Volta's invention of the electrochemical cell

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Volta's memoir of 1800, which describes his invention of the electrochemical cell, is entitled *On the Electricity excited by the mere Contact of conducting Substances of different kinds,*[1] *In a Letter from Mr. Alexander Volta, F. R. S. Professor of Natural Philosophy in the University of Pavia, to the Rt. Hon. Sir Joseph Banks Bart. K. B. P. R. S*. Aside from the title, it was written in French. It had been sent by Volta to his friend Cavallo in London to be communicated to the Royal Society, which had published it in its *Transactions*. This publication was released in London in 1800, while France was at war against the Second Coalition. We do not know of any off-prints of Volta's memoir. The European distribution of this volume of the *Philosophical Transactions of the Royal Society of London*, Volume 90 of 1800, was obviously disrupted by the state of war between France and England and the original edition of Volta's paper is rare.[2]

This memoir is rightly famous. Stressing its importance, Carter and Muir state forcefully in their *Printing and the Mind of Man* (1967):[3]

> *The indispensability and ubiquity of electricity, in one form or another, in Western civilization today emphasize sharply the fact that before 1800 human environment and existence were closer to life in ancient Egypt than to our own. Volta's invention was one of the first and most important causes of this change.*

This invention was not only a major contribution to science but also a genuine game-changer for scientists themselves, who, for the first time, had a source of permanent electrical current. It is worth reiterating that before 1800 the production of electricity was limited to electrostatic devices charged using various methods. Such electricity manifested itself in the sparks and shocks produced upon touching

1. In *Philosophical Transactions*, 90, Part 2, London, 1800, pp. 403–431.
2. What's more, this memoir was printed in the second section of the volume of the *Transactions*, and some libraries possess the first part only. For this reason, the Bibliothèque Nationale de France (BnF Gallica) includes a digitised copy of only the first section.
3. *Printing and the Mind of Man* was published for the first time in 1967 and is based on an exhibition held in 1963. PMM, as its title is usually abbreviated, is considered a classic reference book that provides an overview of the impact of printed books on the development of Western civilisation.

the two poles of a charged Leyden jar, which, at the time, was often known as a battery or charge accumulator. Electrical phenomena were therefore impulsive, discontinuous, brief, and often noisy and violent, being linked to the discharge of the electrical capacity. Volta’s battery, on the other hand, was a low-impedance source and could provide a high and permanent current. What’s more, the technique used to build it was very simple and easily within reach of the ordinary experimenter.

The volt: The unit for electromotive force

The term *volt* was adopted as the unit of electromotive force at the first International Congress of Electricians held in Paris in 1881, in honour of Volta, the inventor of the electrochemical cell.

In addition, two CGS (centimetre–gram–second) systems, the electrostatic system, based on Coulomb’s Law – which expresses the force F between two charges q and q' situated at a distance of r in a vacuum – and the electromagnetic system – based on Ampère’s Force Law (Laplace’s Law + the Biot–Savart Law) between two current-carrying wires (or, equivalently, on the Coulomb force between two magnetic poles, provide equations for the magnitudes of the electric charge as related to the speed of light.

Initially, the British Association for the Advancement of Science had in 1862 adopted the principle of measuring an electrical or magnetic magnitude using the fundamental magnitudes of mechanics: length, mass and time. The CGS unit for electromotive force (emf) was based on an idea formulated by the physicist Franz Neuman in 1825. Following Neuman’s idea, the International Congress of Electricians of 1881 defined the volt as equal to 108 CGS units of emf.

The current definition of the volt in the International System of Units (SI) is as follows: “The volt is the potential difference between two points of a conducting wire carrying a constant current of 1 ampere, when the power dissipated between these points is equal to 1 watt.” In SI units, it is therefore equivalent to $1m^2 \cdot kg \cdot s^{-3} \cdot A^{-1}$, and can also be represented as 1 joule of energy for every coulomb of charge.

The realisation of the volt in the International System is therefore based on the comparison of an electrostatic force with a mechanical force, and the uncertainties linked to this are too great given the requirements of modern science. Thus, for two decades now we have used a different method to represent – or maintain – the volt, just like we have also “maintained” the standard metre (the unit of the metre is now maintained in relation to the frequency of the Caesium atom). This maintenance of the volt depends on the stability of voltage references based on the "Josephson effect", which depends solely on the stability of the frequency and can easily reach 10^{-12}.

The Josephson effect is a supraconductivity effect, a quantic phenomenon that appears at very low temperature in certain metals. In the supraconductive state, electrons are attracted to one another two by two and form pairs, which are called Cooper pairs. The Josephson effect is associated with the movement of these pairs, in a tunnel effect, through an insulating barrier placed between the two supraconductors, known as a Josephson junction.

Since the 18th General Conference on Weights and Measures (held in 1987), national metrology laboratories have used the alternative Josephson effect as a representation of the volt and, through an international agreement, have adopted a conventionally true value for the Josephson constant K_J, K_{J-90}= 483 597,9 GHz/V, applicable as of 1 January 1990. The exactitude of the voltage–frequency relationship $V = (h/2e) \times f$, and its independence vis-à-vis experimental conditions when an alternative voltage is applied to a Josephson voltage, have led scientists to consider the Josephson junction as a precision voltage–frequency converter. That is why the Josephson effect is today used to maintain the volt. The constant of proportionality between frequency and voltage is known as the *Josephson constant*.

This is now described as Volta's discovery of potential difference, known as the Volta effect, which is produced by the contact of two metals with different extraction functions (the energy necessary to extract an electron from its surface). Through this discovery, he had thus also discovered the electrochemical generation of electric current. Of course, the theory behind these phenomena cannot be understood without an understanding of the chemical conception of both the atom (which at the time was almost unknown) and the quantification of the energy of the atom's electronic layers. In 1800 it was therefore impossible for Volta to develop a correct theory explaining the phenomenon. He instead sought to describe his experimental discovery in a long, 270-word sentence, in a style worthy of Marcel Proust:

The astonishing apparatus is nothing but an assemblage of a number of good conductors of a different kind, arranged in a certain manner. Thus, 30, 40, 60, or more pieces of copper, or better of silver, each applied to a piece of tin, or still better of zinc, and an equal number of layers of water, or of some other liquid which may be a better conductor than simple water, as salt water, lye, &c., or of bits of card or leather, &c., soaked in such liquids. Of such layers interposed between each couple or combination of two different metals, one such alternate series, and always in the same order, of these three kinds of conductors, is all that *constitutes my new instrument; which imitates so well the effects of the Leyden phial or electric batteries; not indeed with the force and explosions of these, when highly charged, but only equalling the effects of a battery charged to a very weak degree, of a battery, however, having an immense capacity, but which besides infinitely surpasses the virtue and the power of these same batteries; as it has no need, like them, of being charged beforehand, by means of a foreign electricity; and as it is capable of giving the usual commotion as often as ever it is properly touched.*[4]

This single sentence covers it all: Volta's battery is defined as an autonomous generator with a weak potential difference but a high capacity, and, above all, one capable of delivering a permanent current. All that remained to do was to give the object a name. After explaining that his device is similar to a Leyden jar or the *natural electric organ* of the electric ray (torpedo), Volta christens it the *artificial electric organ*.

… that apparatus, which I have named the artificial electric organ, and which being at the bottom the same as the natural organ of the torpedo, resembles it also in its form, as I have advanced.[5]

The torpedo

The torpedo, or electric ray, is a large fish that can produce electrical pulses of up to 6 kW, with a maximum voltage of around 200 volts. Torpedoes produce bioelectricity using the electric organ which Volta referred to. This organ is formed from cells that can contract. Like all biological cells, the torpedo's cells are surrounded by a membrane that isolates the inside of the cell, or the cytoplasm, from the extracellular surroundings. As the ionic composition of these two environments is different, there is an electrochemical potential difference at the boundaries of the cell. A torpedo's cells have a high concentration of ion channels, a category of membrane proteins which are permeable to one or several ions. The electric organ therefore acts as a condenser that can discharge electric shocks as pulses initiated by a contraction. The torpedo's electric organ is much used in modern neuroscience research to identify ion channels. An ion channel can be selectively permeable to a single type of ion, such as sodium, calcium or potassium. It can also be permeable to several ions simultaneously. Ion channels are present in the membranes of all cells and play an important role in the physiology of electrically excitable cells, such as neurones for example.

4. --Trans. English translation quoted from Oliver Thatcher (ed.), *The Library of Original Sources*, 10 vols., New York: University Research Extension, 1907, 6, pp. 358–361, available at: http://media.bloomsbury.com/rep/files/primary-source-122-volta-and-the-discovery-of-the-battery.pdf
5. --Trans. English translation quoted from http://www.chemteam.info/Chem-History/Volta-1800.html

Volta's text is not a paper on theoretical physics, but rather an account of the work of a brilliant experimenter. At several points throughout the text Volta stresses the need for there to be salt water in the battery in order for it to work better:

> *the clean and dry metallic pieces, and the other non-metallic pieces well impregnated with common water, or, even better, salt water*

> *the column … is in communication with the following couple by a sufficient stratum of moisture, consisting of salt water*

> *but what makes [water] even better still is almost all the salts, and particularly common salt*

And being an experimenter also involves taking risks, particularly when it comes to electricity: Volta tests his battery by dipping his finger into the solution and evaluating for himself the electric "commotion" he feels!

> *However, this force is such that I am able to receive from such a column, consisting of 20 pairs of plates, commotions that affect all of the finger, and even affect it quite painfully*

> *The commotions will be much greater, and will extend along the two arms up to the shoulder*

> *But, if one dips a single finger [into the solution], whether partially or fully, the commotions concentrated in it alone, will be all the more painful, and will sting to the point of becoming unbearable*

VOLTA'S RESEARCH INTO ELECTRICITY

As early as 1769, at the age of 24, Alessandro Volta had begun researching electricity. His first publication included in a scientific journal was made public in 1775. It concerned the electrophorus, a source of electricity produced by electrostatic influence.

In 1778, in a letter to Horace de Saussure entitled *Sur la capacité des conducteurs électriques*, Volta introduced the notion of "electrical tension". This concept enabled him to express the tendency of excess fluid in a body to move to a second body that lacks such fluid. This notion of tension, measured by the *volt*, would of course go down in history.

Pursuing his work on electricity, he developed an electrometric balance, which, in 1787, enabled the definition of a unit of measure of electric tension (voltage) for the first time. He defined this "fundamental degree" as the "electric force" required to unsettle the suspended discs of the balance, "when the disc [was] placed at a distance of two inches from the earthed plane and kept in equilibrium by 12 grains on the other scale. Such an electric force, Volta suggested, should be taken as being … degree 35"[6] (equivalent to 13,350 volts).

But in 1791, Luigi Galvani, an Italian anatomist, published a work entitled *On the Forces of Electricity During Muscular Movement*.[7] This text set out his theory of *animal electricity*: according to this theory, when the nerves and the muscles of a dead frog are touched with a compass whose two ends are made of different metals, the electricity – which Galvani thought to be permanently present in animal bodies – is discharged, making the muscles contract. At the University of Pavia, Alessandro Volta interpreted Galvani's experiment not as evidence of animal electricity, but as a result of the electricity due to the contact of the two metals present in the compass. Volta, who had been elected to the Royal Society that very same year, attacked Galvani's theory of "electric animal fluid" in his *Second Memoir on Animal Electricity* (1792), stating it is "the diversity of metals that counts". He demonstrated his theory by the fact that an arc containing two welded metals produces an acidic taste when placed in contact with both sides of the tongue.

In 1794, Volta's work on the condenser was recognised when he was awarded the prestigious Copley Medal by the Royal Society. But the controversy with Galvani only intensified: with the support of his adepts, Aldini and Valli, Galvani adduced a series of experiments against Volta, which, they claimed, "demonstrated" the existence of "electric fluid" in frogs. Our physicist responded with a series of three letters addressed to Friedrich Gren de Halle, entitled *On the Electricity excited by the mere Contact of conducting Substances of different Kinds*. Galvani reiterated his thesis in 1797, in his *Memoirs on Animal Electricity*, which were dedicated to Spallanzani. Volta responded in his *Letters from Citizen N.N. of Como*, addressed to Aldini. The quarrel between the two men only came to end with the death of one of the protagonists, Luigi Galvani, on 4 December 1798. Volta himself was forced to leave the University of Pavia after it was closed following the invasion of Lombardy by the Austro-Russians in 1799. He returned to Como. "Towards the end of 1799", Volta writes, "[I took] an important step towards the construction of a most

6. Giuliano Pancaldi, *Volta: Science and Culture in the Age of Enlightenment*, Princeton: Princeton University Press, 2005, p. 140.
7. *De Viribus Electricitatis in Motu Musculari Commentarius,* Bologna, Ex typographia instituti scientiarum, 1791.

impressive piece of apparatus”. He had just invented the battery. He was 55 years old.

THE ELECTROCHEMICAL CELL

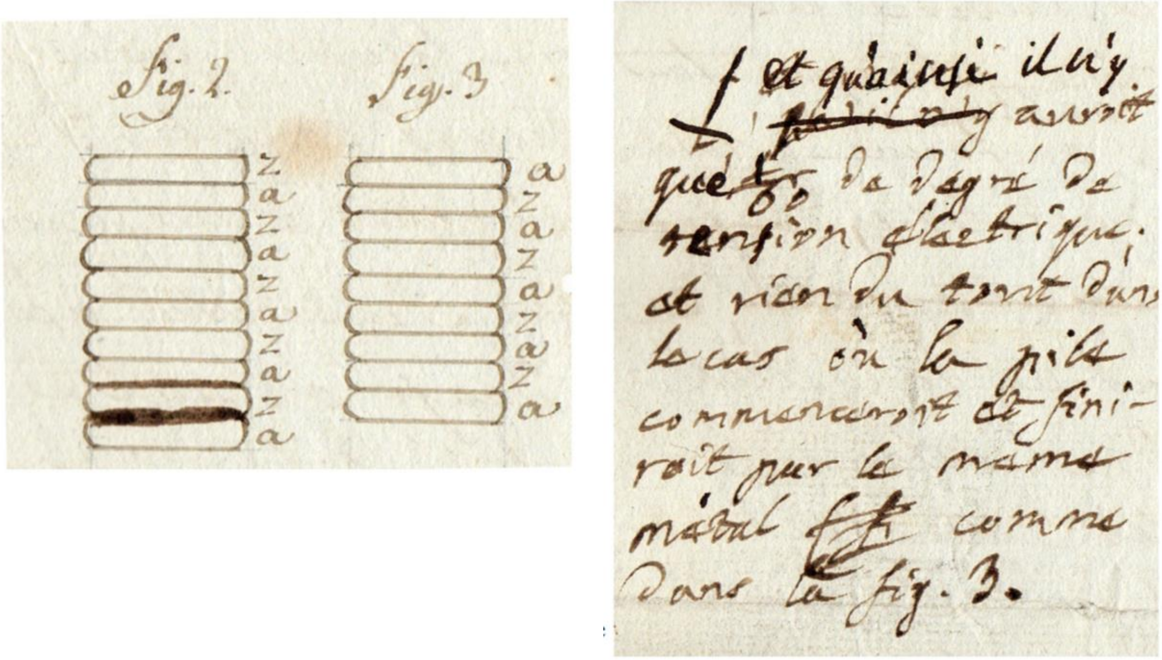

***Figure 1*: Volta’s handwritten corrections to his manuscript of 1802,**
De l’électricité dite galvanique*, which was published in Volume 40 of the* Annales de Chimie *(private collection): “And thus there would be only 1/60 of a degree of electrical tension; and nothing at all in the case of a pile that begins and terminates with the same metal as in Figure 3.” Volta explains that, without the interlaid wet discs, a battery made up of a column beginning with a silver disc and terminating with a zinc disc would have an emf equal to that of a single pair (Fig. 2), and zero emf in the case of a battery that begins and terminates with the same metal, as in Figure 3.*

In 1796, Volta had sought the electromotive force (*emf*) – his own term – of various combinations of metals. He now had to work out how to add together the *emfs* of different pairs. He quickly noticed that piling metal discs on top of one another made no difference, and that metal-only circuits produced an *emf* equivalent to that which the discs at the two ends would produce if they were placed in direct contact. Where did he get the idea to insert two wet discs, and how? No one knows. But on 20 March 1800, he wrote this memoir on the battery and sent it to his friend Cavallo in London, so that it could be delivered at the Royal Society, where it was read on 26 June. It contains the first description of an electrochemical battery producing a continuous current. With this generator, the age of electricity could begin.

In 1802, Volta wrote[8] that his experiments as a whole proved that "the electrical tension reaches, during the contact, nearly the sixtieth part of a degree of my electrometer made with fine straws, when the two metals are zinc and silver;[9] this electricity, as has already been observed, is positive in the former, and negative in the latter".

THE VOLTA EFFECT

The extraction function of a metal is the minimum energy required to extract an electron from a solid object to a point beyond its surface. The *Volta effect* is the term for the potential difference that appears when two metals with different extraction functions are brought into contact. One of the metals will then extract electrons from the other, and the net opposite charges will increase until the potential difference between the two metals is the same as the difference between the values of the extraction functions of the metals. Expressed in electron volts (eV), this function is 4.5 for copper, 4.26 for silver, 5.1 for gold and 3.3 for zinc.

The relationship between the Volta effect and the threshold of the photoelectric effect was identified by Einstein in 1906.[10] Einstein demonstrated that the difference between the threshold frequencies of the photoelectric effect on two metals is proportional to the difference between the extraction functions of those two metals.

This is how the Volta battery works: the oxidation of a zinc atom produces two electrons: $Zn \longrightarrow 2\ e^- + Zn^{2+}$ (oxidation reaction at the anode – the positive pole). These then react with the water molecules in the conductive solution: $2\ H_2O + 2\ e^- \longrightarrow 2\ HO^- + H_2$ (reduction reaction at the cathode – the negative pole). In total, there is an oxido-reduction reaction accompanied by the creation of a potential difference and a current: hydrogen is produced and the zinc disc is gradually consumed.

Using the Volta battery, in 1800 the English surgeon Anthony Carlisle (1768–1842) and William Nicholson (1753–1815) discovered electrolysis by

8. *De l'électricité dite galvanique. Annales de Chimie*, Paris, Vol. 40, page 243, 30 Frimaire an X.
9. The literature on Volta's battery is not always consistent when it comes to this second metal (which does not in fact play a role in the reaction): some texts mention copper, while others mention silver. Volta himself mentions both of these metals in his text, as we saw above. However, as his drawings at the end of the article show a zinc/silver battery, we have described silver as the second metal in this text.
10. *Annalen der Physik*, Vol. 20, 1906, pp. 199–206.

passing an electric current through water. This caused the water to decompose into its constituent elements: hydrogen and oxygen. From 1807 onwards, Humphry Davy at the Royal Institution had a 3,000-unit battery at his disposal, enabling him to discover sodium and potassium that very same year through the electrolysis of soda and potash. The following year he would discover magnesium, strontium and calcium.

Reaction to the discovery

But let's get back to Volta. After victory against the Austrians at Marengo on 14 June 18000, Napoleon reopened the University of Pavia and reinstated its professors. In June, he established Volta's post of professor of experimental physics and president of the cabinet of physics by decree. In September 1801, our physicist travelled to Paris to pay homage to the First Consul on behalf of the University of Pavia. On 7 November 1801 (see illustration below), he gave a demonstration of his experiments at the Academy of Sciences, before an audience that included Napoleon, who was a member of the institution. He also read his important memoir *De l'électricité dite galvanique*, which we have already mentioned. It is worth noting that Volta used the term *galvanic electricity* so as to emphasise that there was no intrinsic difference between the current described by Galvani and that generated by his battery.[11]

Napoleon suggested that the academy should award Volta its gold metal (which it did, on 2 December) and furthermore nominate him as a foreign member (which it also did, on 5 September 1803). Volta also received a bequest and a life annuity.[12] In 1802, Napoleon nominated Volta a member of the Italian National Institute, and in 1805 he awarded him the Cross of the Legion of Honour. He also made him a senator of the kingdom of Italy in 1809 and, last but not least, a count of the kingdom the following year.

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11. In 1814 Volta published an important work to demonstrate this identity: *L'identita del fluido electtrico col cosi detto fluido galvanico vittoriosamente dimostrata con nuove esperienze ed osservazione. Memoria comunicata al Signore Pietro Configliachi*, Pavia, 1814.
12. In 1813 Napoleon ordered the construction of a large, 600-unit battery in the basement of the École Polytechnique.

***Figure 2**: Volta presents his battery to First Consul Bonaparte.*

Napoleon's admiration for Volta

In his *Historical Eloge* of Volta, Arago underlines the admiration that Napoleon felt for the Italian physicist: "By the invitation of General Bonaparte, conqueror of Italy, Volta returned to Paris in 1801. He there repeated his experiments on electricity by contact, before a numerous commission of the Institute. The First Consul assisted in person at the meeting in which the commissioners rendered a detailed account of these remarkable phenomena. Their report was scarcely ended, when he proposed to bestow on Volta a gold medal, in testimony of the gratitude of the French savants. It was contrary to custom, and the established rules of the Academy, to accede to this proposal; but rules are made for ordinary circumstances, and the professor of Pavia had placed himself beyond these. The medal was therefore voted by acclamation; and as Bonaparte did nothing by halves, Volta received on the same day, a sum of 2,000 crowns to defray the expenses of his journey. The foundation of a prize of 60,000 francs, to be awarded to the individual who shall give an impulse to the sciences of electricity or magnetism, similar to that which they first received from Franklin and Volta, is another proof of the enthusiasm which the Great Captain had felt. This impression was lasting, and the professor of Pavia became in the eyes of Napoleon the type of genius. He was speedily decorated with the Cross of the Legion of Honour, and the Crown of Iron, nominated a member of the Italian Council, and raised to the dignity of Count and Senator of the Kingdom of Lombardy. When the Italian Institute presented itself at the palace, if Volta happened not to be among the foremost ranks, the abrupt questions, 'Where is Volta? is he unwell? why is he not present?' showed perhaps too obviously, that, in the eyes of the sovereign, the other members, in spite of all their knowledge, were merely satellites to the inventor of the pile. 'I cannot consent,' said Napoleon in 1804, 'to the retirement of Volta. If the duties of a professor fatigue him, he may diminish them. Let him deliver, if he please, only one lecture in the year, but the University of Pavia would be struck to the heart, were I to permit a name so illustrious to disappear from the list of her members; besides,' he added, 'a good general ought to die on the field of honour.' The good general found the argument irresistible, and the Italian youth, whose idol he was, continued to enjoy his valuable instructions for some years.[13]

Volta's electrochemical cell sparked a cascade of discoveries that would have been impossible without this permanent source of electrical energy.

Here is a list of just a few of the discoveries made in the first decades of the 19th century:

1802: *Humphry Davy*, invention of electrolysis and electrochemistry, thanks to which Davy discovered the following chemical elements: sodium, potassium, calcium and magnesium.

1820: *Hans Christian Oersted*, deflection of a compass by an electrical current

1820: *André Ampère*, the force acting on a current due to a magnetic field

1820: *Biot and Savart*, law determining the force between a current and a magnetic field

1821: *Michael Faraday*, first electric motor

1823: *Johann Schweigger*, galvanometer

1827: *Georg Ohm*, Ohm law of electrical resistance

1831: *Michael Faraday*, electromagnetic induction

1831: *Michael Faraday*, electromagnetic lines of force

1831: *Michael Faraday*, electric dynamo

1831: *Michael Faraday*, electrical transformer

1833: *Michael Faraday*, law of electrolysis

1833: *Joseph Henry*, self-inductance

1834: *Heinrich Lenz*, laws of electromagnetic forces

1840: *Joule and Helmholtz*, electricity is a form of energy

1843: *James Joule*, mechanical and electrical equivalent of heat

13. https://archive.org/stream/edinburghnewphil16edin/edinburghnewphil16edin_djvu.txt

It should be noted that in 1836 the Englishman John F. Daniell (1790–1845) invited his eponymous battery, which used two electrolytes, copper sulphate and zinc sulphate. The Daniell cell, which was safer and less corrosive, would go on to replace the Zn/Ag Volta pile.

Around seven billion batteries are now produced each year.

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