Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2019, Volume 10, Issue 12, Page 1194-1199

http://www.jmaterenvironsci.com

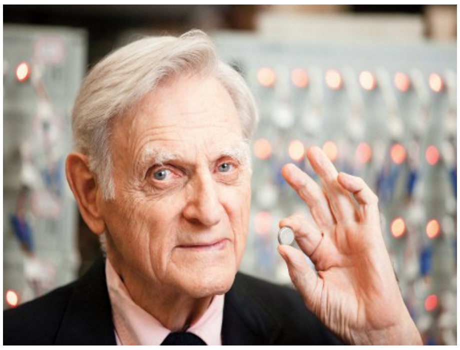
Congratulations to Professors John B Goodenough, M Stanley Whittingham and Akira Yoshino awarded the Nobel Prize in Chemistry 2019 for work on Lithium-ion batteries

Driss Mazouzi[1*] and Belkheir Hammouti[2] (JMES Team)
[1]*Faculté Polydisciplinaire Taza, Universite Sidi Mohamed Ben Abdellah, Morocco.*
[2]*Faculté des Sciences, Université Mohammed 1er, Oujda, Morocco.*
E-mail: driss.mazouzi@usmba.ac.ma

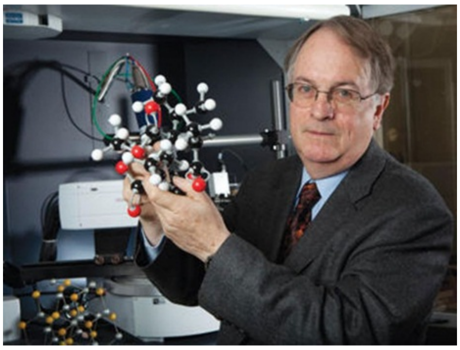
JMES Editors and Members present all wishes and Congratulations to Professors *John B Goodenough, M Stanley Whittingham and Akira Yoshino* awarded the Nobel Prize in Chemistry 2019, *"for the development of Lithium-ion batteries"*.

The 2019 Nobel Prize in Chemistry winners are :

Born in 25 July 1922 in Jena, Germany, **John Bannister Goodenough** is an American professor and solid-state physicist. He is currently a professor of mechanical engineering and materials science at **The University of Texas at Austin**. He is widely credited for the identification and development of the Lithium-ion battery as well as for developing the Goodenough-Kanamori rules for determining the sign of the magnetic superexchange in materials. In 2014, he received the Charles Stark Draper Prize for his contributions to the Lithium-ion battery. In 2019, he was awarded the Nobel Prize in Chemistry, making him the oldest Nobel laureate ever.



Born in 1941 **Michael Stanley Whittingham** United Kingdom, M. Stanley Whittingham is a British-American chemist. He is currently a professor of chemistry and director of both the Institute for Materials Research and the Materials Science and Engineering program at Binghamton University, part of the State **University of New York**. He was awarded the Nobel Prize in Chemistry in 2019.



Born in Suita on January 30, 1948, **Akira Yoshino** graduated from Kitano High School in Osaka City (1966). He holds a B.S. (1970) and a M.S. in Engineering (1972) at Kyoto University, and obtained a Doctorate in Engineering from Osaka University (a Dissertation PhD) in 2005. He is a Japanese chemist. Fellow of Asahi Kasei Corporation and professor of **Meijo University**. He is the inventor of Lithium-ion battery (LIB) often used in cellular phones and notebook computers. He was awarded the Nobel Prize in Chemistry in 2019.

The Nobel prize in chemistry has been awarded to three scientists for their work in developing Lithium-ion batteries. John B Goodenough of the University of Texas at Austin, M Stanley Whittingham of Binghamton University and Akira Yoshino of Meijo University will receive equal shares of the 9m Swedish kronor (£740,000) prize, which was announced by the Royal Swedish Academy of Sciences in Stockholm on Wednesday.

Goodenough, Whittingham and Yoshino become the 25th trio to share the Nobel Prize in Chemistry, in what is a perfect example of scientists discovering the work of others and improving on it to create something truly groundbreaking. They also become the 176th, 177th and 178th men to become Nobel Laureates of Chemistry. While the awards were initially set up to celebrate the greatest achievements in research in the year prior to the award, the trend has on the whole changed to now acknowledge historic research that has resulted in a large impact on life as we know it today. Similarly, most cutting edge research today is carried out by large international collaborations made up of more diverse groups of researchers.

1. Introduction-state of the art :

Electrochemical power sources convert chemical energy into electrical energy. The energy of this reaction is available as electric current at a defined voltage and time. It has to be emphasized that the electrochemical electricity storage has been in use for as long as electricity has been industrially used. In a large compilation of early research, the batteries have been known for more than two centuries since the pioneering work of Galvani and Volta. In 1859, Gaston Plante was introduced the earliest secondary battery, based on the first laboratory primary battery created by Alessandro Volta in 1800, when he stacked zinc and silver disks between a sodium chloride soaked cloth. Advancing from this primary cell, the Pb-acid battery also known as secondary cell, became the first field rechargeable system when it was invented in 1859 by Gaston Plante. The Pb-acid batteries were novel at the time, they suffered from low energy density and would fail at meeting the demands of many power and energy hungry electronic devices in today's world. Next came the Nickel-Cadmium (Ni-Cd) was proposed as an alternative chemistry in the early 1900's and Nickel Metal Hybdride (Ni-MH) became prominent in the latter half of the century. Both batteries improved upon the Pb-acid battery's energy density and were used in many first generation consumer electronics and hybrid vehicles. But Ni-Cd and Ni-MH suffered from several deficiencies. Both nickel and cadmium are toxic materials and the cell voltage for both types of batteries is only 1.2V which limits the energy and power density forthese chemistries [1].

Therfore, the development of industry grow exponentially and progress of science, another possible battery was developed as an alternate energy source has gathered lot of importance in all forms of energy requiring applications. Earlier versions of electrochemical energy storage could not hold enough charge to power the devices in use today while allowing them to remain fot portable electronics, especially in laptops and mobile phones. Recently, the application area has been extended to power tools and battery-assisted electric bicycles, hybrid and fully electric vehicles. That's the way, the Lithium-ion battery (LIB) based on the principle of electrochemical intercalation have become popular and replaced other batteries in the market, due to their high energy density which allows them to be used in the areas of communications, cumputers, electronics and un more power demanding devices such as power tools and transportation. The LIB was accepted immediately because of its high-energy density, good performance, and no memory effect as occurred with nickel-cadmium (Ni-Cd) or nickel-hydride (Ni-MH) batteries. Figure 1 represents a comparison of the various batteries with respect to their volumetric and gravimetric energy densities. It can be observed that, Li-ion batteries provide high values for the above mentioned density characteristics. The significant progress of Lithium batteries is mainly due to the numerous innovations by contribution of scientists chemists, physicists and elecrochemists in matriels, design and safety aspects of the batteries. In addition, relevant research and advanced technology have helped to improve the progress of battery technology.

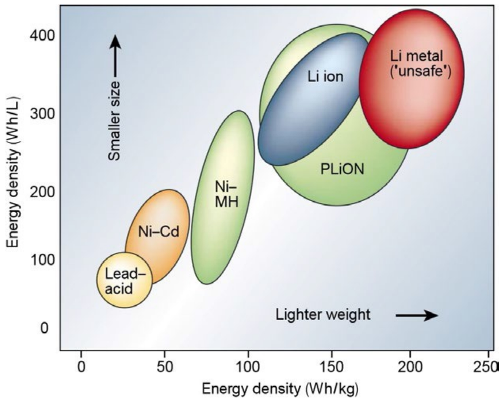


Figure 1: Volumetric and gravimetric energy density (for different battery technologies) [1].

2. History and Overview of Lithium Secondary :

Lithium is the lightest of all metals with a density of only 0.53 g/cm^3, has the greatest electrochemical potential with also her very low standard reduction potential (Li^+/Li couple -3.05 V vs SHE) and provides the largest energy content of the metals give a high cell voltage and capacity (specific capacity 3.86 Ah/g). These properties make the Lithium the most attractive material for use in the rechargeable batteries.

Despite its main characteristics, the research into batteries began modestly and climbed sharply in popularity. The first step in tapping the actual potential of Lithium battery began in the year 1912 by G.N. Lewis who was the dean of the department of chemistry at the University of California Berkeley [2].

In the 1970's, **M.S. Whittingham** and coworkers are a key figure in the history of the development and commercialization of Lithium batteries, discovering the concept of intercalation electrodes [3-6]. The basic process of these batterie involves Lithium oxidation at the anode, with the formation of Lithium ions that travel through the nonaqueous electrolyte to reach the cathode to finally insert into its layer structure. Because the guest Lithium ions keep their charge when intercalated in the TiS_2, to maintain electroneutrality, a modification of the electronic structure of the TiS_2 host also occurs by a variation in the oxidation state of the transition metal, which passes from Ti(IV) to Ti(III). In addition, to allow the electrochemical reaction to go on to multiple cycles, hence to assure the cycle life of the battery, a highly reversible evolution of both the electronic structure (to balance the positive charge of the inserted Lithium ions) and the crystal structure (to prevent the lattice to collapse) is required. Basically, the batteries using intercalation electrodes (e.g., TiS_2) can be regarded as concentration cells where the activity of Lithium varies from zero (at the TiS_2 pristine state) to 1 (at the fully intercalated $LiTiS_2$ state). The total electrochemical process may in fact be written as :

$$xLi + TiS_2 \Leftrightarrow Li_xTiS_2$$

where *x*, the intercalation degree, may vary from 0 to 1 (Figure2). The battery cell was composed of Lithium metal as the anode and TiS_2 as the cathode, with $LiPF_6$ as the electrolyte in propylene carbonate as the solvent. A cell voltage of 2.5 V could be recorded, with a theoretical energy density about 480 Wh/kg.

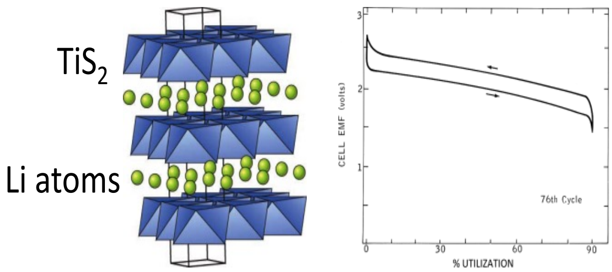


Figure 2: Structure of cathode material Li_xTiS_2, and the 76th cycle of a Li_xTiS_2 cell at 21 °C and at 10 mA/cm^2 [7].

To meet market demands, the concept of the Whittingham battery based Li-metal followed developing in the 1980's. Therfore, it was found that rechargeable batteries using Lithium metal anode are capable of providing both high voltage and excellent capacity. These characteristics led to an extraordinarily high energy density. However, failed due to safety concerns because of the violent chemical reactions that were taking place due to the temperature changes, and the Lithium metal anode was shown to have uneven dendrite or whisker growth during cycling. Such dendrites could pierce the separator sitting between Li-metal and TiS_2 (Figure3). Because of this, a triggering electrical short circuits, ignite organic-liquid electrolytes, and cause combustions or explosions. This severe safety concern halted the development of the battery based Li-metal anode, in spite of numerous research efforts.

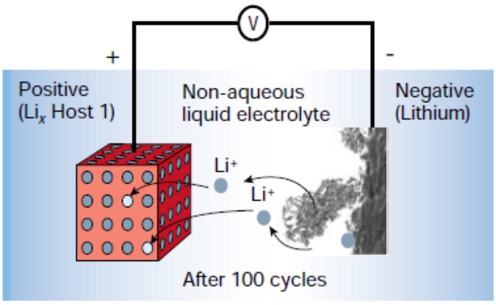


Figure 3: Dendrite formation on Lithium anode [8]

In the 1980's **J.B. Goodenough** whose research team proposed a battery without Li metal. Since Lithium metal constituted a safety problem, attention shifted to the use of a Lithium-intercalation material as an anode, and the Li-based batteries were revived. Goodenough and coworkers filed their $LiCoO_2$ patent for an intercalation cathode material and demonstrated in Materials Research Bulletin a Li-containing layered oxide, Lithium cobalt oxide ($LiCoO_2$, Figure 4) [9-10], as a potent cathode material. The team devised what they say is a dramatic improvement in cathode performance, and, thus the battery's performance. Since the function of the cell relied merely on Li^+ (without metallic Li), it was coined the Li-ion battery. The structure of $LiCoO_2$ consists of layers of Lithium that lie between slabs of octahedra formed by cobalt and oxygen atoms. Goodenough found that by using $LiCoO_2$ as a lightweight, high energy density cathode material, he could double the capacity of Lithium-ion batteries . This material is easy to prepare, cost, good cyclability and to cycle with an average voltage about 3.9 (V vs Li/Li^+) and in which the theoretical reversible capacity can reach 274 $mAhg^{-1}$. A $LiCoO_2$ cathode is now the most common Lithium storage material for Lithium rechargeable batteries.

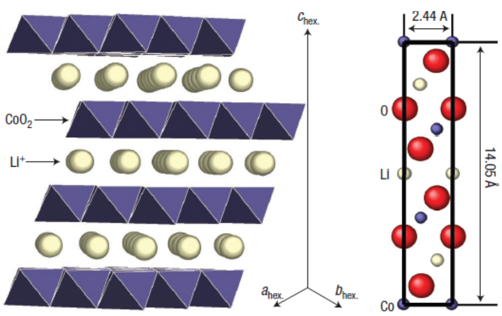


Figure 4: Models of the layered $LiCoO_2$ structure with space group [13].

In the 1985's, **A. Yoshino** and coworkers therefore studied the suitability of several carbonaceous materials as negative electrode [13-15]. Yoshino found that carbonaceous material with a certain crystalline structure provided greater capacity without causing decomposition of the propylene carbonate electrolyte solvent as graphite did. The carbon anodes offer stable morphology resulting in consistent safety properties over their useful life. The reversible intercalation/deintercalation reactions overcome the problem of dendrite formation of Lithium and provide dramatic improvements in safety and cycleability. Especially, the carbonaceous anodes accept Li^+ between the graphite layers to form C_6Li and capable of storing Lithium ions in its structure, which is worth a maximum theoretical capacity of 372 $mAhg^{-1}$ and low average voltage (150 mV vs Li/Li^+). Yoshino developed after successfully a new cell design using an intercalation carbon anode was used as an insertion material for rechargeable batteries and a $LiCoO_2$ cathode and filed patents worldwide, and this invention became an essential constituent technology for fabricating electrodes and assembling batteries. This new combination of component materials enabled stable charging and discharging, over many cycles for a long period. In this idea, Sony since **1991's** developed and commercialize a first Lithium-ion battery, with novel high-powered rechargeable cells were completed. $LiCoO_2$ was used as a cathode-active material and a tailor-made carbonaceous material was developed as an anode. Lithium was inserted in this carbon anode when a cell was charged and Lithium was extracted from the anode during discharge. We gave the name of Lithium-ion battery or LIB to this battery system.

Currently, the commercial cells (shown in Figure 5) will be made up of various sophisticated materials including $LiCoO_2$ (i.e.,cathode), carbonaceous materials (i.e., anodes), polymer films (i.e., separators), adhesives (i.e., binders for cathode and anode materials), and organic solvents and Lithium salts (i.e., electrolytes). They also introduced electronic circuitry to control the charge-discharge, the use of a current interrupt device to interrupt current flow on buildup of excessive internal cell pressure, and the use of a shut-down. Basically, during discharge, Lithium ions, Li^+, carry the current from the negative to the positive electrode, through the nonaqueous electrolyte and separator. During charging, an external electrical power source (the charging circuit) applies a higher voltage (but of the same polarity) than that produced by the battery, forcing the current to pass in the reverse direction. The Lithium ions then migrate from the positive to the negative electrode, where they become embedded in the porous electrode material in a process known as intercalation. When a Li-ion battery is discharged, the positive material is reduced and the negative material is oxidized. The reverse happens on charge. The following equations are in units of moles, making it possible to use the coefficient x (0.5). The charge-discharge process in a Li ion battery is further illustrated graphically in Figure 5.

The cathode half-reaction is :

$$LiCoO_2 \Leftrightarrow Li_{0.5}CoO_2 + 0.5Li^+ + 0.5e^-$$

The theoretical specific capacity (mAh/g) of anode graphite can be estimated as the following :

$$C_{specific} = xF/nM = 0.5\times(96485\ C/mol)/1\times(98\ g/mol) = 137\ mAh/g$$

The anode half-reaction is :

$$C_6 + 0.5Li^+ + e^- \Leftrightarrow Li_{0.5}C_6$$

The theoretical specific capacity (mAh/g) of anode graphite can be estimated as the following :

$$C_{specific} = xF/nM = 1\times(96485\ C/mol)/6\times(12\ g/mol) = 372\ mAh/g$$

The overall reaction is :

$$LiCoO_2 + C_6 \Leftrightarrow Li_{0.5}C_6 + Li_{0.5}CoO_2$$

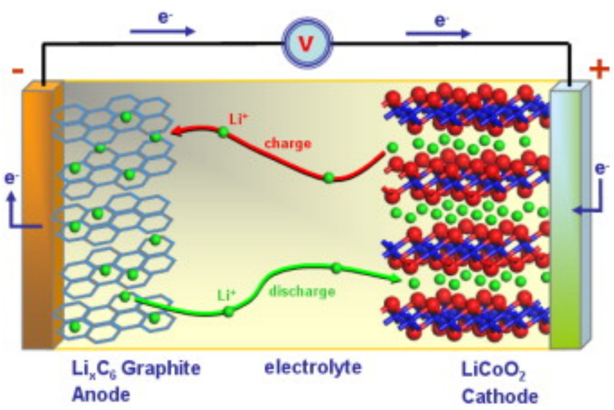


Figure 5: Movement of Li^+ in an electrolyte and insertion/extraction of Li^+ within electrodes in a Lithium secondary battery [16].

In regard to commercialization Lithium secondary batteries, they are classified according to cell shape and component materials as shown in Figure 6. The various forms of batteries include cylindrical, coin, prismatic and the pouch cell geometry [16]. Greneraly, the Li-ion battery is mainly composed of cathode, anode, separator, electrolyte and current collector. Cathode and anode material is the most significant part in the total cost constitution of Li-ion battery, accounting for more than 40%. It has an important influence on Li-ion battery capacity, working temperature, circulation efficiency, and security. Typically, the Li-ion batteries have many advantages, including high voltage, typically in the range of 2.5-4.2 V, high specific energy and energy density (e.g., over 150 Wh/kg and over 400 Wh/l, respectively), high rate capability, high power density, and low self-discharge rate (2-8% per month), long cycle life (>1000 cycles), no memory effect, and a broad temperature range of operation. Li ion batteries can be charged from 20 to 60 °C and discharged from -40 to 65 °C.

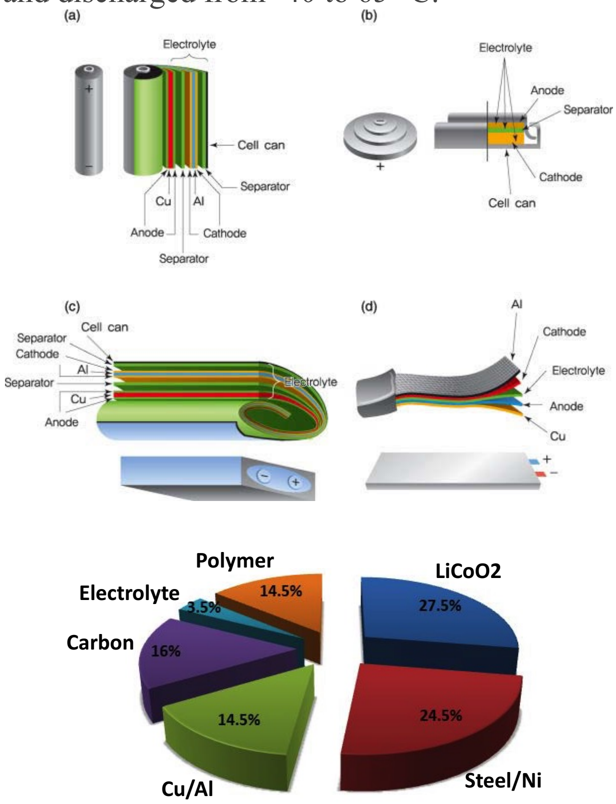


Figure 6: Different shapes of Lithium secondary batteries: (a) cylindrical, (b) coin, (c) prismatic, (d) pouch and distribution of components of Li-ion battery [16].

3. Summary and Outlook :

A great deal of effort has been invested in recent years in the success of commercial Li-ion batteries. Thus, it is the result of intensive research and contribution by many great scientists over few decades. The discoveries of John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino have affected almost everyone in the world. By, the successful adoption of Lithium-ion batteries in most consumer electronic devices and the huge interest in integrating them in electric vehicles or large energy storage for the electrical grid have made the demand and the research and development in this type of battery technology like never before. However, It is an important task to make advance preparations for future batteries by considering the functions of new applications such as electric vehicles, robots, solar, wind, and marine energy, are viewed as a key component of next-generation smart grid technology. Therfore, the research is required to achieve next-generation Li-ion batteries, with, much more environment friendly than when it was first developed. The Academic sections and private companies should invest significantly into the new research and development of Li-ion batteries, which could lead to incrementally advanced products achieving significant direct impacts to our society. Clearly, no one knows what the future holds, but it is certain that nanomaterials and nanotechnology has a lot to offer to Lithium-ion battery technology, and the best is yet to come.

JMES members reiterate their congratulations to the winners of the Nobel Prize in Chemistry 2019

References :

1. B. Scrosati, "History of Lithium batteries", *Journal of Solid State Electrochemistry*. 15 (2011) 7-8.
2. G. N. Lewis, "The potential of Lithium electrode", *Journal of the American Chemical Society*. 192 (1913) 1126-1127.
3. M. S. Whittingham, F. R. Gamble, "The Lithium Intercalates of the Transition Metal Dichalcogenides". *Mater. Res. Bull.* 10 (5) (1975) 363-371.
4. M. S. Whittingham, "Batterie à Base de Chalcogénures". Belgian patent no. 819672, 1975.
5. M.S. Whittingham, "Electrical energy storage and intercalation chemistry". *Science*. 192 (1976) 1126-1127.
6. M. S. Whittingham, "Chemistry of intercalation compounds: metal guests in chalcogenide hosts". *Prog. Solid State Chem*. 12 (1978) 41-99.
7. M. S. Whittingham, C. Siu, and J. Ding., "Can Multielectron Intercalation Reactions Be the Basis of Next Generation Batteries? ". *Acc. Chem. Res.* 51 (2018) 258-264.
8. M. Armand, J. M. Tarascson, "Issue and challenges facing rechargeable Lithium batteries". *Nature.* 414 (2001) 359-367.
9. K. Mizushima, P. C. Jones, P. J. Wiseman, J. B. Goodenough., "Li_xCoO_2 ($0<x<1$): A new cathode material for batteries of high energy density". *Mater. Res. Bull.* 15(6) (1980) 783-789.
10. J. B. Goodenough, K. Mizushima, "Fast Ion Conductors". US patent no. 4357215, 1982.
11. J. B. Goodenough, K. Mizushima, and T. Takeda, "Solid-Solution Oxides for Storage-Battery Electrodes". *Jpn. J. Appl. Phys.,* 19 (1980) 305-313.
12. Y. Shao-horn, L. Croguennec, C. Delmas, E. C. Nelson and M. A. O'keefe "Atomic resolution of Lithium ions in $LiCoO_2$". *Nature Materials.* 2 (2003) 464-467.
13. A. Yoshino, K. Sanechika, T. Nakajima, Japanese patent no. 1989293, 1985.
14. A. Yoshino, K. Sanechika, T. Nakajima, Secondary Battery. US patent no. 4668595, May 26, 1987.
15. A. Yoshino, "The Birth of the Lithium-Ion Battery". *Angew. Chem. Int. Ed.* 51 (2012) 5798-5800.
16. A. K. Shukla, and T. P. Kumar, "Materials for Next Generation Lithium Batteries". *Current Science*. 94 (3) (2008) 317-327

(2019) ; http://www.jmaterenvironsci.com