ACS Energy LETTERS

Cite This: ACS Energy Lett. 2018, 3, 2841−2845

http://pubs.acs.org/journal/aelccp

EDITORIAL

Building Better Batteries: A Travel Back in Time

Electrical batteries are so ubiquitous that one hardly takes note of their unassuming presence all around us. Likewise, we are not consciously aware of the extent of influence they have in various transformations influencing our day-to-day life. For example, it is not always recognized that batteries precede all other forms of inventions in providing a reliable source of electricity. Therefore, we felt that it is interesting and worthwhile to trace the history of the development of batteries through their various transformative stages.

Pedagogically, any device capable of converting its chemical energy into electrical energy using oxidation−reduction (redox) reactions of its active materials, known as electrodes, is now called a battery. A good battery is one that performs a large amount of work per unit volume and weight, is easy to store, is easily accessible, and, most importantly is economical. However, the origin of the term "battery" lies in its use by Benjamin Franklin in 1749 to describe several capacitors (known as Leyden jars, after the town in which it was discovered), connected in series (see Figure 1), to give rise to a consolidated and enhanced source of electrical energy,[1] presumably in analogy to the already existing word to describe a collection of similar equipment working together, such as a battery of artillery guns. Interestingly, today the word "battery", unless specifically qualified to mean something else, invariably signifies electrochemical cells to provide electric energy, and even a single such cell is often called a battery.

Figure 1. Battery of serially connected Leyden jars (Source: https://commons.wikimedia.org/wiki/File:Leidse_flessen_Museum_Boerhave_december_2003_2.jpg).

There is some speculation based on archeological findings of a ceramic pot together with a copper tube and an iron rod in the region of Iraq whether these were used in ancient times as a source of electrochemical energy for electroplating, leading to this collection being popularly known as the "Bagdad Battery". There is, however, no evidence so far to support this speculation, and even the dating of these artifacts is somewhat controversial. The real discoverer of batteries is Allessandro Volta (Figure 2) who, using two metallic electrodes in conjunction with an electrolyte in 1800, invented a way to store electrochemical energy that can be accessed at will to tap electrical energy.[2] This acted as the harbinger of revolutionizing long-distance communications based on the invention of telegraphs in the late 1830s and, much later (in 1870s), of the telephone.

Figure 2. Alessandro Volta with a Voltaic pile in front on the table (Source: http://www.anthroposophie.net/bibliothek/nawi/physik/volta/bib_volta.htm (Public Domain); https://commons.wikimedia.org/w/index.php?curid=1678917).

Voltaic pile, as the invention was then known, had a problem—evolution of hydrogen bubbles due to chemical reactions sticking to the electrode surfaces and leading to a rapid drop in its performance—and therefore, it was of little

Published: November 9, 2018

DOI: 10.1021/acsenergylett.8b01966
ACS Energy Lett. 2018, 3, 2841−2845

practical utility. This problem was solved[3] by John Daniel (Figure 3) in 1836 with the discovery of a two-fluid battery,

Figure 3. John Daniell (Source: By Unknown - King's College, London, Public Domain, https://commons.wikimedia.org/w/index.php?curid=28331882).

named a Daniel Cell after the discoverer, to provide a constant and reliable source of electricity over a long time, thereby being used for telegraphy that was patented the following year.

The troublesome design of separating two fluids to avoid depolarization using a porous separator was first overcome by Johann Christian Poggendorff in 1842 by mixing the electrolyte (sulfuric acid) with the depolarizer (chromic acid).[4] He also used carbon as one of the electrodes, dating possibly the first use of a nonmetal as an electrode.

All of these developments of various designs of cells were based on a single use philosophy, where the electrodes once consumed by the chemical reaction could not be regenerated, defining what was later called primary cells. By contrast, Gaston Planté (Figure 4) discovered in 1859 the rechargeable lead–acid battery that revolutionized the world and defined what is now called secondary cells.[5] The original design used lead as both electrodes. Introducing several important innovations and departures from the standard approach of the time, Georges Leclanché in 1866 introduced a new battery that used MnO_2 as one of the electrodes (Figure 5), signaling the use of the first oxide for this purpose,[6] because lead oxide was not introduced in the lead–acid battery design until 1881. The telegraphic service of Belgium was quick to induct this technology into their service in 1867, indicating an extraordinarily short patent-to-market transition that must be an envy to most inventors of modern times.

Leclanché also introduced ammonium chloride solution as the electrolyte, which was a departure from the predominant use of protonic acids as electrolytes until then. However, the first design of a battery without any protonic acid, called the gravity cell, used two fluids, copper sulfate and zinc sulfate, separated by their relative densities, introduced sometime in 1860s. The invention, surrounded by a certain sense of

Figure 4. Gaston Planté (Source: Di Chevallier - Gallica, Pubblico dominio, https://commons.wikimedia.org/w/index.php?curid=3208411).

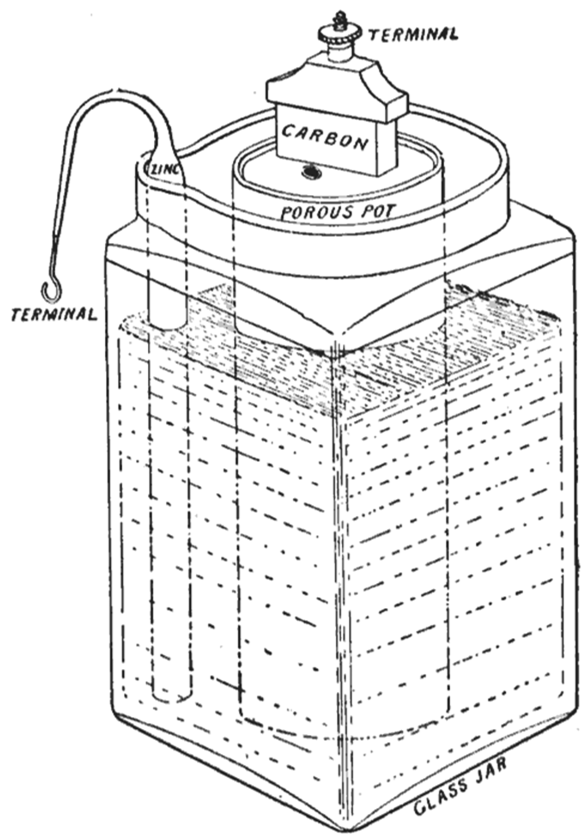

Figure 5. Engraving of a Leclanche cell from the Cyclopedia of Telephony and Telegraphy (1919). (Source: https://upload.wikimedia.org/wikipedia/commons/4/44/Leclanche_cell.gif).

mystery, is attributed to a Frenchman, with the name Callaud, though very little is known about the inventor; we could not find even his complete name in any records. Interestingly, this cell with its mysterious inventor has possibly had one of the most successful applications, having been the preferred source of electricity for telegraphic systems until the 1950s.

A very significant progress in the history of commercialization of batteries is the making of the dry cell that allowed easy

DOI: 10.1021/acsenergylett.8b01966
ACS Energy Lett. 2018, 3, 2841–2845

transportation, storage, and universal deployment in any orientation, in contrast to the cumbersome cells with liquid electrolytes. While historically the Zamboni pile, introduced in 1812, is the first example of a dry cell, its low current capacity made it an impractical device. Replacing the liquid ammonium chloride solution of the Leclanché cell with a paste of ammonium chloride solution in plaster of Paris as the electrolyte, Carl Gassner introduced the first significant dry cell in 1886, patenting his invention in several countries,[7] clearly underlining his understanding of the commercial implications of his invention. There were independent developments of dry batteries around the same time, most notably by Wilhelm Hellesen and Yai Sakizo, with some confusion regarding whom among these three invented the first dry cell. These dry cells are the first truly portable electrical energy devices that not only led to the introduction of the flashlight around 1899 but also encouraged their modern counterparts to continue to change human society in the most fundamental ways by making portable devices that are pervasive in their use.

The year 1899 saw another fundamental shift in the design of batteries, when Waldemar Jüngner used potassium hydroxide solution as the electrolyte,[8] in contrast to all acidic electrolytes used until then, with nickel and cadmium electrodes, giving birth to alkaline batteries. Later on, nickel−cadmium was commercially discarded due to the toxicity of cadmium. The unpopularity of cadmium encouraged the development of nickel−metal hydride batteries, which are not only cadmium-free but can store more charge than nickel−cadmium batteries. On the downside, nickel−metal hydride batteries deliver less power, have a faster self-discharge, and are less tolerant to overcharge.

Jüngner also introduced nickel−iron (Ni−Fe) batteries,[8] and the design was developed[9] further by Thomas Edison (Figure 6) and patented in 1901. It is interesting to note that the primary driving force for Edison's efforts in improving Ni−Fe batteries was based on his desire to make electric cars the most popular mode of transport,[10] and we are now seeing a revival of similar sentiments more than 100 years later. Unfortunately, electric vehicles did not get enough traction at Edison's time primarily due to the advent of the legendary Model T Ford cars with petroleum-based fuel engines. It is tempting to speculate what human civilization would look like today if the history of development of transportation went down the road of electrically driven vehicles with Edison instead of Ford winning the race.

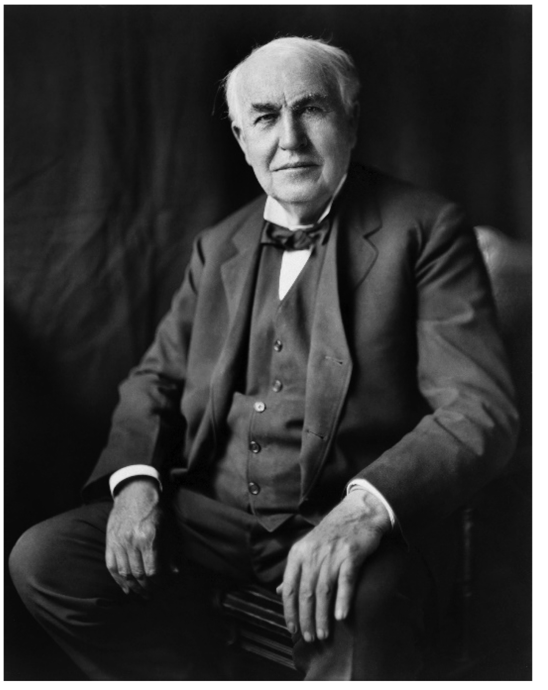

Figure 6. Thomas Alva Edison (Source: By Louis Bachrach, Bachrach Studios, restored by Michel Vuijlsteke. This image is available from the United States Library of Congress's Prints and Photographs division under the digital ID cph.3c05139. Public Domain, https://commons.wikimedia.org/w/index.php?curid=6582301).

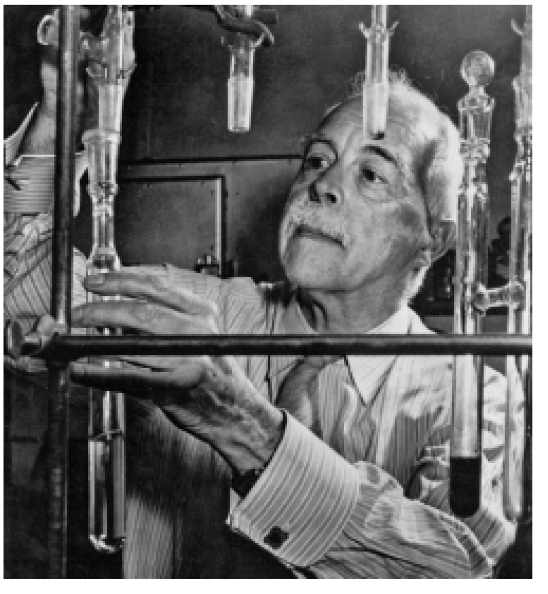

Figure 7. G. N. Lewis in his UC Berkeley lab in the 1940s. Credit: UC Berkeley Lawrence Berkeley National Lab (Source: https://cen.acs.org/articles/94/i15/Five-chemists-should-won-Nobel.html)

Keeping in mind the metrics of energy and power capabilities of any battery per unit mass for the all-important purpose of portable applications, it is surprising that lithium-based batteries were the last to enter the inventive chain of battery technology. It appeals to common sense that lithium is an obvious choice because its low mass and highest electrochemical potential maximize the energy-to-weight ratio. Its small ionic size is also expected to give rise to facile diffusion, enhancing the current delivery capabilities significantly, but lithium batteries were introduced only in the 1970s by several groups, and lithium-ion batteries were first discussed starting 1979. However, the exploration of lithium as an active ingredient of electrochemical cells can be traced back to the work of G. N. Lewis (Figure 7). While his 1912 paper[11] on "The Activity of the Ions and the Degree of Dissociation of Strong Electrolytes" is mentioned often, it is his 1913 paper[12] that specifically investigates "The Potential of the Lithium Electrode". His 1916 paper[13] is also important, describing "Electrical Conduction in Dilute Amalgams", where he explicitly points to the contributions from both ionic and electronic conductivities contributing to the total conductance of the lithium amalgamated mercury sample.

It is finally the works of N. A. Godshall and co-workers[14,15] and those of J. B. Goodenough and co-workers[16] in 1980 and

DOI: 10.1021/acsenergylett.8b01966
ACS Energy Lett. 2018, 3, 2841−2845

onward that established the first successful topotactical insertion/deinsertion of a Li^+-ion in $LiCoO_2$ among several other oxide systems, paving the way for commercialization of the lithium-ion battery technology by Sony in 1991. Lithium-ion batteries of today are iterations of the concept developed by Goodenough. Scientists are also expending their efforts on other alternatives such as sodium-ion, lithium−air, and lithium−sulfur batteries, which have compelling promise but also problems.

In revenue share, Li^+ batteries are next only to lead−acid batteries today; with the advent of electric vehicles and nonrenewable energy sources, its market share is expected to increase rapidly. However, there is also concern about this technology due to its dependence on a scarce commodity, lithium, making this an expensive option; additionally, there are various safety issues connected with the highly reactive nature of this element. Thus, there has always been a search for alternatives based on earth-abundant materials, and there has been some interesting developments in recent times[17] using one such material, namely zinc, with its specific capacity as high as 820 mAh/g, leading to zinc−air and zinc−manganese dioxide-based technologies.

The most pressing challenges today are to invent batteries that can make electric cars travel with a single charge distances comparable to what a conventional car can do with a full tank of fuel or to store and deliver enough electrical energy/power to the grid, all at a competitive cost to become a viable solution. Another problem faced in the realization of electric cars is the requirement of a fast charge acceptance by the battery. While there are recent laboratory level developments of Li ion batteries with spectacularly fast charge-discharge rates, another route to circumvent this problem is with the help of supercapacitors. It is now generally believed that a practical solution will be a capatery—a combination of the superbattery and the suparcapacitor. Unlike a battery, a supercapacitor stores charge in the electrical double-layer. Amazingly, although the concept of the electrical double-layer was established in the 1800s, it took 150 years to become a technical reality. The unique attributes of supercapacitors complement the strengths and weaknesses of the battery very well.

Tracing the history of battery technology, it is evident that breakthroughs have been only a few and slow in coming, particularly in the last 100 years or so. Yet, the impact of batteries on our life is astounding, bringing in a quiet revolution by making portable devices feasible, be it the mundane flashlight or omnipresent portable electronic goods in the form of mobiles, laptops, and music systems (not to forget yesteryear's transistor radios) or the life-saving pace-maker. Right now, we may be transiting through another drastic shift, with the electric vehicle technology posing a serious challenge to IC engine-based transportation. It is also generally accepted that we need rapid and pole-vaulting improvements, if not quantum jumps, in battery technologies to make renewable energy the main source of electricity supply over the grid system. Irrespective of these future improvements and independent of the absence of our realization that it is always the everyday battery that makes the fancy devices work, the present global market[18] for batteries is variously estimated between USD 50 and 120 Billion, underscoring the importance of this technology in supporting modern civilization.

D. D. Sarma*

A. K. Shukla

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bengaluru 560012, India

AUTHOR INFORMATION

Corresponding Author

*E-mail: sarma@iisc.ac.in.

ORCID

D. D. Sarma: 0000-0001-6433-1069

Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

ACKNOWLEDGMENTS

We gratefully acknowledge the important pointers provided by various public domain open resources, particularly Wiki sources, available on the Internet, and the original sources that we could reach following such leads in preparing this article. The figures are taken mostly from various Wiki-related sources, with proper acknowledgements provided in the figure captions.

REFERENCES

(1) Franklin, B. *Experiments and Observations on Electricity (1749)*, Letter IV to Peter Collinson by Benjamin Franklin. https://www.chemteam.info/Chem-History/Franklin-1749/Franklin-1749-all.pdf (2018).

(2) *Milestones: Volta's Electrical Battery Invention, 1799*. ieeeghn.org. IEEE Global History Network. Retrieved Apr 12, 2016; and *Enterprise and electrolysis*. rsc.org. Royal Society of Chemistry. Retrieved 18 Feb 18, 2015. https://en.wikipedia.org/wiki/Alessandro_Volta#cite_ref-5 (2018).

(3) Daniell, J. F. On Voltaic Combinations" and "Additional observations on voltaic combinations" - Letters addressed to Michael Faraday. *Philos. Trans. R. Soc. London* **1836**, *126*, 107−129.

(4) Poggendorff, J. C. Ueber die mit Chromsäure construirten galvanischen Ketten. *Ann. Phys.* **1842**, *133*, 101−111.

(5) Plantè, G. The Storage of Electrical Energy, Reprinted. Kessinger Publishing, 2008 (SN - 9781436521819).

(6) Leclanchè, G. French Patent No. 7865, 1866.

(7) Gassner, C. Germany Patent No. 37,758, Apr 8, 1886, Austria−Hungary Patent No. 64,357 and 35,974, May 21, 1886; Belgium Patent No. 73,872, Jul 16, 1886; French Patent No. 77,465, Jul 17, 1886; England Patent No. 16,810, Dec 22, 1886; United States Patent No. 373,064, Nov 15, 1887.

(8) Jüngner, W. Swedish Patent No. 10,177 (published as SE 10,177 C1), Mar 11, 1899; No. 15,567 (published as SE 15,567 C1), Jan 22, 1901.

(9) Edison, T. A. US Patent No. 678,722, Jul 16, 1901.

(10) Edison, T. A. US Patent No. 750,102, Jan 19, 1904.

(11) Lewis, G. N. The Activity of the Ions and the Degree of Dissociation of Strong Electrolytes. *J. Am. Chem. Soc.* **1912**, *34*, 1631−1644.

(12) Lewis, G. N.; Keyes, F. G. The Potential of the Lithium Electrode. *J. Am. Chem. Soc.* **1913**, *35*, 340−344.

(13) Lewis, G. N.; Hine, T. B. Electrical Conduction in Dilute Amalgams. *Proc. Natl. Acad. Sci. U. S. A.* **1916**, *2*, 634−638.

(14) Godshall, N. A.; Raistrick, I. D.; Huggins, R. A. Thermodynamic investigations of ternary lithium-transition metal-oxygen cathode materials. *Mater. Res. Bull.* **1980**, *15*, 561−570. and Godshall, N. A. Ph.D. Dissertation, Stanford University, May 18, 1980.

(15) Raistrick, I. D.; Godshall, N. A.; Huggins, R. A. US Patent No. 4340652, Jul 20, 1982.

(16) Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B. Li_xCoO_2 ($0 < x < 1$): A New Cathode Material for Batteries of High Energy Density. *Mater. Res. Bull.* **1980**, *15*, 783−789.

DOI: 10.1021/acsenergylett.8b01966
ACS Energy Lett. 2018, 3, 2841−2845

(17) See, for example: *Cheaper Battery Is Unveiled as a Step to a Carbon-Free Grid*. https://www.nytimes.com/2018/09/26/business/energy-environment/zinc-battery-solar-power.html (2018).
(18) *Global Battery Materials Market 2018-2023 by Battery Type, Material, Application*. https://www.prnewswire.com/news-releases/global-battery-materials-market-2018-2023-by-battery-type-material-application-300646280.html (2018). Also see, https://www.freedoniagroup.com/industry-study/world-batteries-3309.htm.

DOI: 10.1021/acsenergylett.8b01966
ACS Energy Lett. 2018, 3, 2841−2845