republic, a sister of the French Republic and inspired to the principles of the Revolution, was established, of which Bologna (formerly belonging to the Papal States) was a part. Every professor of the University was required to swear loyalty to the Republic. Galvani, who disagreed with the social and political disorder brought by the French in Bologna, and who felt this oath of allegiance in full contrast with his religious belief, consistently refused, along with a few other colleagues. As a consequence, he was deprived of his academic and public positions, and his salary was terminated. He died in Bologna, in his brother's house, saddened and in poverty, on December 4th, 1798, the age of 62, at a time when the world was on the eve of the great electrical revolution.

William Nicholson, the first man to produce a chemical reaction (water splitting) by electricity, can be rightfully considered the father of electrochemistry. However, after the exciting months of 1800, he apparently lost any interest in the chemical applications of Volta's pile and continued his activity of writer and translator (from French) of scientific articles and books. In 1809 he published in London *The British Encyclopaedia, or Dictionary of arts and sciences: comprising an accurate and popular view of the present improved state of human knowledge*, consisting of six volumes. During the later years of his life, Nicholson acted as a water engineer for the Portsea Island Waterworks Company. This employment placed him in an affluent position, which, however, from domestic and other causes, he was unable to maintain. Financial problems were such that he spent time in debtor's prison. He died in poverty after a persistent illness, in Bloomsbury, at the age of 61, on 21 May 1815, attended by his old friend Sir Anthony Carlisle. Nicholson was an ingenious inventor and a competent practitioner, whose interests varied from basic research, to scientific divulgation and to practical applications of science. This variety of interests and inconstancy prevented him from attaining a sound scientific and social reputation: he neither became a fellow of the Royal Society nor did he enjoy other public recognition. Nevertheless, science, chemistry in particular, is lastingly in his debt.

Conflict of interest

The authors declare no conflict of interest.

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