Conference paper

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The invention of Volta's Pile and its diffusion in Europe at war in the year 1800

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Abstract: Alessandro Volta built his pile in the winter of 1799 in his country house with no lab and no technical staff because, due to the war against Napoleon, the Austrians had closed the University of Pavia and fired the professors. Volta sent the article on the pile to the Royal Society in March 1800, and through the long process of publication in the journal *Philosophical Transactions* (September 1800), the news spread through the London scientific community. The physician Anthony Carlisle and the chemist and editor William Nicholson were the first to build a battery and used it to decompose water. The great news that electricity could be generated by a simple and easily constructed device was also printed in the daily newspapers, which helped to spread the word throughout Europe and inspired scientists and practitioners to build their own pile and carry out the electrical decomposition of various electrolytes, thus creating the basis for the new discipline of electrochemistry.

Keywords: Alessandro Volta; electrolysis of water; galvanism; pile; William Nicholson; 2022 Alessandro Volta's Heritage.

Introduction

The history of science is primarily assumed by scientists as a sequence and evolution of discoveries, inventions, and theories, documented in books and specialized journals. That of science, however, is not an isolated world, and the laboratory is rarely housed in an ivory tower. Scientific activity, like all human activities, is conditioned by the environment, by external events, and ultimately by the fact that scientists are human beings living in a society with its own problems, fortunes and misfortunes. The *electrical revolution*, *i.e.* the transition from *static electricity*, generated by friction (an uncontrollable form of energy that manifested itself in shocks and sparks, the subject of polite entertainment for wealthy classes of the 18^{th} century) to the *dynamic electricity* of cells and batteries (chemically generated, storable and controllable, with formidable applications and developments in science and society to this day and in the centuries to come) took its start in Northern Italy in the last decade of the 18^{th} century, thanks to two university professors (Luigi Galvani, Bologna, and Alessandro Volta, Pavia), at a time when that region was going through war (the two Napoleonic campaigns) and was at the same time undergoing dramatic social changes [1].

In 1797, after the first Napoleonic campaign and the French occupation of Northern Italy, the Cisalpine Republic was established, inspired by the principles of the Revolution. Bologna, previously belonging to the Papal States, was part of it. Every professor at the local University was required to swear loyalty to the Republic. Galvani, who did not agree with the social and political disorder brought to Bologna by the French, and who felt that this oath of allegiance was completely contrary to his religious convictions, consistently refused, together with a few

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other colleagues. As a result, he was deprived of his academic and public positions, and his salary was cut off. He died in Bologna, in his brother's house, grieving and in poverty, on 4 December 1798 at the age of 62, without being able to attend the triumph of the electric revolution, of which he had been the initiator.

Alessandro Volta conceived and built the pile in the months at the turn of the 19th century, during the second Napoleonic campaign, when the University of Pavia had been closed by the Austrians and the professors dismissed, if not put in jail for collaborating with the French invaders. So, Volta realised his invention in his country home in Lazzate (Como), in an arranged laboratory, without the help of workshop technicians or collaborators, using simple and easily available materials. Even the publication of the results was problematic and adventurous, as he sent the article on the pile to the then most prestigious scientific journal, that of the Royal Society in London, when communications across wartime Europe were interrupted or otherwise difficult. The delay in publication favoured an unofficial dissemination of news about the pile and its construction in a country, Great Britain, of empiricist culture, traditionally prepared for the applications of science and technological development. Philosophers and practitioners built their pile and studied its uses, starting with the electrical decomposition of water. From Great Britain, piles spread throughout Europe. Napoleon himself realised the importance, not only scientific, of the invention. He instituted the 'Prix du Galvanisme' destined for European scientists 'for the best experiment to be done on galvanic fluid', the first winner being Humphry Davy (1807), and financed grandiose projects for the construction of ever more powerful piles. Italy, steeped in humanistic culture and divided into many states, without a national scientific Society, made a marginal contribution to the development of galvanism and of the pile. Curiously, the chemical interpretation of galvanism, and consequently of the pile, which countered the contact theory advanced by Volta and was affirmed only at the end of the 19th century, was proposed in 1799 by another Italian scientist, Giovanni Fabbroni, a Florentine chemist and agronomist in the service of the Grand Duke of Tuscany, Ferdinand III. Fortunately for him and his fellow citizens, the passage of Tuscany under French democratic rule (1801) and the subsequent return to Austrian control (1814) took place peacefully without war and battles. *Malgré tout*, science won and in 1800, with the discovery of water electrolysis by William Nicholson, electrochemistry was born.

Alessandro Volta, professor of Physics and researcher in the science of static electricity

Alessandro Giuseppe Antonio Anastasio Volta was born in Como on 18 February 1745 to a family of minor nobility, the sixth of seven children. The older brothers and sisters all devoted themselves to religious life (a friar, a canon, an archdeacon, two Benedictine nuns). Alessandro was different: from the age of 13 he attended the Jesuit school, then entered the seminary, but at eighteen, quite fortunately for science and for our civilization, he left to devote himself to the study of physics, in particular electricity, as an autodidact. He carried out experiments at home, read current literature, and corresponded with important physicists: Giambattista Beccaria (1716–1781), professor of Experimental Physics at the University of Turin and Jean Antoine Nollet (1700–1770), professor of Experimental Physics at the University of Paris and Director of the *Académie des Sciences*. At the age of 20 Volta was welcomed into the laboratory of his friend Giulio Cesare Gattoni (1741–1809), a canon and amateur physicist, where he could conduct more sophisticated experiments in a better equipped environment. At the age of 24 Volta published his first work on electricity (*"De vi attractiva ignis electrici ac phaenomenis inde pendentibus"* – On the force of attraction of electric fire and on related phenomena – 72 pages) [2], a treatise on electricity, in Latin, that he sent to the most illustrious Italian scientists. In 1774, he was appointed Superintendent and Regent of the Royal Schools of Como and was able to carry out his research in his own laboratory. In 1775 he communicated to Joseph Priestley the invention of a surprising instrument, the electrophorus [3,4]. This apparatus was able to produce electricity not by friction, as in the electrostatic machines of that time, but by induction and was immediately applied to the systematic production of abundant and lasting supply of electricity in all European laboratories. Volta so achieved considerable notoriety and was appointed professor of Physics at the 'Real Ginnasio' (Grammar School) in Como. Volta, a skilled and ingenious experimenter, was also a keen observer of nature. Sailing by boat the reeds on Lake Maggiore, he noticed and collected a gas bubbling from the muddy bottom of the water. Once in the laboratory, he noticed that the gas, in contact with a spark, ignited and burned with a mild and moderate flame: he called the new gas "inflammable air native to marshes" (called by chemists 'methane' since 1866 [5]).

In 1778 Volta was appointed at the University of Pavia as a professor of Physics. In particular, the chair of Physics, formerly held by Carlo Barletti (1735–1800), a Piarist father, was split into that of 'Particular and Experimental Physics', with a pronounced phenomenological character and covering emerging disciplines like: electricity, magnetism, heat, acoustics, meteorology, optics, which was assigned to Volta, and that of 'General Physics', based on solid mathematical foundations and treating classical disciplines (mechanics, hydraulics, astronomy), which remained with Barletti. Volta was a brilliant and attracting teacher, a quality that made the number of students of Physics increase substantially. This urged the University to build a new lecture theatre (today called "Aula Volta", shown in Fig. 1), of the seating capacity of 120, which was also used by Volta for public demonstrations of experiments on electricity.

In contrast to the provincialism of the Italian scientists of the time, who did not like to travel and thus avoided comparison with other cultures, Volta travelled around Europe between 1781 and 1782, supported by a grant from the Austrian government. He visited Savoy, Switzerland, Germany, Belgium, Holland, France and England to buy new instruments for his laboratory and to exchange ideas and build relationships with the leading scientists of the day. In Pavia, Volta continued his research in the field of electrostatics, inventing new devices such as the condenser electrometer and perfecting known apparatus. At the beginning of the last decade of the XVIII century, Alessandro Volta was a renowned professor and a successful and respected researcher in the science of electricity.

From Galvani's frog to Volta's pile: electricity becomes continuous and constant

Discovery of electricity is traditionally credited to Thales, a pre-socratic philosopher, who lived in Miletus (now in Turkey) around VI century BC and noticed that amber, when rubbed with wool, attracted feathers and other light objects. The Latin adjective 'electricus', from which the term 'electricity' derives, was invented by the English scientist and physician William Gilbert (1554–1603), who introduced it in his treatise *'De Magnete'*, published in 1600 [6], and was inspired by the Ancient Greek name of amber: ἤλεκτρον. During the XVIII century electrostatic machines of increasing power and sophistication were built, capable of converting mechanical energy (associated to friction) into the static electricity, which could be released in the form of sparks of varying length or transferred into a Leyden jar, where it could be stored for future use. Such a form of electricity was poorly controllable, did not find any practical and useful application, often being the subject of polite entertainment for ladies and gentlemen who enjoyed seeing sparks and experiencing moderate shocks [7].

Fig. 1: The Physical Theater of the University of Pavia (today, Aula Volta, capacity 120), wanted by Alessandro Volta and built in the period 1785–1787, under the direction of the architect Leopoldo Pollack.

Everything changed in 1791, when Luigi Galvani (1737–1798), professor of anatomy and obstetrics at the University of Bologna, published a pamphlet in Latin entitled "De viribus electricitatis in motu musculari. Commentarius", printed by the University's Institute of Science [8]. Galvani sent the pamphlet (58 pages, 3 figures) to leading Italian scientists, including Volta. Galvani had been studying the effects of electricity on frogs (the animal commonly used at the time as a laboratory guinea pig) for a decade, and in particular he had observed that when a metal arc, especially when made of two different metals, bridged a muscle and a nerve of a "treated" frog (*i.e.* killed and skinned), the frog's legs contracted as if in the grip of toxic convulsions. According to tradition, the discovery took place on 24 March 1786 on the terrace overlooking the garden of Palazzo Zamboni in Bologna, where Galvani lived, as shown in Fig. 2.

To study the influence of atmospheric electricity on the frog's movements in calm weather, Galvani passed a copper hook through the spinal cord of a prepared frog and hung it from the iron balustrade that bordered the terrace. For several hours nothing happened. Galvani, disappointed, moved the frog with a glass rod until it touched the iron railing. Immediately, the animal's lower limbs began to contract, and these muscular movements were reproduced with each new contact between the frog and the iron railing. Galvani formulated the idea that there was an *animal electricity*, an electrical fluid secreted by the brain and carried by the nerves to the muscles. According to Galvani, each animal is a reservoir of electrical fluid, a sort of Leyden jar. Positive electricity has its seat in the nerves (nerve tissue acting like the inner surface of the jar), negative electricity in the muscles (muscle tissue being the outer surface). The metallic arc interposed between these organs is simply the conductor by which the discharge takes place, causing contraction. Volta was strongly impressed, repeated Galvani's experiments and extended them to a variety of animals (mammals, reptiles, birds, insects, worms), each time observing contraction induced by contact with a dimetallic arc (in this way he was also able to excite the song of a cicada) [10]. However, Volta formulated a different theory on the electrical nature of the phenomenon: electricity is generated by the contact of two different metals (*metallic electricity*) [11], and the muscular *or* nervous tissue of the frog behaves as a second species conductor (today, following the nomenclature suggested by Faraday [12], we say 'electrolyte'). The frog (or the animal in question) simply closes the circuit. Volta published these results in the periodical of the Royal Society of London, *Philosophical Transactions* [10] one of the most prestigious scientific journals of the time [13].

The article aroused great interest and Volta in 1794 was awarded the Copley Medal (something equivalent of the Nobel Prize at the time) by the Royal Society "for his several Communications explanatory of certain Experiments published by Professor Galvani". A scientific controversy on the nature of electricity, whether animal or metallic, then arose between Galvani and Volta, a controversy that was also bitter, but always conducted within the limits of mutual respect and esteem.

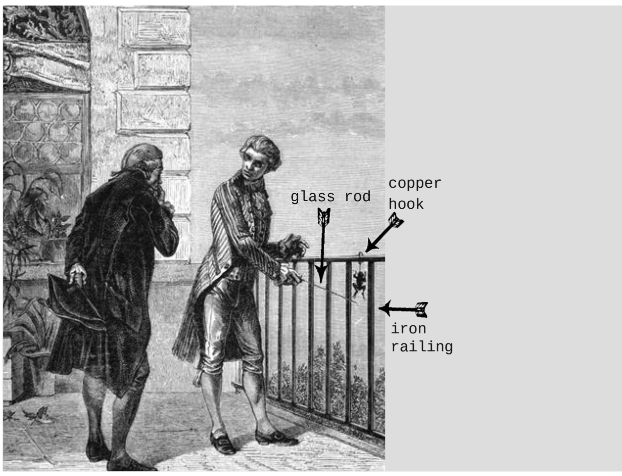

Fig. 2: Galvani shows a friend the experiment with the frog on the terrace of the Zamboni palace, in Bologna, where he lived. Picture adapted from ref. [9].

At this stage, to prove the validity of his theory and put the matter to rest, Volta had to make a device capable of producing a constant current through the contact of two different metals. And he did this in an ingenious way, by building what was later called a *pile*. He carried out pertinent experiments under uneasy environmental conditions (vide infra), in the winter of 1799/1800 and described his work in a communication (in French) submitted to the Royal Society [14]. Volta, among the metals used in his study on frogs and other animals, chose zinc (or even tin, but it proved less effective) and silver (which could be substituted for copper or brass) and made discs of them, 2.5 cm in diameter, as well as discs of cardboard soaked in salt water. Then, he placed the discs on top of each other according to the sequence: silver, zinc, cardboard, silver, zinc, cardboard, and so on. The column, whatever the number of metal pairs, ended with a zinc disc, as shown in the original drawing shown in Fig. 3. Volta observed that a 20-pair column could charge a capacitor to the point of sparking, or giving a shock to anyone who touched the ends of the column with both hands. The shock is stronger if one of the hands is immersed in a basin full of water connected to the silver disk at the foot of the column. The greater the number of Zn/Ag pairs, the stronger the intensity of the shock. Volta stated that his device generates a constant direct current (which is *true*) and that it is the contact between different conductors that gives rise to an *endless* circulation of the electrical fluid – 'un mouvement perpetuel' (perpetual motion, *false*, and contrary to the fundamental laws of physics). Volta's ability to convert a principle (contact of conductors of different natures generates constant electricity) into an effective device is to be admired, but the ingenuity and simplicity of the design (the discs placed in columns, to give an apparatus that is manageable, transportable and beyond all easy to construct) is amazing. But how did he get the idea? What was it inspired by? As explicitly stated in the article, Volta took inspiration from the natural electric organ of the torpedo fish raia. The ability of the torpedo to emit electric shocks had been known since ancient times. The Latin name, *torpēdo, torpedĭnis*, derives from the verb *torpēre*, to remain numb, which was what happened to those who touched the torpedo with their bare hands. Scribonius Largus (ca. 1–ca. 50 AD), the court physician to the Roman emperor Claudius, reported in his *Compositiones Medicae* (a collection of 271 prescriptions) that headaches, even if chronic and unbearable, can be eliminated forever by placing a black, live torpedo on the painful area, thus providing the first example of electrotherapy. Systematic studies on electricity in the 18th century had generated interest in the physiology and anatomy of electric fishes. The most significant studies had been conducted by John Walsh, a British naturalist (1726–1795), who observed that the torpedo raia has two large kidney-shaped electric organs on each side of the head and found that the two sides of each electric organ detain opposite electrical charges [15]. For these and other experiments on electric fishes Walsh received the Copley Medal of the Royal Society in 1774. At Walsh's request, the British surgeon and anatomist John Hunter (1728–1793) dissected and examined the electric organs of several torpedo fishes [16]. Hunter observed that each organ consisted of hundreds of perpendicular *columns*, reaching from the top to the bottom of the body, and varying in their lengths from 0.6 to 3.8 cm. Each column was divided by horizontal *partitions*, placed over each other, at small distances, and forming numerous interstices, which contained a fluid (see Fig. 4a).

Volta was well aware of the findings of Walsh and Hunter and in his paper stated: "We know, by the anatomy which has been made of it, that the electric organ of the torpedo consists of several membranous *columns*, filled from one end to the other with a large numbers of laminae or pellicles, in the form of very thin

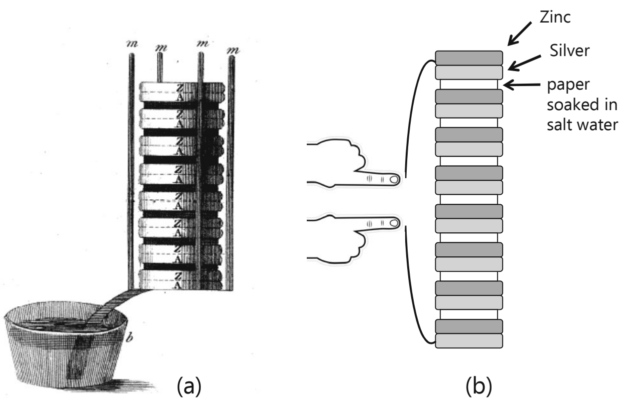

Fig. 3: The column of discs. (a) The original drawing of Volta's generator of current in its most popular version, the column of discs [14]; (b) a simplified drawing of the apparatus. The column is made of eight zinc/silver couple, interfaced by seven cardboard discs impregnated by a saline solution. Notice that, according to the chemical interpretation, the upper zinc disc and the lower silver disc do not contribute to the production of electricity, but act as simple conductors.

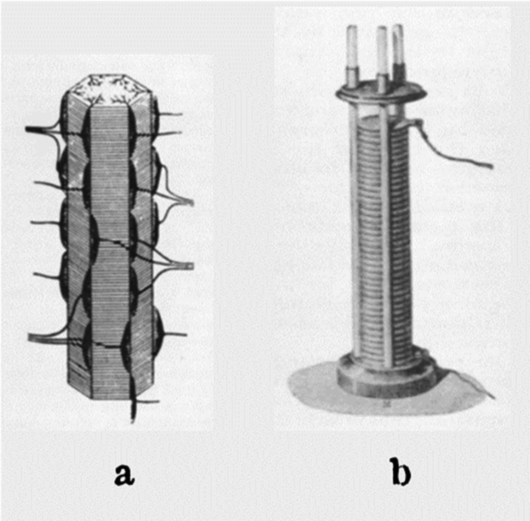

Fig. 4: Drawing showing the similarity of (a) the electrical organ of the torpedo and (b) Volta's pile.

discs, lying on top of each other at very small intervals, in which flows some humour" [14]. Thus, Volta conceived his pile as a replica of the electric organ of a torpedo, deserving therefore the name of 'Organe électrique artificiel' (Artificial electric organ). He stated that the electrical fluid circulating in a circle of conductors, whether the electric organ of the torpedo or the pile, is generated by the mutual contact of conductors of different nature (zinc and silver, in the pile). Since they differ in their power of conducing electricity, when they are brought into contact, they generate an electrical current. Volta proudly concluded that any other interpretation of galvanism had to be definitively rejected.

How Volta's pile works

The 'physical' interpretation of the pile (contact theory) was immediately contrasted with a 'chemical' interpretation. According to the chemical theory, the electric current is not generated by the two metals in contact, but by chemical phenomena that take place in the solution by which the cardboard or cloth disc is soaked. Already in 1799, a year before the construction of Volta's pile was made public, Giovanni Fabbroni (1752–1822), Florentine naturalist and chemist, founder of the Museum of Physics and Natural History of Florence, had observed that a non-oxidizable metal (*e.g.* silver) and an oxidizable one (*e.g.* tin), in contact with each other, placed on the tongue, generate a convulsive sensation [6]. This sensation is not felt if the two metals are separated. Furthermore, if an Ag/Sn dimetallic arc is immersed in water, the immersed tin part is covered with a white layer, made up of tin oxide crystals, while the thickness of this layer increases over time. When immersed in water alone, nothing happened to the zinc wire. Fabbroni suggested that the dimetallic arc caused the decomposition of the water, that the oxygen formed reacted with tin to give the oxide and that the hydrogen was absorbed by silver. According to Fabbroni, it was this complex of reactions that was responsible for the galvanism. From here followed a long dispute between the supporters of the metallic or contact theory (current generated by the contact of different metals: Volta, Davy, Pfaff, Marianini, Fechner, Poggendorf, Zamboni, Matteucci, Karsten) and those of the chemical theory (Fabbroni, Wollaston, Oersted, Becquerel, de la Rive, Schönbein, Faraday, Grove). The controversy lasted for a century and finally ended when oxidation and reduction reactions were clearly established [18], and the electron was discovered as a physical entity [19].

Before discussing the chemical functioning of the pile, it is worth considering a second version of the electricity generator, illustrated in Fig. 5a, that Volta described in his article [14]. It consists of a row of 30–60 cups of any non-conducting material (wood, tortoise shell, earth, or, better, glass), half full of a saline solution, communicating by means of dimetallic arcs made of laminated silver (A) and zinc (Z). Metals were welded together and each one plunged into the liquid of one of two adjacent goblets. By immersing your hands in the two outer cups (larger than the internal glasses so that the hands can enter them comfortably, as shown in the original Fig. 5a), you close the circuit and you feel the typical shock due the passage of electric current from one hand to the other along your body. The intensity of the shock increases with the increasing number of goblets. In a modern perspective, each cup can be considered a *galvanic cell* (see Fig. 5c) and, using the technical language introduced by Faraday in 1833 [11], the metal plates immersed the saline solution are the *electrodes* and the salt dissolved is the *electrolyte*. We know today that the electromotive force does not arise from the contact between the two metal electrodes, but from the chemical processes that take place in the solution. It derives that the two external vessels act as simple conductors and do not contribute to generate the current. Thus, the electricity of the crown cups shown in Fig. 5a and c is generated by three galvanic cells (Zn/electrolyte/Ag), rather than by four metallic arcs Ag/Zn. In the same way, in the pile illustrated in Fig. 3a and b the two highest discs (Zn and impregnated cardboard) and the two lowest discs (Ag and cardboard) are redundant.

The occurrence of chemical processes in a galvanic cell was realised by William Nicholson, English chemist, who was the first to build a pile (with his friend Carlisle, English physician, vide infra), following Volta's recipe [20]. He observed that, when the pile was working, a white layer of oxide formed on zinc discs. He commented: "… I cannot here look back without some surprize, and observe that the chemical phenomena of galvanism, which had been much so insisted on by Fabbroni, *more especially the rapid oxidation of the zinc*, should constitute no part of [Volta's, note of the author] numerous observations".

We are today aware that behind every galvanic cell there is an oxidation-reduction process. If the oxidation process has been recognized (formation of zinc oxide), the reduction process remains to be clearly identified. An important clue is provided by the observation, made by Henry Haldane [21], and confirmed by Humphry Davy [22], that Volta's pile (Zn/NaCl(aq)/Ag) works in the presence of air and even better in an oxygen environment, but does not work either *in vacuo* or in an environment of nitrogen or hydrogen. This suggests that half-reactions (1) and (2) take place at the electrodes:

$$\text{Zn, anode} \quad 2Zn \rightarrow 2Zn^{2+} + 4e^- \tag{1}$$

$$\text{Cu, cathode} \quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{2}$$

$$2Zn + O_2 + 2H_2O \rightarrow 2Zn\,(OH)_2 \tag{3}$$

In a hypothesized temporal sequence, (i) two zinc atoms leaves four electrons on the electrode (anode) and go into solution as Zn^{2+} – half-reaction (1); (ii) the four electrons reach the silver electrode (cathode) where they are acquired by an oxygen molecule in solution, while four hydroxide ions are formed according to the half-reaction

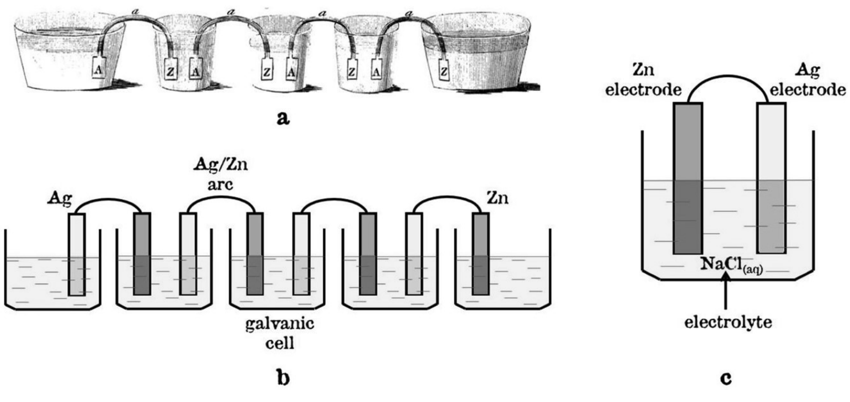

Fig. 5: The crown of cups. (a) The original drawing of Volta's generator of current in its version crown of cups [14]; (b) a simplified drawing of the apparatus. The system consists of four Ag/Zn arcs (the two metals being connected by a copper wire), dipped in five glasses containing salt water; (c) an Ag/Zn galvanic cell. Following the chemical theory, the crown of cups generating electricity is made by three galvanic cells. We know today that the two outer cups do not contribute to the production of electricity and act as simple conductors (if you put your hands in the two outer vessels, you close the circuit and get a shock!).

(2); (iii) the OH^- ions produced in the half-reaction (2) migrate in the solution and interact with the Zn^{2+} ions produced in the half-reaction (1) to form the insoluble hydroxide $Zn(OH)_2$, the white solid forming on the zinc electrode surface or precipitating below it. eq. 3, which describes the overall redox process, results from the sum of the two half-reactions (1) and (2). From a thermodynamic point the cell should provide a respectable emf: $\Delta E° = 1.99$ V, taking into account that at pH = 7 $E°(O_2{}^{0/2-}) = 1.23–0.059$ pH V = 0.82 V, and that $E°(Zn^{2+/0}$ pH = 7) = – 2.81 V, from $E°(Zn^{2+/0}) = 0.76$ V, and $K_{ps}(Zn(OH)_2) = 3 \times 10^{-17}$.

However, Haldane and Davy's observations about the need for oxygen for the pile to function are contradicted by the fact that Volta had coated two connected piles (of twenty Zn/Ag elements each) with wax (or pitch) to prevent the evaporation of water from the cardboard discs. This expedient, which excluded any supply of oxygen from the atmosphere, ensured that the pile would continue to work for weeks («et, j'éspère, après mois» [14]).

Recently, Dick and co-workers reconstructed three Zn/Cu voltaic piles [23], each consisting of three pieces of both copper and zinc, while the interfacing cardboard pieces were impregnated by 1 M NaCl (pH 7), 1 M HCl (pH 0) and 1 M NaOH (pH 14). Each pile was kept in a container, first exposed to air, then purged with appropriate gases. The open-circuit potential of the pile, E_{pile}, was determined with a potentiostat. On purging the container of nitrogen, the value of E_{pile} was observed to decrease substantially: 1 M HCl from 1.6 (in the air) to 1.1 V (under nitrogen); 1 M NaCl from 1.9 to 1.3 V; 1 M NaOH from 2.7 to 1.3 V. On purging the container of oxygen original values were restored. These findings suggest that oxygen reduction plays an important role in determining the electromotive force of voltaic piles.

However, in textbooks and encyclopedia entries dealing with the chemistry of Volta's pile it is traditionally assumed that the half-reaction (4) takes place at the cathode, in which the hydrogen ion of water (whatever its concentration is) is reduced to molecular hydrogen.

$$(\text{cathode})2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

This assumption was first made by Daniell (1790–1845) in his studies in the search for a 'constant pile' [24]. Daniell, professor of chemistry at the East India Company's Military Seminary at Addiscombe, Surrey, built a galvanic cell in which an amalgamated zinc plate and a platinum plate were immersed in water acidulated with sulphuric acid «in the ratio of 100 parts by volume of the former to 24 of the latter (specific gravity 1027.5 g L^{-1})», which corresponds to the respectable concentration 0.46 M. With the electrodes not connected, the amalgamate zinc plate was not oxidized by H^+ and in any case no evolution of H_2 on this electrode was observed. When the two plates were connected by a metal wire, an abundant release of hydrogen was observed on the platinum electrode, a behaviour illustrated by half-reaction (4). We know today that formation of H_2 at the platinum electrode must be ascribed to the high hydrogen overpotential on zinc, which had been further increased by the presence of mercury on the surface. In a first attempt to build the constant battery, Daniell separated the oxidable electrode (still amalgamated zinc) from the non-oxidable electrode (this time copper) by a membranous tube formed of a part of the gullet of an ox [24]. Such a porous barrier allowed ions to pass through but kept the solutions from mixing. When both compartments were filled with a dilute solution of sulphuric acid, the action of the cell progressively decreased due to the adhesion of hydrogen bubbles to the surface of the copper cathode, a process that increased the resistance of the circuit. At this stage, Daniell formulated the genial idea of replacing the dilute sulphuric acid in the cathodic compartment with a solution of copper sulphate. So, it was Cu^{2+} that was reduced on the copper electrode, instead of H^+, creating a conducting metallic layer that guaranteed a constant production of electric current. Indeed, batteries based on this design, with some reasonable modifications (the ox gullet had been replaced by an unglazed porous earthenware cylinder) were satisfactorily used to feed telegraph networks until the late 1860s, when they were replaced by the Leclanché cells. A demonstrative version of Daniell's cell (a beaker containing the zinc electrode dipped in a solution of $ZnSO_4$ and a beaker containing a copper electrode dipped in a solution of $CuSO_4$, connected by a reverse U-shaped tube filled with an electrolyte, *e.g.* aqueous KNO_3 – the salt bridge) is typically illustrated at the beginning of the chapter of electrochemistry of any textbook of general chemistry, providing an explanation of how first batteries worked. No comments are made on the chemistry behind Volta's pile.

Some modern authors, when discussing citrus batteries, have raised the problem of the chemical mechanism of the Volta battery. For example, Goodisman measured a potential difference of 0.91 V between a Zn and a Cu electrode immersed in a 0.25 M solution of citric acid (pK_{a1} 3.13, pH = 2.5), which mimics lemon juice [25]. This value coincides with the $\Delta E°$ value of the $Zn + 2H^+$ redox reaction (0.91 V at pH = 3.13) and is very distant from that of the O_2 + Zn reaction (1.84 V at pH = 3.13). Then, the author observed that the open circuit potential difference for solutions with pH ranging between 3.20 and 10.45 varied linearly with pH with a slope of −0.0648 ± 0.0061, to be compared with RT/nF = −0.0592, a feature common to both $Zn + 2H^+$ and O_2 + Zn reactions. More significantly, hydrogen bubbles were observed to develop on the copper electrode (for pH < 3 also on the zinc electrode, but in smaller quantities).

The results illustrated above show that the chemical interpretation of the Volta pile is quite complicated. It seems probable that both (a) the reduction of H^+ (of H_2O in neutral solution, with consequent formation of $Zn(OH)_2$, as illustrated by eq. 7)

$$\text{Zn, anode} \quad Zn \rightarrow Zn^{2+} + 2e^- \tag{5}$$

$$\text{Cu, cathode}\ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{6}$$

$$Zn + 2H_2O \rightarrow H_2 + Zn\,(OH)_2 \tag{7}$$

and (b) the reduction of dissolved O_2 contribute to the process.

The predominance of either half-reaction of reduction may depend on a variety of factors, primarily the hydrogen overvoltage, which strictly depends upon the nature of the electrode metal and of its surface. This effect had been intuited by Daniell, who in his first battery used amalgamated zinc to prevent the 'local' oxidation of the zinc by H^+ (the amalgamated zinc was no longer needed when the dilute sulphuric acid electrolyte was replaced by a $ZnSO_4$ solution [26]).

The first chemical application of Volta's pile: the electrolysis of water

Volta's communication to the Royal Society on the pile is dated: Como, 20 March 1800. Why Como and not Pavia where Alessandro Volta was an acclaimed university professor and carried out his research? The reason is to be ascribed to the political troubles Lombardy and Northern Italy in general were experienced during the 1796–1800 period: this was in fact the period of Napoleon's Italian campaigns. When in April 1796 General Napoleon entered Italy to fight the Piedmonteses and Austrians, Vienna closed the University of Pavia. The University was reopened by the victorious French in April 1797 with the stated intention of restoring its former glory and bringing the ideas of democracy and revolution. However, when Napoleon moved into Egypt, Austro-Russian troops re-occupied Lombardy (April 1799). This time the University was suppressed and the professors fired. Many of them, who had committed themselves to democratic government and had played a political role in the Cisalpine republic, were imprisoned. Among these was Volta's colleague Carlo Barletti, government commissioner of the province of Pavia under the French rule, who died in prison in February 1800, a few months before the battle of Marengo (14 June 1800) and the return of the French to Northern Italy.

Volta in April 1799, without a salary and without a laboratory, retired to his house in the countryside at Lazzate, 24 km south of Como, 34 km north of Milan; it is there that Volta built the pile, in an improvised laboratory set up at home, without the collaboration of his trusted technician Giuseppe Re and with a limited variety of materials available. This also explains why Volta experienced the effects of the electric discharge on himself and on his sense organs and not on the variety of animals that had been supplied to him by colleagues of the close Institute of Zoology for the 1793 communication to the Royal Society [10].

The work completed, the problem arose of how to get it across war-ravaged Europe to the Royal Society of London for discussion and publication on *Philosophical Transactions*. On 20 March 1800, Volta sent a four-page extended abstract to the regular postal service. Then, on April 1st, he entrusted the complete letter to Pasquale Garovaglio, a merchant from Como who was leaving for London. Sir Joseph Banks (1743–1820), President of the Royal Society in London, received the four-page abstract in the latter end of April, which contained detailed instructions on the construction of the pile. Banks, the eminent botanist, patron of the natural sciences and president of the Royal Society from 1778 until his death in 1820, was deeply impressed, understood that he was faced with a revolutionary discovery and felt the need to share this emotion with some friends and colleagues. Coldly, we can say that Banks' behaviour violated every rule of scientific ethics, which requires every editor of scientific publications, and every reviewer consulted, not to disseminate information about an article or communication until it has been published (and, in the case in question, preliminarily discussed at an official meeting of the members of the Royal Society). However, such editorial malpractice may be understandable when one considers the extraordinary novelty of a discovery that made the production and control of electricity easy and possible for everyone and which, it was felt, would have formidable and immediate consequences for the sciences of physics, chemistry and medicine. Among the privileged people who were allowed to peruse Volta's preliminary letter, the quickest and most receptive was Anthony Carlisle (1768–1840), surgeon at the Westminster Hospital in London from 1793 and destined for a brilliant career (in 1820 he would become Surgeon Extraordinary to King George IV). Interested in the applications of electricity in medicine, Carlisle built a column of 17 half-crowns (silver coins 3.2 cm in diameter and weighing 14.1 g, used in the UK until 1970) and the same number of zinc discs, the metal pairs being interfaced by cardboard discs soaked in salt water, all arranged as indicated in Volta's abstract. Then, uncertain of what to do, on the 30th of April he called for help from his friend William Nicholson (1753–1815), a lively, multifaceted personality, trained chemist, writer and translator of texts on natural philosophy, best known as the founder and editor of "The Journal of Natural Philosophy, Chemistry and the Arts", the first commercial monthly scientific journal (founded in April 1797). This magazine was popular among scientists and practitioners, often preferred even by prestigious authors because it ensured a faster publication than the periodical of the Royal Society and was widespread in Great Britain and Europe. Nicholson was also a renowned scholar of electricity, mentioned by Volta in the letter to Banks as «savant et laborieux physicien» [14].

In a preliminary experiment (30 April) the two philosophers determined the charges on the pile by means of a Bennet's gold leaf electrometer connected to a revolving doubler, by which (see Fig. 6), a negative charge could be assigned the outer silver disc and a positive charge to the zinc disc. Nicholson refers that, after placing a drop of water on the silver plate, in order to make the contact sure, Carlisle observed a disengagement of fine bubbles of gas round the touching wire. Even is the quantity of gas was very minute, the expert chemist Nicholson

Fig. 6: 'Nicholson et Carlisle, à Londres, décomposent l'eau par la pile de Volta, le 2 mai 1800', picture taken from L. Figuier, *Les Merveilles de la Science – Tome 1*, (1867), Fig. 324, p. 629 [27]. More specifically, in the picture, Carlisle (left) and Nicholson are not yet electrolysing water, but using a Bennet's gold leaf electrometer to determine the electrical charges on silver and zinc, an attempt which Nicholson said was unsuccessful. By amplifying the signal with a revolving doubler, a positive charge could be assigned to zinc and a negative charge to silver.

recognized the smell of hydrogen. In a scaled up experiment on 2 May, a brass wire connected to zinc and a brass wire connected to silver were dipped in a vessel containing the water from a nearby river. Hydrogen bubbles developed from the silver connected wire, while the on the zinc connected wire a precipitate formed, first white (zinc hydroxide), then green (copper hydroxide). In hindsight, we can ascribe the phenomena to the occurrence at the electrodes of the following redox processes:

$$\text{Zn (brass anode)} \quad Zn \rightarrow Zn^{2+} + 2e^-$$

$$\text{Cu (brass anode)} \quad Cu \rightarrow Cu^{2+} + 2e^-$$

$$\text{Cu (brass cathode)} \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$\text{overall} \quad M + 2H_2O \rightarrow H_2 + M(OH)_2 \qquad M = Zn, Cu \tag{8}$$

Nicholson realized that electricity had in some way induced the decomposition of water and planned further experiments. Nicholson refers that Carlisle, who looked at the medical and physiological effects of electricity, was no longer interested and on May 6th left the game taking away his pile [20]. Thus, Nicholson constructed two piles, each consisting of 16 discs of laminated silver (0.025 mm thick), 16 discs of laminated zinc (1.1 mm thick) and 15 discs of wetted carboard, all of a diameter of ~5 cm (thus consuming a minimum quantity of the precious metal, according to the traditional tendency of chemists to save). Investigations culminated in an experiment in which two platinum electrodes were dipped in the water containing vessel: a plentiful stream of fine bubbles was observed to form at the silver connected wire and a less abundant stream of bubbles at the zinc connected wire. For Nicholson «… it was natural to conjecture that the larger stream from the silver side was hydrogen, and the smaller oxygen…». To prove the correctness of the hypothesis, Nicholson borrowed Carlisle's pile and put it in series with his two for a total of 57 Ag/Zn pairs. The platinum wires were placed under two inverted tubes filled with water. During the experiment, each gas occupied the upper part of the overturned tube, displacing the water downwards. How to determine the molar ratio between the two gases? Simple – would answer a student taking his first steps in chemistry, who has just studied Avogadro's principle – from the ratio of the two volumes. Nicholson, who could not have known Avogadro's work published eleven years later [28], resorted to a more complicated and laborious method: he weighed the amount of water displaced in each tube: 9.42 g in the tube with the electrode connected to the zinc and 4.48 g in the tube connected to the silver, thus brilliantly confirming the 2:1 ratio established by Lavoisier. The processes taking place at the electrodes are described by the following equations [29]:

$$\text{Pt (anode)}\, 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \tag{9}$$

$$\text{Pt (cathode)}\, 2H_2O \rightarrow O_{2\,(g)} + 4H^+ + 4e^- \tag{10}$$

$$\text{overall} \quad 2H_2O \rightarrow 2H_2 + O_2 \tag{11}$$

With this beautiful experiment, Nicholson had demonstrated the electrolysis of water, paving the way for a new fundamental branch of chemistry: electrochemistry.

However, to be precise, that was not the first experiment in the electrical decomposition of water [30]. In 1789 Adriaan Paets van Troostwijk (1752–1837) and Johan Rudolph Deiman (1743–1808) in Amsterdam took a small glass tube with a diameter of 3.2 mm closed at the bottom, through which a gold wire passed. They filled the tube with distilled water and then placed it upside down in a container filled with distilled water. Then they inserted another gold wire into the open part of the tube to within 1.6 cm of the gold wire welded into the glass. They connected the two gold wires to a powerful friction electrostatic generator and made it produce several discharges. With each discharge the ends of the two wires were illuminated by a spark, while fine bubbles of gas developed on the wires and collected towards the top of the closed tube, forcing the water downwards. When the upper gold thread remained completely uncovered by the water, the spark ignited the gas with detonation, the gas vanished and the water refilled the tube almost completely. Paets van Troostwijk and Deiman formulated the hypothesis that electric discharges decomposed water into flammable air (hydrogen) and vital air (oxygen), providing a strong support to Lavoisier's statement that water was not an element, but was constituted by two elements. The article by the two Dutch scientists was first published in a French journal [31], then taken up in other journals: German [32], Dutch [33], and Italian [34]. A few years later, George Pearson (1751–1828), a British physician and chemist, repeated the experiments of Paets van Troostwijk and Deiman and communicated his research in the session of the Royal Society of 2 February 1797, then published in *Philosophical Transactions* [35]. Pearson's communication was taken up and republished in three successive sections by Nicholson in his journal [36]. Nicholson, therefore, knew well the effect of electricity on water. It derives that the discovery of electrolysis did not arise from the acute but casual observation by Carlisle of the fine hydrogen bubbles that formed in the drop of water used to improve an electrical contact [20]. Nicholson had well in mind the decomposition of water induced by electric discharges described by Paets van Troostwijk and Deiman and was eager to repeat the experiment with Volta's pile, a machine that guaranteed continuous and controllable electricity. With the intuition and competence of a talented chemist he carried out the experiment in the proper conditions and was able to separate and qualitatively and quantitatively characterize the products of the decomposition of water (what his friend Carlisle, interested in the physiological effects of the electrical shock, would never have done). It was Nicholson's work that demonstrated to the scientific community the potential of Volta's pile as a powerful chemical instrument.

The subtle game of scientific communication at the turn of the 19th century

Nicholson was well aware that he had achieved a great scientific result and was impatient to report it in his journal. However, professional ethics prevented him from publishing a research work carried out with an apparatus described in a Communication not yet discussed in a meeting of the Royal Society and not yet published. He later wrote in the July issue of his journal [20]: "For motives of delicacy to the inventor of the most curious and important combination hereafter to be described, I forbore giving an account of its construction and effects in the last number of this Journal, *though it has now been a subject of great attention among philosophers for near two months*". The same delicacy was not shown by his colleague Carlisle who recounted in detail the experiments with Volta's pile (even those in which, according to Nicholson's testimony [20], he had not physically participated) to Alexander Tilloch (1759–1825), the Editor of *The Philosophical Magazine*, the other commercial scientific journal published in London (established by Tilloch in June 1798). In the May issue of Tilloch's journal, a 120-word article entitled 'Galvanism' (written by the Editor) appeared in which it was said that Mr. Carlisle had built a device made of 40 or 50 half-crowns and as many zinc discs and pieces of wetted pasteboard [37]. Detailed instructions were given for its construction. It was also said that if two platinum wires connected to the apparatus were immersed in water, both oxygen and hydrogen were liberated. Neither Volta nor Nicholson were mentioned in the report! The news circulated among philosophers and the simplicity of the device and its low cost stimulated many of them to build it and to carry out water decomposition.

A further decisive contribution to the diffusion of the pile and its applications beyond the philosophers reading *The Philosophical Magazine* was given by Thomas Garnett (1766–1802), a Scottish physician, professor of experimental philosophy, mechanics and chemistry at the Royal Institution. The Royal Institution of Great Britain, founded in 1799 and based in London's Albemarle Street, aimed to develop new technologies to improve the quality of life and to disseminate scientific knowledge to the general public through courses and public lectures accompanied by experimental demonstrations, in line with typical Enlightenment ideals. It was Garnett's job to give regular lectures on current scientific topics, and, after learning about the pile and its applications, he borrowed the device from a philosopher friend – Edward Charles Howard (1774–1816), a talented chemist awarded the Copley Medal in 1800 for the discovery of mercury fulminate and its explosive power [38]. The lecture was held on the evening of Wednesday 28 May: Garnett reconstructed the pile on the bench by placing one by one 40 half-crowns, 40 zinc plates and 39 wet paper discs one on top of the other. Then, he called a volunteer at the bench and gave him a shock with the pile. Finally, he carried out the electrical decomposition of the water with copious development of gas bubbles. Resounding success! The only fly in the ointment: he attributed the invention and discovery to 'some French philosophers'. The next day, the unfortunate attribution reached the ears of Sir Joseph Banks, one of the founders of the Royal Institution, who flew into a rage (partly because he was aware that he and his editorial misconduct were at the root of the whole unpleasant affair). On 30 May, a short article appeared in the London *Morning Chronicle* reporting on Garnett's lecture and in particular describing in detail the construction of the pile. Probably misunderstanding a suggestion made by Banks himself, the reporter credited Volta not only with the pile but also with the electrolysis of water. Nicholson read the article. This time he was the one who flies into a rage and wrote a resentful letter to the *Morning Chronicle*, which was published on 3 June. In the letter Nicholson claimed the discovery of water electrolysis and commented with bitter irony: "The Royal Institution is to become an office for collecting the conversations of philosophers and immediately publishing them in the daily papers". The word 'conversation' suggests that Nicholson himself may have publicized his discoveries among colleagues, out of human vanity.

Around mid-June, Volta's complete letter brought by Garovaglio reached the hands of Banks who presented it at the meeting of the Royal Society on 26 June. Now that Volta's letter had been read and made public, Nicholson felt free to publish his article on the pile and on its applications in the July issue of his journal [20]. It should be noted that the abstract of the paper in Table of Contents mentions 'a *pile* of plates of zinc, silver and wetted card'. It was therefore Nicholson who coined the term 'pile', which supplanted 'appareil à colonne', 'appareil électromoteur' and 'organe électrique artificiel' used by Volta [14]. The 'pile' was immediately accepted by all, including Volta himself'. The following article in the same issue of Nicholson's journal dealt again on the pile and with electrolysis experiments done with a hundred elements apparatus on a variety of electrolytes, in particular a solution of muriate of ammonia (NH_4Cl). The author, William Cruickshank (1750–1811), was professor of chemistry at the Royal Military Academy, Woolwich and may have learnt of the pile from the note in the May issue of the *Philosophical Magazine* [37]. In the abstract of the article reported in the Table of Contents, written by the Editor (Nicholson), the classic expression 'Volta's pile' appeared, which since then was extensively used in the scientific literature.

Afterwards, the chemical applications of galvanic electricity multiplied: in the August-to-December monthly issues of Nicholson's journal there were eight articles on investigations carried out with Volta's pile, three of which by Humphry Davy (1778–1829), then Superintendent of the Pneumatic Institution of Bristol, a 22-year-old rising star in chemistry. Of particular interest is the communication by Lieutenant Colonel Henry Haldane (1756–1825), which appeared in the September issue [21]. Haldane was an American Revolutionary War veteran who had participated in the Battle of Yorktown and had been taken prisoner by the American Patriots. After retirement, among other intellectual activities, he did amatorial research in chemistry. Having learnt of Volta's pile from the May 30 *Morning Chronicle* article he built an Ag/Zn battery of fifty elements and carried out significant experiments, observing among other things that the pile did not work if placed in vacuo. Haldane had sent his communication in time for publication in the month of July, but Nicholson, while acknowledging its originality, had decided to postpone it to the September issue to allow the author to read the other works on the subject (his, in particular!) and avoid overlapping. Finally, in September, Volta's complete letter was published in *Philosophical Transactions* (in French, although Volta, in the accompanying letter, had asked Banks to translate the letter into English). English translation of the article appeared in the September issue of Tilloch's magazine [39]. In the same issue there was an article titled "Experiments in Galvanic Electricity, by Messr. Nicholson, Carlisle, Cruickshank, & c.", written by Tilloch himself [40]. The Editor's article described and summarized the experiments of Nicholson, Carlisle and Cruickshank illustrated in the July issue of Nicholson's journal. In the opening lines, Tilloch apologizes for not mentioning Nicholson's name along with Carlisle's in the note on Galvanism appeared in the May issue of *The Philosophical Magazine* [37], but he «knew not the fact». This casts a bad light on Carlisle's scientific deontology but, in any case, closes the circle.

Volta after the pile

While piles were being built in London, Lombardy was still suffering the adversities and the troubles of war. On 14 June 1800 at Marengo, Napoleon's army definitively defeated the Austrians, who were driven out of Lombardy. In the autumn, the University of Pavia was opened again under the French control and the necessary financial support was guaranteed to professors and students. However, communications with England remained problematic and Volta was not able to learn anything about the fate of his letter to the Royal Society, through either scientific journals or newspapers. In particular, because of the wars, the *Morning Chronicle* was no longer sent to Europe. However, on August 8, the May 30 *Morning Chronicle* article on pile presentation was reprinted in the *Courier de Londres*, the newspaper of French expatriates from Revolution, printed in London. The *Courier de Londres* regularly arrived in Paris and the article in question was reprinted on 17 August in *Le Moniteur*, the most authoritative French newspaper, distributed in all regions controlled by France, including Lombardy. A copy of the French newspaper reached Alessandro Volta in Como on 31 August, five months after his letter to the Royal Society was sent to London through the merchant Garovaglio. It was the first news for Volta that his pile had been reproduced in Britain and used to decompose water in hydrogen and oxygen. Three days later (September 3, 1800) Volta received a letter by Marsilio Landriani (1751–1815), formerly Regius Professor of Physics at the Brera College in Milan, then Embassy Counsellor at the Augsburg Court in Vienna. The letter, dated Vienna, August 14, 1800, was the reply to a letter from Volta in which the Italian physicist had summarized the communication he had just sent to the Royal Society. In the letter, Landriani reported that he had learnt of Nicholson's water electrolysis experiment through Nikolaus von Jacquin (1727–1817), a Dutch scientist, Professor of Botany and Chemistry at the University of Vienna, who had probably read Nicholson's paper in the July issue of the *Journal of Philosophy, Chemistry & Arts* [20]. Landriani reports that he witnessed Jacquin's successful electrical decomposition of water carried out with a pile. At Volta's request, the letter by Landriani was published in the first available issue of Brugnatelli's *Annali di chimica e storia naturale* [41]. In the same issue of the *Annali*, Volta published his letter of reply to Counsellor Landriani, dated 22 September, in which he expressed his satisfaction with the success of his column apparatus and his gratitude to Nicholson for using it in the beautiful experiment on the electrical decomposition of water [41]. He also reported that he had asked Banks to pass on his communication to his colleagues Bennet, Cavallo and Nicholson so that «they would repeat his experiments, multiply and vary them». With the benefit of hindsight, we can observe that Volta's suggestion to Banks was successful, at least as far as Nicholson was concerned, albeit by a less direct and more circuitous route.

The pile and the study of its applications spread rapidly in Europe and the United States of America and Volta's fame grew everywhere to unusual levels for a scientist. Napoleon, a fervent admirer of science and convinced, according to Enlightenment ideals, that science could contribute to social progress and the well-being of populations, invited Volta to Paris. Volta went in Paris in November 1801, accompanied by his friend and University colleague Luigi Valentino Brugnatelli (1761–1818), professor of General Chemistry, and illustrated his investigations and discoveries on electricity, 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 21Brumaire, 1 Frimaire of the Republican Calendar). Napoleon took part in all the three meetings of the Class, as well as the diplomatic corps, and the most distinguished French scientists (see Fig. 7).

The First Consul rewarded Volta with a medal, and later with the title of Senator of the Kingdom of Italy (1805) and the title of Count of the Italian Kingdom (1810), with attached generous salaries. Volta was also appointed *Chevalier de la Légion d'Honneur* (1805) and Knight of the Italian Royal Order of the Iron Crown (1806).

In Pavia Volta asked to reduce his teaching, due to family commitments in Como (he had married at the age of 49, had three young children and wanted to take care of their education). In 1804, the Barnabite abbot Pietro Configliachi (1777–1844) succeeded Volta to the chair of physics. Volta still worked in the University, delivering courses and seminars. After the Austrian Restoration (1814), he maintained his post and was appointed as Dean of the Faculty of Physics and Mathematics. He continued to attend the Cabinet of Physics, but his research activity was substantially reduced. May be, he was aware of not being able to compete in the development of the pile with

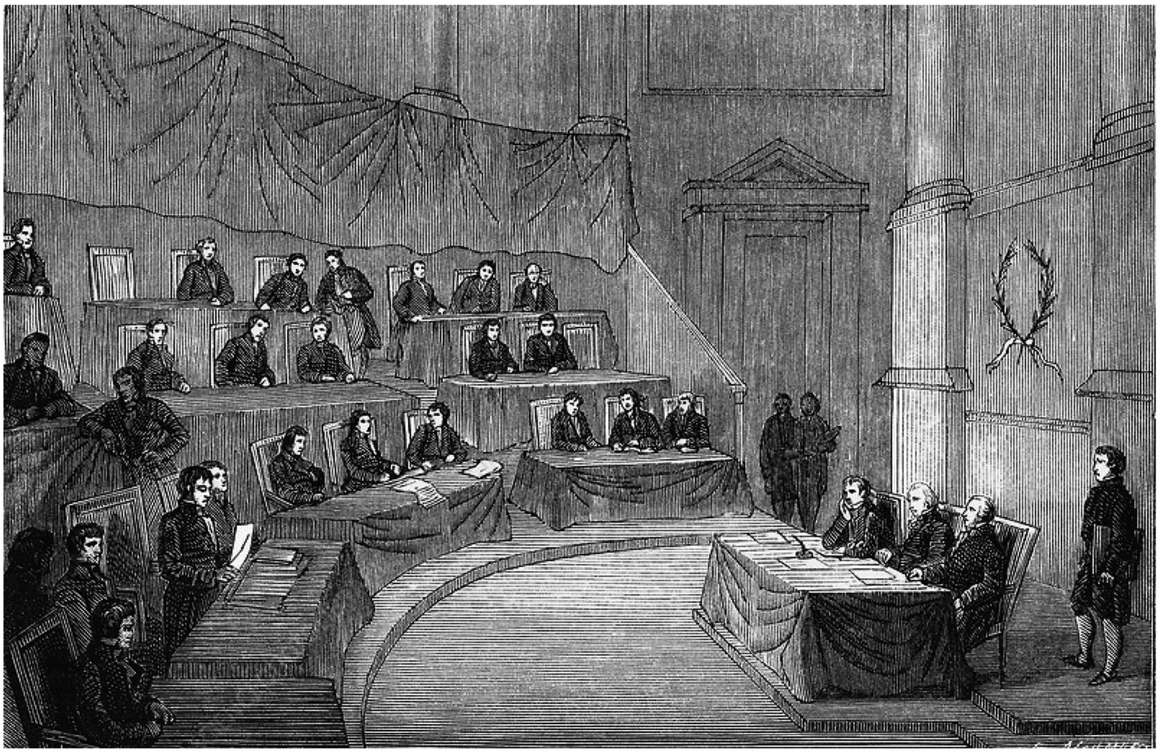

Fig. 7: Volta addressing the French Academy of Sciences in the presence of the First Consul Napoleon Bonaparte (November 1801). Volta is third from the left in the front row, standing. Napoleon is the fifth from the left in the first row, seated. As usual, he keeps his left hand on his stomach to ease the pain caused by the ulcer. Picture taken from L. Figuier, *Les Merveilles de la Science – Tome 1*, (1867), Fig. 326, p. 633 [27].

much more aggressive and organized European research centres, operating in countries with a more consolidated and widespread scientific and technological tradition than Italy in the 19^{th} century [42]. In 1819 he retired from the University, in 1827 he died in Como at the age of 82.

Conclusions

To understand Alessandro Volta's idea of scientific work, it is useful to consider his portrait in old age, painted by an unknown artist, probably following the instructions of Volta himself (see Fig. 8).

In the foreground, on a small table, the two most important inventions of Volta, of maturity (the pile) and of youth (the perpetual electrophorus). In the background, in Volta's hands a volume containing letters and articles describing the results of the research. Finally, the ribbons of honours pinned on the jacket (the *Légion d'Honneur*, red; the Italian Royal Order, green and yellow). The arrangement of the three classes of objects illustrates the temporal sequence of scientific work: first the experiment, then the publication with the description and interpretation of the results, finally, public recognition. But it is more likely that Volta meant the hierarchy of activities, the most important of which was experimental work, the manual construction of devices. In this respect, it is significant that Volta was able to build the pile, probably the scientific device that had the greatest impact on society, in difficult conditions, in an improvised laboratory set up in a country house, alone ('the laboratory in the kitchen'). In the paper, he described its construction in plain, understandable language that seemed aimed more at amateur practitioners than at philosophers. Volta, first a seminarian, then self-taught, did not have a solid mathematical background and, perhaps for this reason, he was not particularly interested in theory. For him, the important thing was to invent devices that worked. As he wrote in his letter to Banks in 1800 [14], "This

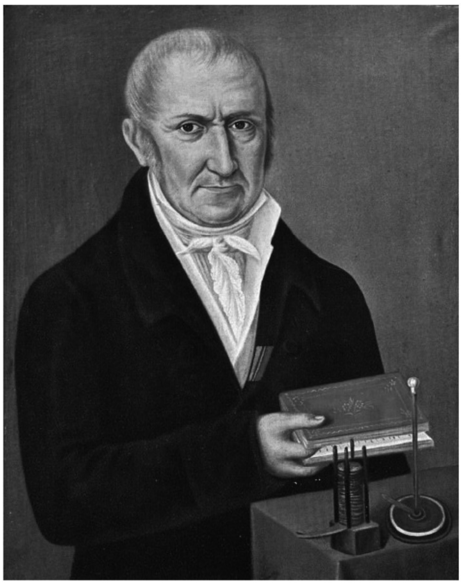

Fig. 8: Portrait of Alessandro Volta as an old man, oil by an unknown artist, Camnago, Volta family.

circulation of the electric fluid (that produced by the pile, Author’s note) may appear paradoxical, may not be explicable; but it is none the less true and real, and one touches it, so to speak, with the hands”. A sentence that definitively establishes the primacy of experiment over theory.

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