

Fuel cells, batteries, and the development of electrochemistry

Vladimir S. Bagotsky

Received: 21 September 2010 / Revised: 30 November 2010 / Accepted: 30 November 2010 / Published online: 4 January 2011
© Springer-Verlag 2010



The Volta pile—the first electrochemical battery

In March 1800, the Italian physicist Alessandro Volta (1745–1827) reported the construction of a device which could produce an “inexhaustible electric charge” [1]. Now known as the Volta pile, this device was the first example of a practical electrochemical power source (battery).

No special oxidizer was used in the Volta pile, and this role was played by water molecules which were reduced at the silver cathode to gaseous hydrogen. As a result of such a weak oxidizer, the open circuit voltage (OCV) of a single cell in this pile was only about 0.4 V. If a high discharge current was needed, very large batteries had to be built. One

pile manufactured in 2003 comprised 2,100 individual cells.

The Volta pile was of extraordinary significance for the development of many new fields of science and technology in the nineteenth century. This pile allowed for the first time to realize a continuous flow of electrical charges (an electrical current).

The development of different battery types

In order to circumvent the limited possibilities of the original Volta pile in the following period, other battery types were developed with the introduction of special oxidizers. In 1836, J. F. Daniell (1796–1845) developed a cell with an oxidizer in the form of copper ions in a copper-sulfate solution. Cells with the use of nitric acid as oxidizer were developed in 1838 by W. R. Grove (1811–1896) and in 1841 by R. Bunsen (1811–1899). Cells containing sodium bichromate dissolved in sulfuric acid were developed in 1843 by Ch. Poggendorff (1824–1876) and in 1856 by Grenet.

A considerable improvement of electrical batteries was achieved after the replacement of liquid oxidizers (mainly in aqueous solutions) by solid oxidizers (mainly by oxides of different metals). In 1865, the French engineer G. L. Leclanché (1839–1882) made a battery containing manganese dioxide as oxidizer (positive electrode) and zinc as a reductant (negative electrode) and an aqueous solution of ammonium chloride as electrolyte [2]. In the following, this liquid electrolyte was replaced by an electrolyte solidified by different gelling agents. These “dry” Leclanché cells proved to be very simple in manufacture and reliable in use. As early as 1868, more than 20,000 such cells were being manufactured. A further advance in battery technology was

V. S. Bagotsky (✉)
A.N. Frumkin Institute of Physical Chemistry and
Electrochemistry,
Russian Academy of Sciences,
Moscow, Russia
e-mail: vbag@mail.ru

the development of rechargeable batteries. In 1859, the French scientist Gaston Planté (1834–1889) made the first prototype of a lead–acid rechargeable battery [3]. An alkaline nickel–cadmium rechargeable battery was developed in 1901 by the Swedish engineer W. Jungner (1869–1924) [4], and an alkaline nickel–iron battery was developed in the same year by the well-known American inventor Thomas A. Edison (1847–1931) [5]. Up to the seventh decade of the nineteenth century, electrochemical batteries remained the only sources of electrical current and power.

The development of electrochemical thermodynamics

The development of a variety of batteries taking place in the second half of the nineteenth century led to basic work in electrochemical thermodynamics. In 1847–1851, Herman von Helmholtz (1821–1894) and William Thomson (Lord Kelvin, 1824–1907) established a connection between the OCV of batteries and the thermal effect of the chemical reaction proceeding during discharge. Experimental discrepancies between the values of these two parameters were explained later by Josiah Willard Gibbs (1839–1903) who took into account the reaction enthalpy and established the concept of free enthalpy (the Gibbs energy) [6].

For an analysis of the OCV of batteries, the notion of electrode potential was of prime importance. In 1886, Friedrich Wilhelm Ostwald (1853–1903; Nobel Prize, 1909) gave a clear description of this notion [7]. At his suggestion, his student Walther Nernst (1864–1941; Nobel Prize, 1920) investigated the thermodynamic equilibrium conditions at electrode surfaces, and in 1889, derived his famous equation

$$E = E^0 + (RT/F) \log c_j$$

linking the electrode potential E with ion concentrations c_j in solution [8]. Thus, the long development of different types of batteries resulted in the formation of a new important branch of electrochemistry and physical chemistry—*electrochemical thermodynamics*.

The development of electrodynamics and emergence of another electrical power source

After the appearance of the Volta pile and other improved versions of batteries, extended experiments with the new phenomenon of a continuous electrical current became possible, and soon, different properties of this current could be established: in 1820, Ampère's law of interaction

between electrical currents; in 1827, Ohm's law of proportionality between voltage and current; in 1831, Joule's law of the thermal effect of electrical current; in 1831, Faraday's laws of electromagnetic induction, and many others. These achievements led to the development of the *theory of electrodynamics* and the practice of electrical engineering and, as a result, to the appearance of a revolutionary new power source: the electromagnetic generator invented in 1866 by Werner von Siemens (1816–1872) which soon surpassed their predecessors both in electrical and economic parameters.

The emergence of a large-scale electrochemical industry and the development of electrochemical kinetics

After the development of the electromagnetic generator, a large-scale production of electric power became possible (“grid-electricity”). Electric power could now be used in different branches of industry. In particular, many new industrial electrolysis processes were developed and soon organized at a large scale: after 1883, chlor-alkali electrolysis and after 1888, the electrolytic production of aluminum. The necessity to increase the efficiency of these processes led to the beginning of investigations in *electrochemical kinetics*. In 1905, Julius Tafel (1862–1918) established his well-known equation

$$\eta = a + b \cdot \log i$$

linking the overvoltage η of electrochemical processes with the current density i on the electrodes [9]. Many subsequent investigations in this field were devoted to the interpretation of the values of the constant “ b ” in the Tafel equation: in 1930 (M. Volmer, 1885–1965 and T. Erdey-Gruz, 1902–1976 [10]); in 1933, Alexander N. Frumkin (1895–1976) [11].

The development of fuel cells

As a logical consequence of the development of electrochemical thermodynamics, F. W. Ostwald in 1894 proposed to use electrochemical cells for large-scale power production as an alternative to conventional power generation in thermal power stations and introduced the term *fuel cell* [12].

In the following years, this term was used not only for such large-scale installations but also for smaller electrochemical power sources into which the reactants–oxidizer and reducing agent (mostly gasses and/or liquids)—are continuously fed to the electrodes at a rate proportional to the current load. In 1839, the British scientist William

Robert Grove (1811–1896) described a cell with gas (hydrogen and oxygen) electrodes [13]. This cell is now regarded as the first prototype of such a fuel cell. At that time, this cell had no practical importance. Numerous attempts to develop efficient fuel cells with different fuel types during the last decades of the nineteenth century and the first decades of the twentieth century ended without appreciable results. The power densities obtained with these cells were rather low, and most importantly, the service life of the cells was too short.

The first practical breakthrough was achieved in 1958 when the English engineer Francis Th. Bacon (1904–1992) built the first large power unit (5 kW) with hydrogen/oxygen fuel cells [14]. In order to accelerate the electrochemical processes and thus to achieve a high power output, in this battery, high temperatures (200–240 °C) and elevated working gas pressures (2–4 MPa) were used. Owing to the high gas pressure, the battery had a heavyweight construction. Bacon's battery demonstration attracted great attention from the scientific community, and in many countries, research and design work in this field started on a large scale.

The main purposes of these attempts were a sharp increase in the efficiency (power density and service life) of fuel cells and an increase in the range of possible reactants for them (including organic compounds such as natural gas oil products a.o.). To achieve these goals, it was necessary to increase the rate of the electrochemical reactions in fuel cells and to use reactions with different types of reactants. Investigations in the field of these problems led to the emergence of two new important branches of electrochemistry: (1) *Electrocatalysis* (which is mainly concerned with investigating all factors influencing the value of the constant “*a*” in the Tafel equation) [15, 16], (2) *Electrochemical macrokinetics* (mainly investigating the influence of the electrode's porous structure on the efficiency of reactions with gaseous and/or liquid reactants) [17, 18].

Thus, it can be seen that at all stages of the development of electrochemistry, theoretical investigations have been stimulated by the practical use of various electrochemical devices (batteries, fuel cells, electrolyzers, etc.), and the theoretical concepts that were developed in turn contributed significantly to the development of applied electrochemistry.

The future development of fuel cells in no small degree depends on the possibility to solve two fundamental problems in the field of electrocatalysis:

1. *Developing new catalysts for the electrochemical reduction of oxygen.* Considerable energy loss occurs during fuel cell operation due to the irreversibility of this reaction. The metabolic reduction of oxygen in the human body occurs under conditions close to reversibility and without energy losses, despite the fact that it too has electrochemical components.

2. *Developing highly selective catalysts for electrochemical reactions.* Platinum metal catalysts generally used in fuel cells are highly active but not selective. In contrast, enzymes as natural catalysts are highly active and, at the same time, highly selective. The use of selective catalysts for the two fuel cell electrodes would give the possibility to realize single-compartment fuel cells in which the fuel and the oxidizer are supplied together to the fuel cell. Such cells would be easier and cheaper to manufacture than today's fuel cells. Following the leads provided by nature, it may be possible to achieve adequate solutions to these problems.

Reminiscences of the author

The author of this article worked in the fields of both fundamental and applied electrochemistry and thus had an opportunity to experience the mutual influence in the developments of these two fields. Beginning in 1938, he studied electrochemistry at the Moscow Lomonosov State University, and in 1947, wrote his PhD thesis under the supervision of Prof. Alexander N. Frumkin (1895–1976) who, according to the statement of the British scientist Prof. Roger Parsons, “dominated electrochemistry over fifty years of the twentieth century.” In the following three years, he worked as junior scientist at the University's Chair of Electrochemistry, investigating the mechanism of different electrochemical reactions. In 1952, together with Profs Frumkin, Kabanov, and Iofa, he wrote a book on electrochemical kinetics which was the first monograph ever published on this topic [19].

In 1950, during the odious Soviet campaign against “rootless cosmopolitans in science,” he was fired from the university and had to switch to a job in applied electrochemistry. For 15 years, he worked at the Moscow Industrial Institute of Power Sources where he was engaged in the development and organization of industrial production of new battery types. He supervised the development of new batteries for MIG jet fighters, for Russian ICBMs, sputniks, and spacecrafts. He took an active part in the preparations for launching, in 1956, of the first Sputnik and, in 1962, of the first space flight by Yuriy Gagarin. For these achievements, he was awarded honorary decorations of the Soviet Union and the scientific degree of Doctor of Science (an analog of the German Dr. habil).

In 1965, he again switched to fundamental electrochemistry and became a senior scientist and department chief at the Institute of Electrochemistry of the USSR Academy of Sciences (now A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences). In this institute, his main activities were

devoted to two problems: (1) investigation of the mechanism of electrocatalytic reactions of anodic oxidation of simple organic compounds such as methanol a.o. (together with the group of Dr. Yu. B. Vassilyev) [20], (2) research in the field of macrokinetics of reactions in systems with distributed parameters such as porous electrodes a. o. (together with the group of Dr. Yu. M. Volfkovich) [21]. Both these problems, though not related directly to the development of fuel cells, were aimed at better understanding and optimization of processes in fuel cells.

During more than 15 years, up to the death of Prof. Frumkin in 1976, the author of this article was a deputy of Prof. Frumkin as the head of the Scientific Council for Fuel Cells of the USSR Academy of Sciences. This council was coordinating fuel cell research activities in different universities and research centers. As a result of these efforts at the Ural Integrated Electrochemical Plant and the S. P. Korolev Rocket and Space Corporation, an alkaline 10–15 kW hydrogen/oxygen fuel cell battery “Photon” for the Russian space shuttle project “Buran” was developed. After the discontinuation of the Buran project, the experience gained when developing the photon battery was subsequently used for building power units for test models of electric cars.

After his retirement from the A. N. Frumkin Institute, in 1998, the author of this article for health reasons joined, together with his wife, the family of their daughter in California, where he underwent a heart surgery. In California, he wrote two books which were published by John Wiley & Sons, Hoboken, N.J.: in 2005, “Fundamentals of Electrochemistry”, second edition and in 2009, “Fuel Cells: Problems and Solutions.”

Now, at the age of 90, he is writing (together with Dr. Yu. M. Volfkovich and Dr. A. N. Filippov from Moscow) a new book for Springer-Verlag, London, entitled “Porous

materials and powders: Structural and wetting properties and their application.”

References

- Volta A (1800) *Philos Trans* 2:430
- Leclanché G-L (1876) *Compt Rend* 83:54
- Planté G (1859) *Compt Rend* 49:402
- Jungner W (1901) Swedish patent 1556722
- Edison TA (1901) US patent 678722
- Gibbs JW (1874–1878) *Trans Conn Acad Arts Sci* 3:108, 343
- Ostwald W (1886) *Elektrochemie: ihre Geschichte und Lehre*. Veidt & Co., Leipzig, 1886 (Engl transl: Ostwald W (1980) *Electrochemistry history and theory*, 2 vols. Amerind Publ, New Delhi)
- Nernst W (1889) *Z Phys Chem* 4:129
- Tafel J (1905) *Z Phys Chem* 50:641
- Volmer M, Erdey-Gruz T (1930) *Z Phys Chem* 150A:203
- Frumkin A (1932) *Z Phys Chem* 160A:116
- Ostwald W (1894) *Z Elektrochem* 1:122
- Grove W (1839) *Philos Mag* 14:447
- Bacon FT (1960) *Ind Eng Chem* 52:301
- Binder H, Koehling A, Sanstede G (1972) *From electrocatalysis to fuel cells*. G. Sanstede (ed) University of Washington Press, Seattle, WA
- Lipkowski J, Ross PhN (eds) (1998) *Electrocatalysis*. Wiley, New York
- Chizmadzhev YuA, Markov VS, Chirkov YuG (1971) *Macrokinetics of processes in porous media (fuel cells)* [in Russian]. Nauka, Moscow
- Gurevich IG, Volfkovich YuM, Bagotsky VS (1974) *Porous electrodes with liquid reagents* [in Russian]. Sc and Technol Publ, Minsk
- Frumkin AN, Bagotsky VS, Iofa ZA, Kabanov BN (1952) *Kinetics of electrode reactions* [in Russian]. Moscow University Publishers, Moscow
- Bagotsky VS, Vassiliev YuB, Khazova OA (1977) Generalized scheme of chemisorption, electrooxidation and electroreduction of simple organic compounds on platinum group metals. *J Electroanal Chem* 81:229–238
- Volfkovich YuM, Sosenkin VE, Bagotsky VS (2010) Structural and wetting properties of fuel cell components (Review). *J Power Sources* 195:5429–5441