

Pillars of Modern Electrochemistry

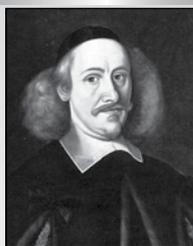
by A. K. Shukla and T. Prem Kumar

Although there is some archaeological evidence which suggests that some form of a primitive battery (sometimes called a Baghdad battery) was used for electroplating in Mesopotamia ca. 200 BC, electrochemistry as we know it today had its genesis in the pile of crowns of Alessandro Volta in 1800. The inspiration for his studies might have come from the famous frog leg experiments of Galvani, who, however, was content to conclude that the phenomenon was of biological origin. A metamorphosis took place with seminal contributions from John Daniell and Michael Faraday. From such humble beginnings, electrochemistry today has matured into a multidisciplinary branch of study. Built on the precision of physics and depth of materials science, it encompasses chemistry, physics, biology, and chemical engineering.

The uniqueness of electrochemistry lies in the fact that the application of a potential or electric field can help overcome kinetic limitations at low temperatures. Moreover, electrochemical processes can be tuned to obtain chemically and sometimes stereochemically-specific products. Electrochemical reactions are also sensitive to electrode-surface characteristics and electrolyte composition, which opens up several analytical and characterization avenues. Like many forward thinkers who have strived to make life easier for us to live, history pages are littered with the names, some of them long forgotten, of those who have made electrochemistry what it is today. This article is an attempt to provide a glimpse of these pillars of electrochemistry through their contributions.



William Gilbert



Otto von Guericke



Charles-Augustin de Coulomb

Birth Pangs

It was only in the sixteenth century that electricity began to be understood. The English scientist **William Gilbert** (1544-1603), known as the “father of magnetism” for his work on magnets, was among the first to experiment with electricity. He devised methods to produce as well as strengthen magnets. The first electric generator was constructed by the German physicist **Otto von Guericke** (1602-1686) in 1663. The device generated static electricity by friction between a large sulfur ball and a pad. By the mid-1700s the French chemist **Charles François de Cisternay du Fay** (1698-1739) discovered two types of static electricity. He found that like charges repel each other while the unlike charges attract. Moreover, he suggested that electricity consisted of two fluids: a vitreous form (from the Latin *vitrum* for glass) or positive electricity; and a resinous form or negative electricity. Later in the century, the two-fluid theory of electricity was opposed by the one-fluid theory of **Benjamin Franklin** (1706-1790). In 1781 **Charles-Augustin de Coulomb** (1736-1806) propounded the law of electrostatic attraction. Coulomb, the SI unit of charge, is named in his honor.

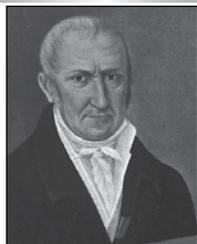
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It was at this time, when insights into the new phenomenon of electricity were growing, that electrochemistry had its birth pangs with the Italian physician and anatomist **Luigi Galvani** (1737-1798) proposing what he called animal electricity. In a 1791 essay titled *De Viribus Electricitatis in Motu Musculari Commentarius*, Galvani proposed that animal tissue contained an unknown vital force, which activated nerves and muscles when touched with metal probes. According to Galvani, animal electricity was a new form of electricity in addition to the natural electricity produced by lightning (or by the electric eel and torpedo ray) and the artificial static electricity produced by friction. The idea of an animal electric fluid was rejected by Alessandro Volta, who argued that frog's legs responded to differences such as metal temper and composition. However, Galvani stood by his version and even demonstrated muscular action with two pieces of the same material.

Interestingly, Galvani's experiments at the University of Bologna on the physiological action of electricity involved not only live frogs but also frog legs that had been detached from the body. He showed that muscle contractions in frogs and other animals could be triggered by an electric current from a Leyden jar or a rotating static electricity generator. The twitching of the frog's legs marked the experimental phenomenon that has come to be known as bioelectrogenesis. In fact, Galvani's experiments not only helped establish the basis for the biological study of neurophysiology, but also led to a conceptual change by acknowledging nerves as electrical conductors rather than as mere water pipes, as held by the Descartes school. Galvani's name came to be associated with galvanization (a technique of administering electric shocks, although another term, faradism, was also used for the technique). The word galvanization has shed this archaic meaning, and is applied at present to a protective treatment of steel with zinc. Galvani is also immortalized in the English word galvanize, which means to stir up sudden/abrupt action.

Nineteenth Century: The First Half



Alessandro Volta

The credit for laying the cornerstone of modern electrochemistry must, however, go to **Alessandro Giuseppe Antonio Anastasio Volta** (1745-1827), a professor of natural philosophy at the University of Pavia, who showed in the early 1800s that animal tissue was not necessary for the generation of current. He argued that the frog legs used in Galvani's experiments served only as an electroscope and suggested that the true source of stimulation was the contact between dissimilar metals.

He called the electricity thus produced metallic electricity. In fact through his voltaic piles, consisting of alternating discs of dissimilar metals, he effectively demonstrated the first electrochemical battery. The epochal invention formed the basis of modern batteries and a host of other galvanic phenomena including corrosion and sacrificial anodes. It also marked the first time that a continuous electric current was generated. Volta, whose work effectively rejected Galvani's animal electricity theory, coined the term galvanism. Napoleon Bonaparte honored Volta with the title of Count of Lombardy. Volta is also credited with the discovery and isolation of methane. Alessandro Volta is immortalized in the unit *volt*, a nomenclature that dates back to 1881.

Volta described his invention in a letter dated 20 March 1800 to **Sir Joseph Banks** (1743-1820), then President of the Royal Society. It was titled "On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds." Banks showed the letter to **Anthony Carlisle** (1768-1842), a London surgeon. Enter chemist-engineer **William Nicholson** (1753-1815), a friend of Carlisle, and together they assembled a voltaic pile. In their attempt to determine the charges on the upper and lower plates with the help of an electroscope, they put drops of water on the uppermost disc (for better contact!), and to their surprise found bubbles of gas evolving. Soon they found that the battery's terminals dipped in water generated hydrogen and oxygen. They had discovered electrolysis or chemical reaction driven by electric current.

Months later, **Johann Wilhelm Ritter** (1776-1810) improved upon the experiments of Carlisle and Nicholson and created a set-up to collect oxygen and hydrogen separately. Subsequently, he also invented the process of electroplating. In fact, Ritter might have made his discoveries earlier than Carlisle and Nicholson, but could not possibly have published the results because of his duties as an apothecary. Ritter's observation of thermoelectric potential (the electrical potential at the junction of two dissimilar metals kept at different temperatures) in 1801 also anticipated the 1821 discovery of thermoelectricity by the Estonian-German physicist **Thomas Johann Seebeck** (1770-1831).^{*} Ritter's experiments on the electrical excitation of muscles included subjecting himself to high voltages, which might have led to his early death. In this same time period, English physicist and chemist **Henry Cavendish** (1731-1810) made his famous quantitative experiments on the composition of water and also came out with a version of the Ohm's law for electrolyte solutions. He is also known for the famous Cavendish experiment for the measurement of the density of the Earth. Not too comfortable with publicity, Cavendish lacked the acclaim that is due to a person of his scientific caliber. In fact, several of his findings were not published. For example, he recognized that the force between a pair of electrical charges is inversely proportional to the distance between them, the credit for which goes to the French physicist Coulomb. There are at least two physical structures that should recall him to the present generation: a square in London, named after him, and the Cavendish Physical Laboratory at Cambridge University.



Sir Humphrey Davy

The technique of electroplating was unveiled by Italian chemist **Luigi Brugnatelli** (1759-1828) in 1805. His experiments on gold plating were performed with a Voltaic pile as the power source. Because he was rebuffed by Napoleon Bonaparte, Brugnatelli was forced to keep his results in low profile. Meanwhile, **William Hyde Wollaston** (1766-1828) and **Smithson Tennant** (1761-1815), in their attempt to use electrochemistry to purify platinum, ended up discovering other elements: palladium and rhodium (Wollaston) and iridium and osmium (Tennant). Drawing inspiration from Ritter, Carlisle, and Nicholson, **Sir Humphrey Davy** (1778-1829) used electrolysis to isolate metals such as sodium, potassium, calcium, magnesium, and lithium. He concluded that electricity induced chemical action and that chemical combination occurred between oppositely charged substances.



Jöns Jakob Berzelius

^{*}Seebeck, however, failed to recognize that an electric current was generated when a bimetallic junction was heated. In fact, he used the term thermomagnetic current to describe his discovery. The Seebeck effect forms the basis of the thermocouple, which is among the most accurate devices for measuring temperature. The opposite phenomenon, the Peltier effect, which is the generation of a temperature difference brought about by a current in a circuit with two dissimilar metals, was observed a decade later.

A contemporary and rival of Davy, **Jöns Jakob Berzelius** (1779-1848) also made important contributions to electrochemistry. Berzelius found that electrolysis resulted in the formation of elements at the poles of the cell, which led him to suggest that atoms were charged and compounds were formed by neutralization of charges. This was his dualism theory, which, however, did not apply to organic compounds. Berzelius also established the law of definite proportions. He is also credited with the discovery of several new elements including cerium, selenium, and thorium. It was he who created a logical system of symbols for elements (H, C, Ca, Cl, O, etc). With the work of Davy and Berzelius, chemistry was never to be the same again!



André-Marie Ampère

A momentous discovery was made in parallel by Danish natural philosopher **Hans Christian Ørsted** (1777-1851), who observed the magnetic effect of electric current in 1820. **André-Marie Ampère** (1775-1836), who took the cue from Ørsted, conducted extensive experiments and formulated his findings mathematically. Then came another formulation connecting voltage, current, and resistance—Ohm's law—which came through the work of the German physicist **Georg Ohm** (1787-1854) in 1827. Ohm's discovery was initially ridiculed by his contemporaries. However, by 1833 the fundamental importance of Ohm's law in electrical circuit analysis was recognized and Ohm came to be considered the Mozart of electricity.



Michael Faraday

Michael Faraday (1791-1867) is considered to be one of the greatest scientists in history. Some refer to him as the greatest experimentalist ever, especially because his work on electricity found expression in day-to-day technology. Farad, the SI unit of capacitance, and the Faraday constant, are named after him. He invented the dynamo, predecessor to today's electric generator. His concept of lines of flux emanating from charged bodies and magnets provided a way to visualize electric and magnetic fields, and was crucial to the successful development of electromechanical devices, which dominated engineering and industry for the remainder of the 19th century. The Faraday effect, a phenomenon he named diamagnetism, was also his discovery. In his work on static electricity, Faraday demonstrated that charge resided only on the exterior of a charged conductor, and that the exterior charge had no influence on anything enclosed within a conductor, a shielding effect we now use in Faraday cage. Faraday worked extensively in chemistry too, discovering substances such as benzene and the first clathrate hydrate, liquefied gases such as chlorine, and proposed the system of oxidation numbers. He also discovered the laws of electrolysis, by which he quantified electrochemistry, and popularized terminology such as anode, cathode, electrode, and ion, terms largely created by **William Whewell** (1794-1866). He rejected the traditional fluid theory of electricity and proposed that electricity was a form of force that passed from particle to particle in matter.



Antoine-Cesar Becquerel

A major problem with the Volta pile was that it could not provide current for a sustained period of time. In 1829 **Antoine-Cesar Becquerel** (1788-1878) constructed a constant current cell, which was a forerunner of the well-known Daniell cell. His acid-alkali cell could deliver current for an hour. Becquerel's studies on electrodeposition of metals helped validate Faraday's laws of electrolysis. The credit for solar cell technology must be given to Becquerel,

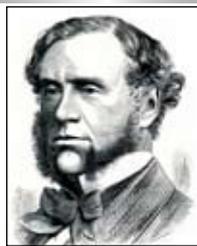
who in 1839 showed that light impinging on an electrode immersed in a conductive solution would create an electric current. In 1830, **William Sturgeon** (1783-1850), another scientist who worked on sustained current generation, produced a battery with longer life than that of Volta by amalgamating the zinc. Mercury was found to be a cure for polarization, a process by which a thin film of hydrogen bubbles formed over the positive electrode. The thin gas film led to high internal resistance in the Volta pile, resulting in reduced current flow. In 1832 Sturgeon constructed an electric motor. The same year witnessed **Hippolyte Pixii** (1808-1835), a French instrument maker, build the first dynamo. Later, using Sturgeon's commutator, Pixii built a direct current dynamo, which was the first practical mechanical generator of electric current.



John Frederic Daniell

In 1836, **John Frederic Daniell** (1790-1845) unveiled a two-fluid battery, which was the first battery to provide a constant and reliable source of current over a long period of time. Daniell used a copper vessel that served both as the positive pole and the container. Inside the copper vessel was an earthen pot with a zinc rod (the negative pole) and dilute sulfuric acid. The copper vessel was then filled with a solution of copper sulfate. The porous pot served as a barrier, preventing mixing of liquids. Although Daniell is famous for his invention of the two-fluid battery, he is less known for his 1820 invention of the dew-point hygrometer for the measurement of relative humidity.

The technique of electroforming was introduced in 1838 by **Boris Jakobi** (1801-1874). Jakobi applied his technique to the printing and coinage industries. Soon an electroforming shop was set up at the Governmental Papers Department, which was noted for depositing 107,984 kg of copper and 720 kg of gold for decoration of architectural monuments and cathedrals in St. Petersburg and Moscow.



Sir William Robert Grove

Sir William Robert Grove (1811-1896) invented the first fuel cell in 1839. Grove is also credited with the invention of the Grove's nitric acid cell: zinc in dilute sulfuric acid as the anode and platinum in concentrated nitric acid as the cathode, separated by a porous pot. Because the cell could sustain high current output, it became a favorite with the early American telegraph industry. But it was replaced by the Daniell cell because of the poisonous nitric oxide it emitted and because of its inability to deliver currents at constant voltage (the voltage dropped as the cell discharged due to depletion of nitric acid). However, his invention of the gas voltaic battery, the forerunner of modern fuel cells,* made him the "father of fuel cells." In his experiments that led to the invention, he sought to reverse



Robert Bunsen

the electrolytic splitting of water, to recombine hydrogen and oxygen to produce water and electricity. His background in law and science opened up the practice of patent and related laws.

In 1841, **Robert Wilhelm Eberhard Bunsen** (1811-1899) led the way for large scale exploitation of fuel cells by replacing the expensive platinum in the Grove's cell with a carbon electrode. The modified version was popularly known as the Bunsen

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*Although the first fuel cell was constructed in 1839, the term fuel cell came into vogue only in 1889 with Ludwig Mond and Charles Langer's attempt to build the first fuel cell using air and industrial coal gas as feed gases.

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battery. To students of science, the name Bunsen is associated with a burner, although the actual credit for the burner should go to a technician by name Peter Desaga of the University of Heidelberg. It must be pointed out that Bunsen fine-tuned the design of the burner to suit experiments in physics that he carried out with Gustav Kirchoff, a Prussian physicist. The two invented the Bunsen-Kirchoff spectroscope.

This was just about the time when the German chemist **Friedrich Wöhler** (1800-1882) overthrew the vitalism theory that a vital force was necessary to make organic compounds by synthesizing urea from ammonium cyanate. **Adolf Wilhelm Hermann Kolbe** (1818-1884) also was another chemist who believed that organic compounds could be made from inorganic ones. He converted carbon disulfide, an inorganic compound into acetic acid, an organic compound, in several synthetic steps. Kolbe also made salicylic acid (the Kolbe-Schmitt reaction). Kolbe was the first to apply electrolysis for organic synthesis. He showed that electrolysis of carboxylic acids led to decarboxylation. Loss of carbon dioxide during the reaction led to dimerization of the resulting alkyl radicals to symmetric compounds (Kolbe synthesis).

During 1842 and 1843, **George Gabriel Stokes** (1819-1903) published a series of papers on the motion of incompressible fluids. They became fundamental to our understanding of electrolyte solutions. Sometime around 1845, in what was to mark a revolution in industrial electroplating, John Wright showed that potassium cyanide was a suitable medium for plating silver and gold. In 1857 electroplating was applied to costume jewelry, and soon electroplaters cashed in on a booming economic jewelry market.

One of the foremost physicists of the nineteenth century, Prussian-born **Gustav Robert Georg Kirchoff** (1824-1887), formulated what are today known as Kirchoff's laws. When he announced the laws in 1845, he was still a student, although in their final forms the laws became known only in 1854. The laws help in calculating the currents, voltages and resistances in multi-loop electrical networks. The laws embody the principle of conservation of charge and energy. In association with Robert Bunsen, Kirchoff introduced the spectroscopic method of chemical analysis, leading in the process to the discovery of cesium (1860) and rubidium (1861) as well as unfolding a new technique for discovery of new elements.

Nineteenth Century: The Second Half

In 1853 **Johann Wilhelm Hittorf** (1824-1914), a German physicist, noticed that some ions traveled more rapidly than others under an applied current. This finding led to the concept of transport number. A couple of years later, **Adolph Fick** (1829-1901), at a mere 26 years, building on the Fourier's theory of heat equilibrium, developed a mathematical concept by which he showed that diffusion is proportional to concentration gradient. That was in 1855. However, experimental proof of the concept was not established for the next 25 years. He was proficient in physiology, mathematics, and physics, and made another distinctive contribution in the form of a monograph entitled *Medical Physics*, in which he dealt with several topics including mixing of air in the lungs, heat economy of the body, physiology of muscular contraction, and thermodynamics of circulation. Medical physics had to wait for nearly a century for another monumental book, which came through **Otto Glasser** (1894-1964). Cardiologists note that Fick made a distinctive contribution in 1870 when he described how mass balance could be used to measure cardiac output, thereby presenting a mathematical basis of physiological activity.

Electrochemists connect the name **Josiah Latimer Clark** (1822-1898) with the standard Clark cell used for measuring the standard electromotive force. This English engineer was a very versatile inventor, known for his work on wireless telegraphy, particularly the Anglo-American Atlantic cable. It was Clark who introduced the notion of volt as the unit for voltage. In 1872, Clark invented the first standard cell with mercury and zinc amalgam electrodes in a saturated solution of zinc sulfate. It had a large temperature coefficient of -0.00115 V/°C. Moreover, it was prone to cracking where the platinum lead entered the glass cell. Today, we use the Weston cadmium cell as the standard for the potentiometric measurement of standard electromotive force.

Between 1858 and 1860 the American inventor and industrialist **Isaak Adams, Jr.** (1836-1911) pioneered the technique of nickel plating, which immediately was exploited on a commercial scale. He was the son of Isaac Adams, Sr., the inventor of the Adams power press. Adams also had other credentials as an inventor: the vacuum-tube carbon burner incandescent electric bulb, which he invented in 1865, 14 years prior to a similar invention by Edison-Swann; breech-loading rifles; and copper plating on steel for bonding rubber to steel.



Gaston Planté

The year 1859 witnessed an invention that was to revolutionize the world of portable power: the lead-acid battery by the French physicist **Gaston Planté** (1834-1889). Planté's storage battery used lead plates as electrodes and delivered limited currents because the positive electrode had very little of active material. In 1881 **Camille Alphonse Faure** (1840-1898) replaced Planté's solid lead plate with a paste of lead oxide, which led to faster formation kinetics and improved efficiency. The significance of Planté's invention can be gauged by the fact that the technology of the lead-acid battery has changed little since its invention except for changes in electrode design and casing materials, and that other battery chemistries are yet to approach the lead-acid battery in terms of certain electrical capabilities and economy.

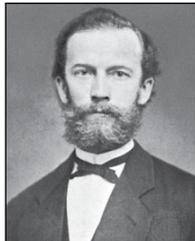
Seven years later, in 1866, French scientist **Georges Leclanché** (1839-1882) patented a primary cell with a porous pot containing manganese dioxide and carbon as the positive, and a zinc rod as the negative. The electrodes were immersed in an electrolyte of ammonium chloride. The Leclanché wet cell was the forerunner to the zinc-carbon dry cell which became the world's first widely used primary power source. Leclanché's cell was rendered dry by the German scientist **Carl Gassner** (1839-1882), when he cleverly configured the cell with zinc as a container and negative electrode. Gassner also employed zinc chloride in the cathode mix so as to reduce the wasteful corrosion of zinc during idling. The market for dry cells



Georges Leclanché

received a boost with the use of tungsten filament in flashlights in 1909.

Gabriel Lippmann (1845-1921) received the 1908 Nobel Prize in Physics for inventing the color photographic plate, but to electrochemists he is associated with the capillary electrometer, which he invented in 1872. This instrument, based on the extreme sensitivity of mercury meniscus in a capillary tube to applied potential, was subsequently exploited for measuring electrocardiograms. His versatility of interests can be noted in the fact that he was also the inventor of the coelostat (a long-exposure instrument that allows a region of the sky to be photographed by compensating for Earth's movement) and conducted research in various areas including piezoelectricity, seismology, and induction in resistance-less circuits. Lippmann was a research advisor to Marie Curie and a professor to Pierre Curie.



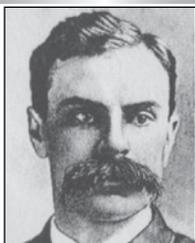
Friedrich Kohlrausch

Between 1875 and 1879, the German physicist **Friedrich Wilhelm Georg Kohlrausch** (1840-1910) working with solutions of a variety of salts and acids developed the law of independent migration of ions. He was the first to apply alternating current for electrochemical investigations. By using alternating current, he was able to avoid deposition of decomposition products on the electrode surface and obtain results with high precision.

Kohlrausch also demonstrated that ionic conductivity increased with dilution. He was also noted for his work on autoionization of water, thermoelasticity, and thermal conduction and for his precision measurements of magnetic and electrical properties.

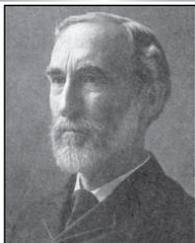
The time was when the electricity was still in its infancy and the identification of the electron itself was to happen ten years later. At this time emerged a man who contrived to answer a question by Maxwell whether the resistance of a coil excited by an electric current was affected by the presence of a magnet.

Edwin Herbert Hall (1855-1938), an American physicist well ahead of his time, discovered what we call the Hall effect in 1879. The discovery remained a curiosity for nearly a century until the emergence of semiconductors that could produce significant Hall voltages. Today, Hall effect is used in the primary circuit of electronic ignition systems.



Edwin Herbert Hall

This was also a momentous period for the growth of electrochemistry, marked by its marriage with thermodynamics. The architect of this transformation was the American scientist **Josiah Willard Gibbs** (1839-1903). (**Ed. Note:** In 1967, there was a serious discussion about renaming ECS as the J. Willard Gibbs Society.) He was a true genius and drew on the concepts of great men like **Johannes Diderik van der Waals** (1837-1923) and drew accolades from peers such as Maxwell. Even his first paper was a classic and contained his famous formula $dU = TdS - PdV$. Interestingly, Yale University's first doctoral degree for an engineering thesis was awarded to Gibbs. He is also known for his contributions to astronomy and electromagnetic theory.



Josiah Willard Gibbs

The nature of electricity came in for much debate during this period. The British physicist **James Clerk Maxwell** (1839-1871) believed that electricity was the result of polarization of the ether or of the medium through which electric current flowed. However, in 1881 the German scientist **Hermann von Helmholtz** (1821-1894) basing

his theory on Faraday's laws of electrolysis, which relates the charge to the amount of metal deposition, argued that the existence of atoms implied the particulate nature of electricity. However, proof of the existence of such a particle (electrons) seemed to contradict Helmholtz theories of electrodynamics, which were based on the supposed properties of the ether. At any rate, the discovery of radio waves by **Heinrich Rudolf Hertz** (1857-1894), a student of Helmholtz, helped cement the theories of Faraday, Maxwell, and Helmholtz. Decades later, Albert Einstein's general and special theories of relativity helped dismantle the concept of the pervasive ether.

Maxwell's successor at King's College, London, **William Grylls Adams** (1836-1915), along with his student, Richard Evans Day, found in 1876 that selenium upon exposure to light produced electricity, by a process we recognize today as



Svante Arrhenius

photoelectric effect. He thus became the first to demonstrate that light could be used to generate electricity without heat or moving parts.

In his thesis published in 1884, Swedish physical chemist and the 1903 Chemistry Nobel Prize winner **Svante August Arrhenius** (1859-1927) suggested that dissolving electrolytes in water resulted in varying degrees of dissociation of the electrolytes into ions. The degree of dissociation depended not only on the nature of the electrolyte but also on its concentration—the greater the concentration, the lesser the dissociation. The concept of activity coefficient, a quantity that relates the actual number of ions at any concentration to their number upon high dilution, was born out of Arrhenius's studies. His collaboration with **Ludwig Eduard Boltzmann** (1844-1906) and **Jacobus Henricus van't Hoff** (1852-1911) led to theories on the ebullioscopic properties of solutions. Latvian chemist **Friedrich Wilhelm Ostwald** (1853-1932), the 1909 Nobel Prize winner, extended Arrhenius's theory to the electrical conductivity and dissociation of organic acids. Ostwald also propounded a theory of solutions based on ionic dissociation. In 1884 he came out with a definition of catalysis. Ostwald is also credited with the invention of the viscometer.



Jacobus van't Hoff



Friedrich Ostwald

The application of electrolysis for winning aluminum from aqueous solutions of aluminum salts ended up in the formation of aluminum hydroxide. However, in 1886 two young scientists, **Paul Louis Héroult** in France and **Charles Martin Hall** in the United States (both born in 1863 and died in 1914), working independently, succeeded in producing aluminum from a melt of aluminum oxide in cryolite. The inventions went through a patch of patent litigations before Héroult and Hall agreed to bury their differences. Their electrolytic process opened up a new world of industrial applications for rust-resistant aluminum, which was until then considered a prized metal used in fine jewelry.



Paul Louis Héroult

The theory of electrolytic dissociation formulated by Arrhenius inspired another architect of modern electrochemistry: **Walther Hermann Nernst** (1864-1941). In 1888, Nernst came out with a theory connecting the electromotive force in an electrochemical cell to the free energy of the chemical reaction that produces the current. He also demonstrated that solvents with high dielectric constants promoted the ionization of substances. His experiments with solutions led him to suggest conditions under which solutes precipitated from solutions. The theory of solubility product is also his making. He devised a method to measure dielectric constant and demonstrated that solvents with high



Charles Martin Hall



Walther Nernst

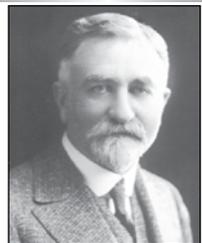
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dielectric constants facilitated ionization of substances. Students of physical chemistry know him through the Nernst equation.

Tutored by Hermann Kolbe at Marburg and Robert Bunsen at Heidelberg, **Ludwig Mond** (1839-1909) became a well known chemist and industrialist. Initially, his interests were in the production of elemental sulfur, alkali, and ammonia. He also developed a process (the Mond process) for the generation of producer gas. In 1889, he and his assistant Carl Langer developed a hydrogen-oxygen fuel cell with thin perforated platinum electrodes. Both Mond and Langer were instrumental in popularizing fuel cells. In their attempt to use coal gas as a fuel in fuel cells, they discovered the formation of nickel carbonyl (the molecules described by Lord Kelvin as metals with wings) from the carbon monoxide in the coal gas and the nickel in the electrode. This observation formed the basis of the Mond process for the extraction of nickel through a carbonyl route.

In 1890, inventive genius and businessman **Herbert Henry Dow** (1866-1930), best known for his work on halogen chemistry, developed an electrolytic method for the production of bromine from brine. Today, the method is known as the Dow process. An offshoot of this work was an electrolytic production route for chlorine. Slowly, and with the establishment of the Dow Chemical Company, he ventured into chlorine chemicals, organics, and later into magnesium metal and calcium. By capitalizing on the brine sourced from the ancient seas in the Midland region of the U.S., Dow opened avenues for mining sea resources.



Herbert Henry Dow

The first to record a human electrocardiogram with the Lippmann's mercury capillary electrometer was **Augustus Desire Waller*** (1856-1922), the French physiologist who in 1887 thought up the idea of using the body itself as an electrical conductor. **Willem Einthoven** (1860-1927) improved upon Waller's experiments and instrumentation. In 1893, **Edward Weston** (1850-1936) developed a standard cell that was to become the international standard for the calibration of voltmeters. The cell was less sensitive to temperature fluctuations than the previous standard, the Clark cell, and had the additional advantage of possessing a voltage very close to a volt: 1.0183 V.



Edward Weston

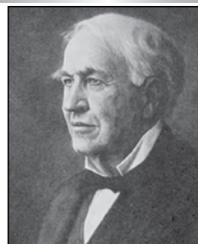
Based on his work on electrolysis, **Fritz Haber** (1868-1934) in 1898 showed that different products could be obtained by maintaining the potential of the electrode at different values. He explained his findings with nitrobenzene, which became a model compound for other investigators. He also worked on the quinone-hydroquinone transformation, which became the basis for Biilmann's quinhydrone electrode for measuring



Fritz Haber

*The first human electrocardiogram was recorded by Alexander Muirhead (1848-1920), but it was Waller who did it in a clinico-physiological setting. Moreover, Muirhead used a Thompson siphon recorder for his measurements while Waller used Lippmann's capillary electrometer.

the acidity of solutions. Haber is also credited with the invention of the glass electrode, a contribution he made with Cremer, one of his associates.



Thomas Edison

This was also a period that witnessed as many as 1,093 inventions by a single person, **Thomas Alva Edison** (1847-1931), nicknamed the "Wizard of Menlo Park." Although he is most popular for inventing the incandescent bulb and the phonograph, his unveiling of the nickel-iron accumulator was no less a contribution. Simultaneously, and independently of Edison, **Waldemar Jungner** (1869-1924) in Sweden patented the nickel-iron battery. In 1899 Jungner replaced the iron electrode with the more efficient cadmium electrode. It is interesting to note that in 1899 the world record for road speed was held by the electric vehicle! However, with rapid advancements in internal combustion engineering, the bottom fell off the electric vehicle market in the next three decades.



Julius Tafel

The year 1898 marked a turning point in organic electrochemistry with Swiss chemist **Julius Tafel** (1862-1918) demonstrating the use of lead as an electrode for the reduction of organic compounds. Tafel, who was both an organic chemist and a physical chemist, made seminal contributions to organic electrochemistry and established the Tafel equation connecting the rates of electrochemical reactions and overpotential. The Tafel equation was unique in that it could be applied to irreversible electrochemical reactions that could not be described by thermodynamics. The several contributions he made in organic chemistry include reduction with amalgams and the Tafel rearrangement. Tafel is also known for introducing the hydrogen coulometer for measurement of electrochemical reaction rates and pre-electrolysis as a method for purifying solutions.

Twentieth Century: First Half

Thermodynamic considerations and ionic transport were the focus of this period. In one of the first approaches to characterizing aqueous solutions, **H. Friedenthal** in 1904 suggested the use of hydrogen ion concentrations. In what is probably the beginning of the concept of *pH*, Friedenthal also found that the product of the concentrations of hydrogen ions and hydroxyl ions in aqueous solutions was always 1×10^{-14} . It must be pointed out, however, that the concept of *pondus hydrogenii*, or *pH*, itself was introduced five years later by the Danish chemist **Søren Peder Lauritz Sørensen** (1868-1939).

In what was to mark the beginning of bioelectrochemistry, **Julius Bernstein** (1839-1917), of the University of Berlin, demonstrated that the action electric potential in nerves was the result of a change in ionic properties of the nerve membrane. He proposed his membrane hypothesis in two parts, the first one in 1902 and the second in 1912. His theory was based on the work of Helmholtz and **Du Bois-Reymond** (1818-1896), the "father of experimental electrophysiology." Bernstein's work on the propagation of nerve impulses and trans-membrane potential led to great interest in bioelectricity and in the theory of nerve action in particular. It is noteworthy that Bernstein's work was the last nail on animal electricity, and came at a time when electricity was trying to rid itself of the shadow of biology.

In 1910, **Robert Andrews Millikan** (1868-1953) determined the charge on an electron by his famous oil drop experiments. The following year, **Frederick George Donnan** (1870-1956) established the conditions for

equilibrium between two electrolytic solutions separated by a semi-permeable membrane. Today, Donnan's name is associated with both the nature of the equilibrium and the potential across the membrane.



Jaroslav Heyrovsky

Around 1922, Prague evolved into the "Mecca of electrochemistry." On February 10 of that year, **Jaroslav Heyrovsky** (1890-1967), sometimes called the "father of electroanalytical chemistry," recorded a current-voltage curve for a solution of sodium hydroxide using a dropping mercury electrode and ascribed the current jump between -1.9 and -2.0 V to the deposition of sodium ions on mercury. This marked the beginning of polarography, which took roots in his early work with F. G. Donnan on the electrode potential of aluminum, leading Heyrovsky into work on liquid electrodes that provide a continuously renewable electrode surface. Later, he teamed up with **Masuzo Shikata** (1895-1964) and designed the first recording polarograph. In 1959, Heyrovsky was awarded the Nobel Prize for his seminal work on this electroanalytical technique. Polarography led to a spurt in the growth of the theory of electrochemical reactions and mass transport in electrolyte solutions, and laid the fundamentals of all voltammetric methods employed in electroanalysis. In 1929, Heyrovsky along with Emil Votocek of the Prague Technical University, founded the journal, *Collection of Czechoslovak Chemical Communications*. Slovakian physical chemist and mathematical physicist **Dionyz Ilkovic** (1907-1980), a research assistant to Heyrovsky, was one of the co-founders of polarography. The basic equation of polarography, the Ilkovic equation, goes by his name.

Relationships between molecular structure and electrical properties were also beginning to be unraveled. In 1923, **Johannes Nicolaus Bronsted** (1879-1947) in Denmark and **Thomas Martin Lowry** (1874-1936) in England propounded, independently of each other, a theory on acids and bases. According to them, an acid was a compound with a tendency to donate a proton (or hydrogen ion), while a

base was one that combined with a proton. The same year also witnessed Dutch-American physicist **Petrus Josephus Wilhelmus Debye** (1884-1966) and German physicist and physical chemist **Erich Armand Arthur Joseph Huckel** (1896-1980) elucidating fundamental theories concerning the behavior of strong electrolyte solutions. According to them, electrolyte solutions deviate from ideal behavior due to ion-ion attractions. They suggested that ions in solutions have a screening effect

on the electric field from individual ions, which gave rise to the Debye length. Huckel is also famous for the Huckel rule for determining ring molecules and for the Huckel method of approximate molecular orbital calculations on π -electron systems.

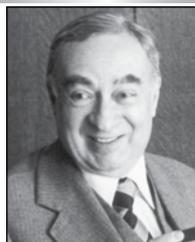
Debye won the 1936 Nobel Prize in Chemistry for his contributions to molecular structure, for dipole moment relationships and for diffraction of X-rays and electrons in gases. In 1916, he showed that X-ray diffraction studies could be done with powder samples, eliminating in the process the need to prepare good crystals. This has come to be known as the Debye-Scherrer X-ray diffraction method. The originality and extent of Debye's contributions are reflected in the many concepts that carry his name: the Debye-Scherrer method of X-ray diffraction, Debye-Huckel theory, Debye theory of specific heat, Debye-Sears effect in transparent liquids, Debye shielding distance, Debye temperature, Debye frequency, and the Debye theory of wave mechanics. He is also immortalized by the CGS unit for dipole moment (debye), the Dipole Moment monument in Maastricht, and the American Chemical Society award in his name.



Petrus Debye



Alexander Frumkin



Veniamin Grigorevich Levich



Thomas Percy Hoare



Ulick Evans



Herbert H. Uhlig



Carl Wagner

Around this time, **Alexander Naumovich Frumkin** (1895-1976), popularly known as the "father of electrochemistry in Russia," made vital contributions to our knowledge of the fundamentals of electrode reactions—particularly the influence of the electrode-electrolyte interface on the rate of electron transfer across it. Based on his studies on the adsorption of organic compounds on mercury, Frumkin proposed an adsorption isotherm that has come to be known as the Frumkin isotherm. He also introduced the concept of potential of zero charge. He joined hands with **Veniamin Grigorevich Levich** (1917-1987), an associate of theoretical physicist **Lev Davidovich Landau** (1908-1968), in relating his experimental results to theory. The collaboration led to the development of the rotating disc electrode and to a quantitative analysis of the polarographic maximum.

Electric traction received a boost with the invention of the so-called Drumm traction battery. This was a nickel-zinc alkaline battery invented by **James J. Drumm** (1897-1974) and it became popular with its use in a suburban train in Ireland. In 1932, **Francis Thomas Bacon** (1904-1992) introduced the use of an alkaline electrolyte and inexpensive nickel electrode in fuel cells. Twenty-seven years later, in 1959, he demonstrated a practical five-kilowatt fuel cell.

The quantitative measurement of electrochemical corrosion got established with a 1932 publication of **Thomas Percy Hoare** (1907-1978) and **Ulick Richardson Evans** (1889-1980). Evans, the 1955 ECS Olin Palladium Award winner, described in the *Biographical Memoirs of Fellows of the Royal Society* as the "father of the modern science of corrosion and protection of metals," laid the foundations of the electrochemical nature of corrosion. His 1937 book *Metallic Corrosion, Passivity, and Protection* is probably the most comprehensive book ever written by a single author on corrosion science. In 1933, in a paper on the oxygen electrode, Hoare showed how equilibrium potential could be determined from Tafel plots. Hoare was the first recipient of the U. R. Evans award (1976) of the Institution of Corrosion Science and Technology. **Herbert H. Uhlig** (1907-1993) was another champion of corrosion science. He helped establish the ECS Corrosion Division. His *Corrosion Handbook* published in 1948 continues to serve generations of corrosion scientists and engineers even half a century after its publication.

Described by F. Mansfeld as "an under-appreciated giant in the world of electrochemistry and corrosion," German electrochemist and materials scientist **Carl Wagner** (1901-1977) is also remembered as the "father of solid-

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state chemistry" for pioneering work in a variety of fields including tarnishing reactions, catalysis, photochemistry, fuel cells, semiconductors, and defect chemistry. Wagner formulated in 1943 the mechanism of ionic conduction in doped zirconia, which laid the foundations for the field of solid state ionics. His contributions to corrosion were fundamental to our understanding of the diffusion-limited growth of scales on metals at high temperatures as well as of other diverse aspects such as local cell action, passivity, alloy oxidation, and cathodic protection. His other contributions include solid state coulometric titration, theoretical and experimental aspects of mixed ionic and electronic conduction, and the introduction of an interaction parameter to describe cross-thermodynamic effects in solutions.

In 1937, **Arne Wilhelm Kaurin Tiselius** (1902-1971) turned another page in the history of electrochemistry with his work on the moving boundary, which was later to become zone electrophoresis. He received the 1948 Nobel Prize for his work on electrophoresis for the separation of proteins and amino acids. In 1938 American electrical engineer **Hendrik Wade Bode** (1905-1982) made an impact in electrochemistry through the Bode plot, which is used extensively in electrochemical impedance analysis of electrochemical systems.

By 1938, Belgian electrochemist and thermodynamicist **Marcel Pourbaix** (1904-1998) had constructed his famous potential-*pH* diagrams, also called Pourbaix diagrams. His work underpins the importance of thermodynamics in corrosion science, electrochemical refining, batteries, electrodeposition, and electrocatalysis. In 1952 he founded the Commission of Electrochemistry of the International Union of Pure and Applied Chemistry, which in the following year laid down the rules that govern the signs of electrode potentials.



Marcel Pourbaix

Much of the theory behind cyclic voltammetry and electrochemical impedance spectroscopy came from the work of the English electrochemist **John Edward Brough Randles** (1912-1998). His 1947 work on the cathode ray polarograph (oscilloscope) marked the beginning of linear sweep voltammetry, the solution to the peak current that comes through the famous Randles-Sevcik equation. (Sevcik was a Czech scientist, who along with Paul Delahay, developed several instruments with triangular sweeps. As an aside, it must be mentioned that it was Delahay who in the 1950s introduced chronopotentiometry.) The same year (1947) Randles published an analysis of an impedance circuit containing diffusion and interfacial electron transfer, which opened up a method to study fast electrode reactions. Randles was not given to much publishing, but his papers lent remarkable insights into the mechanism of electrochemical processes. The equivalent circuit used in the analysis is known as the Randles equivalent circuit, but in all fairness must be termed the Randles-Ershler circuit, for Dolin and Ershler had published similar results in the Soviet Union in 1940, which, however, were not easily available to the West due to the raging Second World War.

Enter British engineer Francis Thomas Bacon. During his years at C. A. Parsons & Co., Ltd., an electrical company based in Newcastle-upon-Tyne, he became the first to develop a practical hydrogen-air fuel cell and suggested its use in submarines. Unlike Grove's cell, which used an acid electrolyte and solid electrodes, Bacon's fuel cell had a less corrosive KOH electrolyte and pressurized porous gas-diffusion electrodes. The first practical application of his technology was to come

years later in Apollo missions, which relied on fuel cells for in-flight power, heating, and drinking water (a product of the electrochemical reaction). It is interesting to note that Bacon was the recipient of the first Grove medal in 1991.

Second Half of the Twentieth Century and Later

If thermodynamics of electrochemical systems dominated the first half of the twentieth century, kinetics of electrochemical reactions began to be recognized as an important branch of theoretical electrochemistry in the second half. The credit for connecting electrochemical thermodynamics and kinetics must go to English physical chemist **John Alfred Valentine Butler** (1899-1977). He, along with German surface chemist **Max Volmer** (1885-1965), and Hungarian physical chemist **Erdey-Gruz Tibor** (1902-1976), laid the seeds of the phenomenological basis of electrochemical kinetics. The Butler-Volmer equation is a product of their contribution to theoretical electrochemistry. People in Berlin are familiar with Max-Volmer Institute at the Technical University of Berlin and the Max-Volmerstrasse. In 1951, Butler teamed up with R. W. Gurney in introducing the concept of energy levels in electrochemical calculations. Butler's contributions to biochemistry are less well known, especially his work on the kinetics of enzyme action. Electrode kinetics also gained tremendously through the work of the German electrochemist **Klaus-Jürgen Vetter** (1916-1974), who made path-breaking interpretations of the exchange current density, electrochemical reaction order, and the Flade potential.

In the late 1950s, electroanalytical techniques came of age with the study of the hanging mercury drop electrode by Polish chemist **Wiktoria Kemula** (1902-1985), whose seminal work in electroanalytical chemistry led to extensive investigations in polarography, amalgam electrochemistry, stripping voltammetry, cyclic voltammetry, and electron transfer. Dutch physical and analytical chemist **Izaak**

Maurits Kolthoff (1927-1962), popularly known as the "father of analytical chemistry" helped transform analytical chemistry from an art with empirical recipes to an independent scientific discipline. Among his contributions to electroanalytical chemistry are conductometric titrations, potentiometric titrations, potentiometric analysis, polarography for environmental trace metal analysis, ion-selective electrodes, electron transfer and precipitation reactions,



Izaak Kolthoff

and chemistry of nonaqueous media. He nurtured an edifice of analytical chemistry and a galaxy of students, which included such boldface names as James J. Lingane and Herbert A. Laitinen. The amalgamation of ideas and concepts from diverse areas such as thermodynamics, kinetics, stereochemistry, electrochemistry, *pH*, and acid-base reactions that Kolthoff brought into analytical chemistry was of such import that Lingane once said, "...analytical chemistry has never been served by a more original mind, nor a more prolific pen, than Kolthoff's."

Parallel developments were also happening in electrochemical instrumentation, the most significant among them probably being the invention of the potentiostat by the German engineer-physicist **Hans Wenking** (b. 1923). Basing the bulb amplifier, which he designed in 1952, as the core of his invention, Wenking made his contribution to electrochemistry through the potentiostat. Until 1957, the potentiostats were used at the Max Planck Institute at Göttingen for corrosion studies. Later, Wenking along with Gerhard Bank, began manufacture of the instrument. Potentiostats have come a long way in their circuitry, but the Wenking potentiostat remains a common trade name

and serves electrochemistry in myriad ways: corrosion measurement, controlled electrolysis, and electrochemical passivation.



Heinz Gerischer

As Germany continued its contribution toward the growth of electrochemistry, there emerged another great name: **Heinz Gerischer** (1919-1994). The study of electrochemistry and photoelectrochemistry at semiconductor electrodes and the electrochemistry of excited states owe their origin to this genius. In 1960 and 1961, he made a detailed mathematical analysis of redox reactions at metal and semiconductor electrodes, by which he showed that electron transfer across the electrode-electrolyte interface occurred through tunneling. With a strong background in chemistry and physics, he toyed with several concepts, many of which were only beginning to be unraveled: the double-potential step (or a.c. modulation) to study very fast electrochemical reactions, interfacial electrochemistry, single crystal electrodes, and low energy electron diffraction (which his assistant Gerhard Ertl, b. 1936, pursued), ultra-high vacuums, and time-resolved spectroscopy. His work on electrode kinetics covered a lot of ground in the interpretation of the mechanisms of electrode processes. For example, he introduced the potentiostatic transient technique for the study of reaction mechanisms.

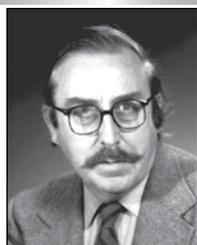
Scientific research in the just-independent India of the 1950s was considered more of an oddity of human endeavor than a profession. But that did not deter Indian electrochemist **Kadarundalige Sitharama Gururaja Doss** (1906-1989) pioneering a.c. effects on adsorption and electrode kinetics. He also introduced the techniques of tensammetry (independently of Breyer) and the redox-kinetic effect, now termed faradaic rectification. The impact



Sarukkai Krishnamachari Rangarajan

of these techniques in adsorption studies, kinetics of fast reactions, and electroanalysis of trace metals is well known. One of his illustrious protégés, **Sarukkai Krishnamachari Rangarajan** (1932-2008) was well known for his unified approach to modeling interfacial phenomena at the macro, molecular, and electronic levels.

This period also saw arguably the finest collaboration between a student and a teacher in electrochemistry, featuring **Brian Evans Conway** (1927-2005) and **John O'Mara Bockris** (b. 1923). They were instrumental in bringing electrochemistry from its moribund state of the Second World War era to modernity through their monumental multi-volume *Modern Aspects of Electrochemistry*. Incidentally, another student of Bockris, the Indian electrochemist Amulya K. N. Reddy also helped bring electrochemistry to the fore by compiling Bockris's lectures into *Modern Electrochemistry*, a two-volume book and arguably a classic. Bockris and Conway were the trail-blazers of electrode kinetics in the western world. Conway was a "complete" electrochemist in that he worked on nearly all aspects of electrochemistry: the electrified interface, ion solvation, adsorption, electrode kinetics, oxide film formation, electrocatalysis, rechargeable batteries, and electrochemical capacitors.



Brian Conway



John O'Mara Bockris



Karl V. Kordesch

Austrian inventor and electrochemist **Karl V. Kordesch** (b. 1922) is a familiar name to researchers in the area of batteries and fuel cells. He is the inventor of the alkaline primary cell (that has largely replaced the zinc-carbon dry cells in flashlights) and the key promoter of the RAM (rechargeable alkaline manganese dioxide) battery technology. In the 1960s, he became the first to develop the Apollo Fuel Cell, an alkaline fuel cell with a circulating electrolyte.

This was also the time when quantum electrochemistry was taking roots with path-breaking investigations by Georgian scientist **Revaz Dogonadze** (1931-1985). He was the first to recognize electron transfer processes as quantum mechanical transitions between two electronic states. His research group was the first to suggest a quantum mechanical model for proton transfer in polar solvents, which led to the formulation of a quantum mechanical theory of chemical, electrochemical, and biochemical processes in polar liquids.



Rudolph Marcus

But it was **Rudolph Marcus** (b. 1923), an American theoretical chemist, who put quantum electrochemistry on the map. He won the 1992 Nobel Prize in Chemistry for his theory of electron transfer in chemical systems.

Today electrochemistry looks set to shift gears with parallel advancements in materials science and characterization techniques. For example, there is increasing thrust toward exploiting nanoscopic materials and architectures. Expectations in

this direction are high because surface plays a key role in electrochemical processes. Continual developments in the synthesis and characterization of materials have also led to welcome changes in electrochemical research. In closing, we have made a chronological sequence of noteworthy developments in electrochemistry although this approach might rob the interconnections between them. The scientists who are portrayed as pillars of electrochemistry here have either made seminal contributions or helped sprout what were previously only just suggestions. We do hope that our list is comprehensive; undoubtedly there are inadvertent omissions. For these we apologize in advance and would welcome comments.

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