

Development of lithium-ion batteries – 2019 Nobel Prize for Chemistry

Three scientists, John B. Goodenough (University of Texas, Austin, USA), M. Stanley Whittingham (Binghamton University, USA) and Akira Yoshino (Mejo University, Japan) have been awarded the Nobel Prize in Chemistry 2019, for the development of lithium-ion batteries (LIBs).

The trio, however, treaded different paths to achieve their goals that not only revolutionized portable electronics but enabled the development of electric cars and the storage of energy from renewable sources. It all started almost fifty years ago during the oil crisis when scientists and engineers across the world were looking for alternate energy sources for fossil fuels. Stan Whittingham was trained in solid state chemistry in Inorganic Chemistry Laboratory, University of Oxford, UK. He along with his advisor Peter G. Dickens worked on the intercalation of different ions into several complex metal oxides and explored its use as potential new electrodes. While the field of solid state chemistry research was dominant in Europe in 60s and 70s, the young graduate opted for the post-doctoral position with Robert A. Huggins at Stanford University, US, to work on the chemistry of ion transport in various solid compounds. The chemistry lab at Oxford was mostly confined to synthesis and structures and limited property measurements whereas the materials laboratory at Stanford was more of interdisciplinary in nature and provided the support to investigate detailed properties. Huggins and Whittingham studied the thermodynamic and kinetic aspects and transport properties of the synthesized solids and of different solid electrolytes, in particular ' β -alumina', a solid electrolyte which showed significant ionic conductivity. A concluding statement from one of their papers records, 'A further unusual and particularly useful characteristic of this class of materials is the ability that they afford for the synthesis of different solid electrolytes themselves. The technique of ion exchange within solids means that one can think in terms of preparing a material, or perhaps even a device, with one composition, and by use of ion exchange methods, convert it to something else *in situ*', probably suggesting that they had some inkling towards its application. They further

worked on the transport properties of intercalated bronzes which revealed high diffusivity of monovalent alkali and silver ions inside the channels.

It is quite possible that an opportunity to participate and present at NATO sponsored first international meeting on 'Fast Ion Transport in Solids' in 1971 at Beligrate (Italy) helped Whittingham to decide his future course of direction. The truly interdisciplinary event involved major players active in all aspects of motion of ions in solids. The meeting eventually led to the birth of a new field known as 'Solid State Ionics' which further expanded to cover a wide range of technologies which includes chemical sensors for environmental and process control, electrochromic windows, mirrors and displays, fuel cells, high performance rechargeable batteries for stationary applications and electrotraction, chemotronics, semiconductor ionics, water electrolysis cells for hydrogen economy and other applications. The meeting provided him the right platform to get exposed to the nascent field presenting a myriad of practical applications ranging from batteries, fuel cells, sensors, etc. These events probably influenced him to accept the job at Exxon Research and Engineering Company, Linden, New Jersey rather than the academic position offered by the Department of Materials Science, Cornell University.

At Exxon, the materials group got sufficient infrastructure and financial support to initiate a programme on alternative energy production and storage. Initially, they studied the intercalation of a range of metals and other electron do-

nors into the van der Waals gap of the layered transition metal disulphides. Aqueous solutions of the alkali metal and ammonium hydroxides would react with TaS_2 resulting in a considerable expansion of the interlayer distance and an enhanced superconducting transition temperature. Very little was known of the chemical nature of these compounds. Significantly, this reaction could be readily reversed on heating indicative of the salt-like nature, $\text{M}^{x+}\text{TaS}_2^{x-}$, of the intercalates. They prepared a series of Li_xMS_2 compounds by reacting layered disulphides with *n*-butyl lithium. The experiments suggested that they could harness the energy created during intercalation. They opted for the lighter TiS_2 which can act as the host for lithium because the layers are held by weak van der Waals forces. Subsequently they built a cell and measured the voltage which turned out to be much higher. Lithium was supplied as the negative electrode in the form of the metal in a flat plate and as ions in a non-aqueous electrolyte of lithium perchlorate dissolved in propylene carbonate, an organic solvent. During discharge, lithium ions were inserted between the layers of the titanium disulphide whilst they were removed from the plate of lithium metal. The reaction occurred very rapidly and in a highly reversible manner at ambient temperatures as a result of structural retention. Titanium disulphide thus has become one of a new generation of solid cathode materials. They further carried out a systematic and thorough investigation of thermodynamic properties to understand the cathodic behaviour of the intercalation compounds.



John B. Goodenough



M. Stanley Whittingham



Akira Yoshino

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They noted, 'If nonstoichiometric phases are formed on discharge, then the rate of reaction and reversibility are likely to be enhanced as it is unnecessary to nucleate new phases. Reversibility is thus optimized when a single ternary phase is formed which is nonstoichiometric and exists over the entire phase region from reactant to final product, as in Li_xTiS_2 ; the structure of this phase should remain essentially unchanged during reaction and no chemical bonds should be broken. These criteria become less important at higher temperatures. As the group VIA anions form such compounds much more often than the halides it is amongst the former that reversible ambient temperature cathodes are likely to be formed.' This gave a powerful cell and soon large batteries of them were being demonstrated at commercial auto shows as a tentative way to power electric vehicles. Thus Stanley Whittingham invented the first rechargeable LIB, patented in 1977 and assigned to Exxon. The battery had high energy density and the diffusion of lithium ions into the titanium disulphide cathode was reversible, making the battery rechargeable. In addition, titanium disulphide has a particularly fast rate of lithium ion diffusion into the crystal lattice. Exxon threw its resources behind the commercialization of a $\text{Li}/\text{LiClO}_4/\text{TiS}_2$ battery. Unfortunately, after a few cycles, lithium dendrites grew across the strongly oxidizing LiClO_4 liquid electrolyte, shorting the cell and blowing it up. Safety concerns left Exxon to abandon the project. Whittingham and his team continued to publish their work in academic journals of electrochemistry and solid-state physics. He eventually left Exxon in 1984 and spent four years at Schlumberger as a Manager. In 1988, he accepted the position of Professor at the Chemistry Department, Binghamton University, USA to pursue his academic interests. He continues to work on LIBs and is currently the Director of both the Institute for Materials Research and the Materials Science and Engineering program at Binghamton University.

Goodenough graduated from the Physics Department in 1952 under Clarence Zener (inventor of diode) and moved to Lincoln Laboratory at MIT where he spent the next 24 years. During his tenure at MIT, he worked in various labs including the Digital Computer Development Group, the Magnetism and Resonance Group and the Electronics

and Materials Group. The vast experience provided him the opportunity to oversee pioneering work on computing and conducting seminal research on the electrical and magnetic properties of oxide materials. Initially, he was involved in the development of the ferromagnetic memory cores of the first random access memory (RAM) of the digital computer along with electrical engineers. His other major contribution is the formulation of fundamental rules of magnetism, now known as the Goodenough–Kanamori rule (1955) which helped rationalizing the magnetic properties of a wide range of materials on a qualitative level. Later he concentrated on the fundamental aspects of solid state chemistry and wrote two landmark books – *Magnetism and the Chemical Bond* (1963) and *Metallic Oxides* (1973). During the oil crisis in the early seventies, he started investigating materials to enable energy conservation and electrical energy storage. Around this time, he identified several framework oxides that supported fast sodium ion transport. A classic example is that of sodium zirconium phosphate, $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$, commonly referred to as NASICON.

In 1976, John Goodenough was offered the post of head of the Department of Inorganic Chemistry in the University of Oxford; the department where Whittingham learnt his fundamental solid state chemistry. By this time, there was significant activity amongst the researchers of US, Europe and Japan to utilize the concept of the lithium ion battery devised by Whittingham, in particular to overcome the reactive lithium. Goodenough diagnosed the double problem of trying to replace the metallic lithium negative electrode in that type of battery with an intercalation host. Doing so, whilst retaining a sulphur containing positive electrode, lowered the voltage too far. Around this time, many groups were exploring electrochemical insertion of lithium into various transition metal oxide hosts. The objectives were twofold: a low-temperature synthetic route to oxides containing high valence states of heavier transition-metal ions of a long series and to determine lithium ion mobilities high enough to sustain large voltages reversibly at reasonable current densities. Earlier studies on a large number of solid electrolytes led Goodenough to recognize that lithium ions in close-packed oxygen arrays are likely to be

mobile. He thought the 1:1 ordered rock-salt based LiMO_2 ($M = \text{V}, \text{Cr}, \text{Co}$ and Ni) series that showed a comparable layered structure to that of TiS_2 would be ideal. Goodenough suggested his visiting scientist, Koichi Mizushima from Japan, to employ these oxides instead of sulphide. With funding from the United States Air Force and the European Energy Commission, his team had both lithium cobalt oxide or lithium nickel oxide as new positive electrodes and achieved four volts from a single cell. They promptly patented the idea but were unable to convince battery manufacturers. So Goodenough tried an electronics company. As cell phones became smaller with miniaturized electronics, they became hungrier for power as colour screens and internet connectivity were added. What was missing was a battery of sufficient energy concentration that would fit in these devices. Goodenough was one of the early few who brought solid state chemistry and materials science to the fore of battery technology. The Sony Corporation, Tokyo, appreciated the potential of a single cell that could deliver four volts, even if some of that had to be relinquished by incorporating the lithium at the negative electrode into an intercalation host. The question remained as to which kind of host will restrain the reactive guest of lithium at the negative electrode. After ten years at Oxford, Goodenough returned to US to University of Texas at Austin as Virginia H Cockrell Centennial Chair of Engineering and still passionately continues his research on LIBs.

Akira Yoshino, a chemist from Kyoto University, took up the job at Asahi Chemical Industry Co. in 1981. At this time, many groups were experimenting with lithium as the positive electrode (anode) which posed considerable problems – the system was highly flammable and prone to short-circuiting over the course of multiple charging/discharging. He began his research employing polyacetylene, an organic conductor as a negative electrode. Around the same time, R. Yazami and P. Touzain from France demonstrated the reversible graphite-lithium negative electrode for electrochemical generators. Yoshino extended this concept of intercalation and arrived at the right composite material after studying a series of carbonaceous materials in a systematic way. The secondary battery thus fabricated based

on this new combination enabled stable charging and discharging, over many cycles for a long period. This invention (1985) led to the construction of a new secondary battery using LiCoO_2 as the positive electrode and lithium intercalated carbon as the negative electrode. Yoshino also demonstrated for the first time how to test the safety of the developed batteries. In 2017, Yoshino joined Mejo University as Professor.

Whittingham laid the foundation by systematically developing methods of solid-state electrochemistry to assemble the first prototype rechargeable battery. Goodenough discovered a new compound, lithium cobalt oxide and revolutionized the design of a powerful battery than the early prototype. With Goodenough's cathode as a basis, Yoshino

devised the first commercially viable and safe lithium-ion battery by employing petroleum coke, a carbon material that, like the cathode's cobalt oxide, can intercalate lithium ions. It is to be acknowledged here that the three brilliant individuals could not have achieved the success but for the support of the large interdisciplinary team. Goodenough's original lithium cobalt oxide structure is still used in the lithium ion batteries virtually found in every smart phone and tablet around the world. Other variations of the cathode material, lithium manganese oxide designed in his laboratory and refined at Argonne National Laboratory are used in electric cars. His lithium-iron-phosphate cathode is used in many modern power tools.

The Nobel committee, in awarding the prize to 'the trio', called this breakthrough a 'decisive step towards the wireless revolution'.

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Out of breath: molecular description of cellular responses to hypoxia – 2019 Nobel Prize for Physiology or Medicine

Living organisms need to adapt to changes in the environment in order to ensure their survival. To do this effectively, an essential requirement is the ability to sense changes in environmental conditions and respond to these with appropriate adjustments in physiology. Examples of changes that need to be sensed include illumination, temperature and chemicals in our surroundings in the form of taste and smell. In addition to these specific sensory stimuli, animals respond to relatively ubiquitous elements of the environment such as air and water and the cells and tissues of living creatures need to be able to detect changes in these and tune ongoing cellular function appropriately.

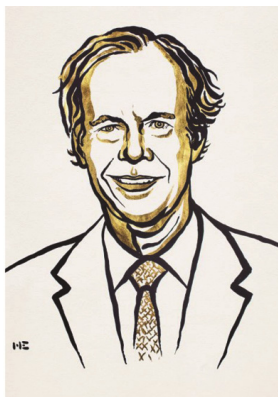
We are all surrounded by air and one of its key constituents is oxygen. Oxygen was discovered in the late eighteenth century by Carl Scheele; it was isolated by Joseph Priestley and Antoine Lavoisier who also named it 'oxygen'. Oxygen forms 20.9% of air and is essential for animal life due to its role in the biochemical reactions that convert nutrients into energy within cells. Oxygen is made available to cells through air inhaled into the respiratory system from where it is absorbed into the bloodstream. Here it is bound to haemoglobin in red blood cells and transported via circulation to the

tissues of the body where it dissociates, enters into cells and is used in the biochemical reactions of cellular respiration. In some tissues such as muscle, oxygen is also stored bound to myoglobin.

Given its critical role in cellular biochemistry, animals have evolved multiple mechanisms to ensure that their cells and tissues have adequate amounts of oxygen available. At the level of the whole animal, this is most evident in the well-recognized phenomenon of animals breathing heavily during intense exercise, an effort to enhance the supply of air and thus oxygen to their lungs. These are key mechanisms to ensure adequate

blood flow to and oxygenation of tissues and the importance of these discoveries was recognized by the award of a Nobel Prize in Physiology or Medicine to Corneille Heymans in 1938.

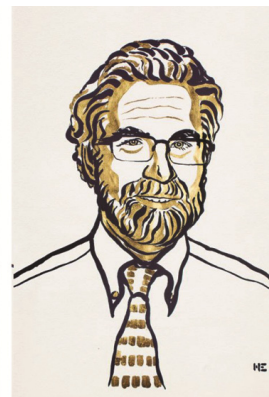
In addition to these immediate mechanisms, chronic deprivation of oxygen, for example, by living at high altitudes, has long been recognized to result in adaptive changes in animals. The Nobel Prize in Physiology or Medicine for 2019 has been awarded for discoveries on the mechanisms by which animals cells respond to changes in oxygen levels. The prize has been awarded to Gregg Semenza (Johns Hopkins University School of



William G. Kaelin Jr



Sir Peter J. Ratcliffe



Gregg L. Semenza

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