



Scientific Background on the Nobel Prize in Chemistry 2019

## LITHIUM-ION BATTERIES



## Lithium-Ion Batteries

The Royal Swedish Academy of Sciences has decided to award **John B. Goodenough**, **M. Stanley Whittingham**, and **Akira Yoshino** the Nobel Prize in Chemistry 2019, for the development of lithium-ion batteries.

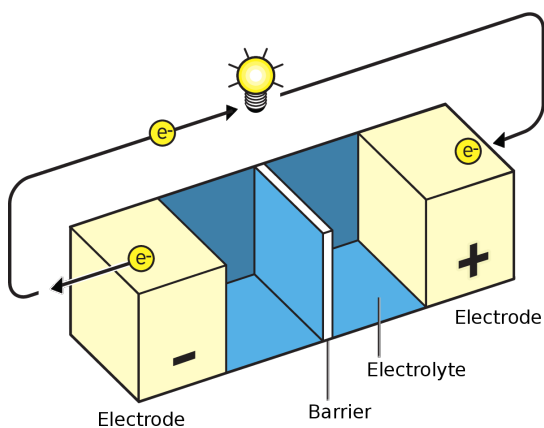
### Introduction

Electrical energy powers our lives, whenever and wherever we need it, and can now be accessed with evermore ease and efficiency - even in the absence of nearby power outlets. We increasingly move in unbound and wireless ways, and enjoy high mobility in a potentially healthier local environment. This dramatic development has been made possible by efficient energy storage devices, where high-capacity batteries enable, for example, a variety of electrically-driven tools and vehicles. In principle, we all can enjoy the use of mobile phones, cameras, laptops, power tools, etc., relying on efficient batteries to power them. As a consequence of modern battery technology, electric vehicles are also becoming increasingly popular, and we are in the middle of a switch away from vehicles powered by fossil fuels. In addition, efficient energy storage is an important complement to fluctuating energy sources, such as wind and sunlight. With batteries, the supply-demand chain can thus be balanced over time, even in situations when no energy can be produced.

To a large extent, these developments have been made possible by the lithium-ion battery. This type of battery has revolutionized the energy storage technology and enabled the mobile revolution. Through its high potential, and high energy density and capacity, this battery type has already contributed to improving our lives, and arguably will continue to do so in the years to come. However, battery development is very daunting and challenging in general, and perhaps particularly so when it comes to lithium-based cells. Ever since Alessandro Volta presented his famous “pile” around 1800,<sup>1</sup> tremendous effort has been invested in the development of batteries. Many scientists and engineers, working in academia, industry, and even independently, have contributed to this development, realizing that the identification of solutions for efficient batteries is a highly difficult task. The development has thus been relatively sluggish and only very few efficient battery configurations have been successfully designed over the years. For example, we still rely on the lead–acid battery discovered in the mid-19th century.<sup>2,3</sup> Nevertheless, due to several ground-breaking multidisciplinary scientific discoveries, encompassing electrochemistry, organic/inorganic chemistry, materials science, etc., these challenges could indeed be met, and the lithium-ion battery become a reality that essentially changed our world.

## Background

The working principle of a battery is relatively straightforward in its basic configuration (Figure 1). The cell is composed of two electrodes, each connected to an electric circuit, separated by an electrolyte that can accommodate charged species. Frequently, the electrodes are physically separated by a barrier material that prevents them from coming into physical contact with one another, which would cause the battery to short-circuit. In the discharge mode, when the battery serves to drive the electric current, an oxidation process takes place at the negative electrode (anode), resulting in electrons moving from the electrode through the circuit. A complementary reduction process takes place at the positive electrode (cathode), replenished by electrons from the circuit. The cell voltage largely depends on the potential difference of the electrodes, and the overall process is spontaneous. For rechargeable (secondary) batteries the process can be reversed and external electricity can be used to produce complementary redox reactions at the electrodes. This process is energy-dependent and non-spontaneous.



**Figure 1.** Working principle of basic battery in the discharge mode (Galvanic element). Spontaneous redox processes at the electrodes result in electric current through the circuit. In the charge mode (electrolytic cell), electricity-driven redox processes take place at the electrodes resulting in reversal of the spontaneous process.

The voltaic pile was made of alternating discs of two metals, one of which tin or zinc and the other copper or silver, separated by layers of cardboard or leather soaked in an aqueous electrolyte.<sup>1</sup> Each pair of metal discs and an electrolyte layer made up a battery cell, and the pile was composed of about 20 stacked cells. During operation, in the case of the Zn/Cu cell, the zinc metal acted as an anode, releasing electrons to the circuit and producing metal ions (oxidation), whereas the opposite electrode reaction was dependent on the working conditions. In the presence of air, the copper metal became partially oxidized to CuO, and reduction of CuO to Cu took place at the electrode. In the absence of air, the protons in the electrolyte were instead reduced to hydrogen



gas at the copper surface. The cell voltage was approximately 0.8–1.1 V, depending on air exposure.<sup>4</sup> The voltaic pile was essentially a primary battery and not rechargeable. When connecting the poles of the whole device, Volta could demonstrate how the resulting current could generate a spark. After a demonstration of the discovery to Napoleon Bonaparte, the First Consul of the Cisalpine republic was so impressed that he immediately made Volta a count.<sup>5</sup>

The ubiquitous lead–acid battery, still used as a starter battery in cars, was studied by Wilhelm J. Sinsteden as early as 1854 and demonstrated by Gaston Planté in 1859–1860.<sup>2–4,6</sup> The battery has a working principle similar to the voltaic pile exposed to air, but was the first so called secondary battery that could be recharged. The term secondary was derived from early studies by Nicolas Gautherot, who in 1801 observed short secondary currents from disconnected wires used in electrochemical experiments.<sup>7</sup> The lead–acid battery is based on two lead electrodes, at least one of which partially oxidized to lead oxide ( $\text{PbO}_2$ ), separated by a sulfuric acid-containing electrolyte. During discharge, oxidation takes place at the lead electrode (anode), producing electrons, protons, and lead sulfate ( $\text{PbSO}_4$ ), whereas the lead oxide is reduced to  $\text{PbSO}_4$  at the cathode. In this case, the cell potential is about 2 V, and a typical 12-V car battery is composed of six cells connected in series.

Another milestone in battery development came in 1899, when Waldemar Jungner described the first nickel-iron (Ni-Fe) and nickel-cadmium (Ni-Cd) batteries.<sup>8,9</sup> Shortly after, Thomas A. Edison also described such batteries.<sup>10</sup> These alkaline batteries became predecessors to the later nickel-metal hydride (Ni-MH) battery, which was commercialized in 1989.

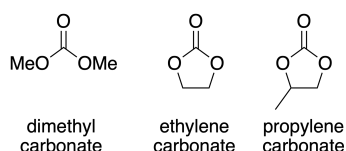
## Lithium

By the mid-20th century, the limited energy densities and capacities of the developed batteries inspired the search for better configurations, and lithium became a target. This metal, discovered by Johan August Arfwedson and named by him and Jöns Jakob Berzelius in 1817,<sup>11,12</sup> was considered to have excellent properties to serve as a battery element (Figure 2). With atomic number 3, lithium is the lightest metal with a density of only 0.53 g/cm<sup>3</sup>. It also has a very low standard reduction potential ( $\text{Li}^+/\text{Li}$  couple -3.05 V vs SHE), thus making it suitable for high-density, high-voltage battery cells. However, lithium is a relatively reactive metal, which has to be protected from water and air, for example. The taming of lithium was therefore of utmost importance for the battery development.

1 H		
3 Li	4 Be	
11 Na	12 Mg	
19 K	20 Ca	21 Sc
37 Rb	38 Sr	39 Y

**Figure 2.** Lithium and the periodic table.

Early studies regarding the electrochemistry of lithium occurred already in 1913 by Gilbert N. Lewis,<sup>13,14</sup> but the interest in lithium for battery applications became most evident in the 1960s and 1970s. To use lithium, water and air had to be avoided, and non-aqueous electrolytes had to be developed. This was not trivial, and factors, such as inertness, melting point, redox stability, solubility of lithium ions and salts, ion/electron transfer rates, viscosity, etc., had to be considered. Studies of non-aqueous electrolytes were described in 1958, when William S. Harris, supervised by Charles C. Tobias, defended his Ph.D. thesis on the electroplating of different metals in different cyclic ester solvents (Figure 3).<sup>15</sup> Of the solvents tested, propylene carbonate showed potential properties for electrochemical applications with alkali metals, and was, e.g., used in combination with lithium halides. This discovery was gradually accommodated by the community and carbonates have remained useful as electrolytes to this day. Around the same time, Y. Yao and J.T. Kummer studied ionic conductivity in solids, and showed that sodium ions can move at the same rate in solids as in salt melts.<sup>16</sup> Kummer also proposed the use of this configuration for batteries in a patent from 1969.<sup>17</sup> At the same time, John Newman developed a theory for ion transfer in electrochemical cells.<sup>18</sup>



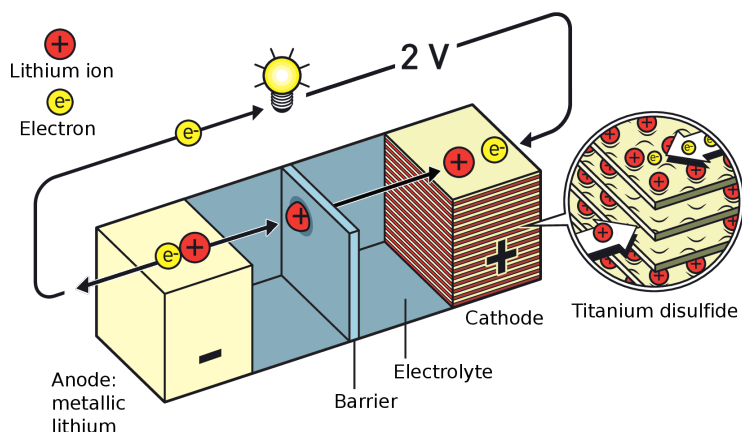
**Figure 3.** Carbonate solvents used for batteries.

A conference held in Belgirate, Italy, arranged by Brian C. H. Steele in 1972 came to be particularly important to the development. This meeting gathered the leading battery scientists at the time, and solutions to taming lithium for energy storage devices were discussed. Of particular interest was the use of lithium ions as electrolyte components, preserving the stoichiometry in the proposed secondary batteries.

## Intercalation cathodes

At the time, it was assumed that metallic lithium should serve as the anode in the batteries and special focus was therefore put on identifying matching cathode materials. Following the studies on ionic conductivity in solids, materials with high reduction potential that were able to accommodate lithium ions at high transfer rates were of special interest. For this reason, a range of lithium-containing structures were studied, and the behavior of the materials upon alkali metal intercalation under reductive conditions was evaluated. This challenge was certainly not trivial, as these materials should ideally fulfil a range of prerequisites to enable subsequent, efficient incorporation in batteries.<sup>19</sup> The materials should thus: 1) have accessible electronic band structures enabling a large, constant intercalation free energy change over the entire stoichiometry range; 2) be able to accommodate the guest ion over a wide stoichiometric range with minimal structural change (topotactic intercalation); 3) display high diffusivity of the alkali ion within the structure; 4) allow the intercalation reaction to proceed reversibly; 5) display good electronic conductivity; 6) be insoluble in the electrolyte, and display no co-intercalation of electrolyte components; and 7) be able to operate under close to ambient conditions.

Of particular interest were the metal chalcogenides of the type  $\text{MX}_2$ , as some of these became known to have layered structures with potential binding sites for lithium. One of the members of this family, titanium disulfide ( $\text{TiS}_2$ ) was shown to be able to host lithium ions by Walter Rüdorff in 1965.<sup>20</sup> This structure was lamellar with  $\text{TiS}_2$  arranged in layers, between which lithium ions could become intercalated. Rüdorff could demonstrate chemical intercalation through the treatment of the materials with lithium dissolved in liquid ammonia, resulting in the structure  $\text{Li}_{0.6}\text{TiS}_2$ . The intercalation effect was further demonstrated by Jean Rouxel and coworkers,<sup>21</sup> and by **M. Stanley Whittingham** and Fred Gamble,<sup>22</sup> who could show that lithium can be chemically intercalated in the  $\text{Li}_x\text{TiS}_2$  material over the whole stoichiometric range ( $0 < x \leq 1$ ) with a small lattice expansion effect. The material was analogous to  $\text{CdI}_2\text{-NiAs}$ , and the lithium ions progressively occupied the octahedral sites of the interlamellar spaces (van der Waals gaps). These promising studies inspired **Whittingham** to explore electrochemical intercalation in such materials,<sup>23</sup> and as early as 1973 propose such materials as electrodes in batteries (with Exxon Research and Engineering Company).<sup>24</sup> A working, rechargeable battery was subsequently demonstrated in 1976 (Figure 4).<sup>25</sup>

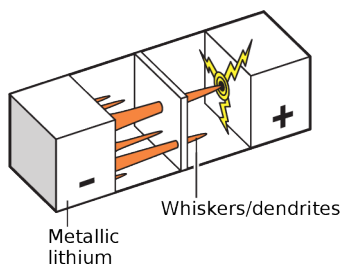


**Figure 4.** Lithium-based battery using  $\text{Li}_x\text{TiS}_2$  as the cathode.

The battery cell was composed of lithium metal as the anode and  $\text{TiS}_2$  as the cathode, with  $\text{LiPF}_6$  as the electrolyte in propylene carbonate as the solvent. A cell electromotive force (emf) of 2.5 V could be recorded, showing an initial current density of  $10 \text{ mA/cm}^2$ , and the results indicated the single-phase reaction:  $x \text{Li} + \text{TiS}_2 \rightarrow \text{Li}_x\text{TiS}_2$ . The reaction proceeded by intercalation of the lithium ions into the titanium disulfide lattice with an estimated diffusion coefficient of  $10^{-7} \text{ cm}^2/\text{s}$ . The reverse process could furthermore be demonstrated, starting with the lithiated  $\text{LiTiS}_2$ -electrode, showing complete reversibility. In a more applied example,  $\text{TiS}_2$  powder was mixed with Teflon and attached to a steel support surrounded by a polypropylene film and lithium metal. When immersed in a mixture of dimethoxyethane and tetrahydrofuran containing  $\text{LiClO}_4$ , the cell was cycled at a low charge/discharge ratio for 1100 times without significant loss of reversibility.

These results became the starting point for the development of commercial batteries, and large cells of up to 45 Wh were developed at Exxon.<sup>26</sup> These cells initially used lithium as the anode,  $\text{TiS}_2$  as the cathode, and lithium perchlorate ( $\text{LiClO}_4$ ) in dioxolane as the solvent, but because the perchlorate proved unstable, it was later replaced by tetramethyl borate despite a less optimal lithium plating with this electrolyte.

However, the reactive metallic lithium could not be completely tamed with this setup and lithium dendrites were formed at the metal surface upon repeated charge-discharge cycles (Figure 5). The dendrite growth could unfortunately be large enough to penetrate the separation layer and reach the opposite electrode, resulting in a short circuit and a potential fire hazard. The problem proved difficult to solve, and the commercial development of such batteries essentially came to a halt.



**Figure 5.** Formation of lithium whiskers/dendrites potentially leading to short-circuiting.

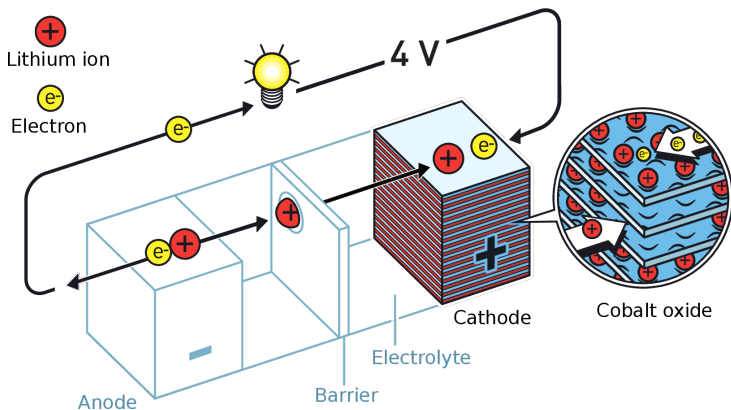
In part for this reason, scientists turned their focus to alternative solutions and an “ion transfer cell” configuration (a.k.a. “rocking chair” cells),<sup>27</sup> in which both electrodes can accommodate ions, was increasingly proposed.<sup>28</sup> The principle of this type of cell had been demonstrated by Rüdorff in 1938, where hydrogen sulfate ions were electrochemically shuttled between two graphite electrodes.<sup>29</sup> In this type of cell, metallic lithium is avoided and both electrodes are made from intercalation materials able to accommodate lithium ions. Ions also were well-known to become intercalated in carbon materials, such as graphite,<sup>30,31</sup> and such materials appeared particularly attractive. Although the cell emf and the capacity of the intercalation electrode would be lower than for metallic lithium, the configuration would be considerably safer. The capacity of these materials was also attractive, as they were able to accommodate up to one lithium ion per six carbon atoms.

However, reversible electrochemical lithium-ion intercalation in graphite proved not to be straightforward, and co-intercalation of the electrolyte components led to exfoliation and destruction of the electrodes. The materials could thus not be effectively used in the cells, and the quest for better materials or better electrolytes continued.

In parallel with the anode development, better cathode materials were also sought after in order to acquire a higher cell emf in combination with anodes of higher potential than metallic lithium. A breakthrough came in 1979/1980 when **John B. Goodenough** and his co-workers at Oxford University, UK, discovered that  $\text{Li}_x\text{CoO}_2$ , another intercalated metal chalcogenide of type  $\text{MX}_2$ , could serve as a cathode material (Figure 6).<sup>32,33</sup> The structure of the material was analogous to  $\text{Li}_x\text{TiS}_2$  with van der Waals gaps between the cobalt dioxide ( $\text{CoO}_2$ ) layers in which lithium ions could be bound without dramatic lattice expansion. **Goodenough** reasoned that when X in  $\text{MX}_2$  is a small electronegative element, a resulting cation uptake process would be associated with a large negative free-energy change and a high cell voltage. With an X of oxygen, the situation was deemed especially promising, also given that lithium ions were proposed to be sufficiently mobile in close-packed oxygen arrays. The reasoning proved to be correct, and the  $\text{CoO}_2$  material showed a very high potential of  $\sim 4\text{--}5$  V relative to  $\text{Li}^+/\text{Li}$  and an approximate diffusion constant for lithium ions of about  $5 \times 10^{-9}$   $\text{cm}^2/\text{s}$  at room temperature. The electrochemical studies were



carried out in this case with an electrolyte composed of  $\text{LiBF}_4$  in propylene carbonate using lithium metal or  $\text{Li}_{0.1}\text{V}_2\text{O}_5$  as counter/reference electrodes.



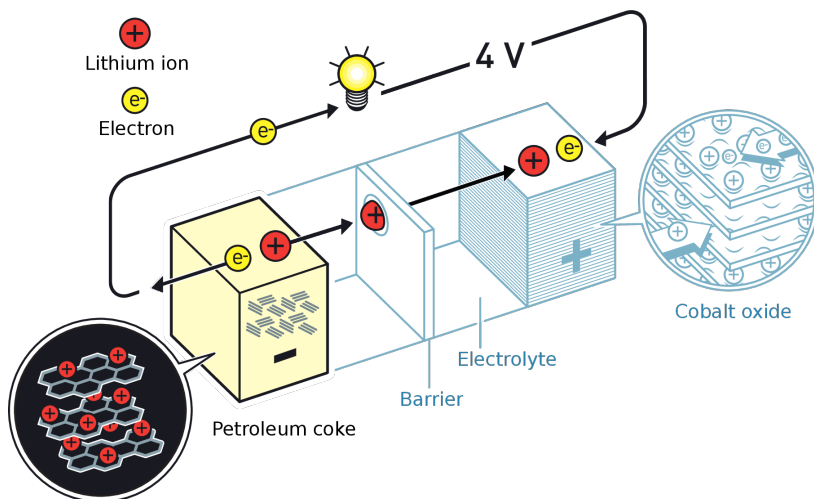
**Figure 6.** Lithium-based battery using  $\text{Li}_x\text{CoO}_2$  as the cathode.

#### Carbonaceous anode materials - ion transfer cell batteries

This discovery enabled the use of anode materials with higher potentials than lithium metal, furthering the search for suitable carbonaceous materials. Considering the difficulty of solving the problem of the electrochemical intercalation of graphite, other options were investigated instead. A breakthrough came in 1985,<sup>34,35</sup> when a group led by **Akira Yoshino** at Asahi Kasei Corporation, Japan, identified that certain qualities of petroleum coke were stable under the required electrochemical conditions. **Yoshino** had initially made attempts with the relatively recently discovered conducting polymer poly(acetylene) as anode material, but soon turned his eye on vapor-phase-grown carbon fibers (VGCF) and eventually heat-treated petroleum coke. The latter material was known to contain a mixture of crystalline (graphitic) and non-crystalline domains, and the researchers could identify particularly stable, yet high-performing, qualities with specific degrees of crystallinity. The surrounding regions were assumed in this case to protect the crystalline domains from exfoliation, and lithium ions could be efficiently and repeatedly intercalated in the materials. Furthermore, the materials showed sufficiently low potential relative to  $\text{Li}^+/\text{Li}$  ( $\sim 0.5$  V), while being able to accommodate a large amount of lithium ions.

With these effective anode materials, **Yoshino** could develop an efficient, working lithium-ion battery based on the ion transfer cell configuration (Figure 7). The identified carbonaceous material was thus used as an anode and **Goodenough's**  $\text{Li}_x\text{CoO}_2$  material (typically containing small amounts of tin) was used as a cathode. Separator layers composed of polyethylene or polypropylene were used, and the electrolyte was composed of  $\text{LiClO}_4$  in propylene carbonate. In order to test the new configuration's safety, **Yoshino** devised a testing unit by which a weight could be remotely dropped on the batteries. It could thus be shown that the newly developed

batteries were damaged without causing any fires or explosions, whereas batteries based on anodes of lithium metal reacted more violently.<sup>36</sup>



**Figure 7.** Ion transfer cell lithium-ion battery configuration.

These discoveries and developments ultimately led to the release of a commercial lithium battery in 1991.<sup>37</sup> The battery was based on a petroleum coke-based anode material,  $\text{Li}_x\text{CoO}_2$  as the cathode, and a water-free electrolyte composed of  $\text{LiPF}_6$  in propylene carbonate. The charging voltage was high (up to 4.1 V), with a recorded energy density of  $\sim 80$  Wh/kg or  $\sim 200$  Wh/L. Compared to other batteries that were on the market at the time, the lithium battery quickly became very competitive and essentially paved the way for the upcoming mobile revolution.

At around the same time, it was found that graphite could actually be used in combination with a suitable electrolyte composition.<sup>38</sup> By using solvents containing ethylene carbonate, hitherto generally disregarded due its higher melting point, a solid electrolyte interphase (SEI)<sup>39</sup> was formed at the surface of the graphite electrode during the charge/discharge cycle, thereby protecting the carbon material from exfoliation and further decomposition. This discovery was rapidly adopted by the community, and a next generation lithium-ion battery based on graphite as the anode material could be developed. With this anode material, batteries with charging voltages of 4.2 V were produced soon after, resulting in energy densities of  $\sim 400$  Wh/L.

The development of the lithium-ion battery did not stop with these seminal and important discoveries, but many improvements and alternatives have since been reported. For example, new cathode materials have continuously been identified for use in specific battery applications, and two such materials have originated from **Goodenough's** group: the spinel material  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  and the olivine material  $\text{Li}_x\text{FePO}_4$  (LFP).<sup>40,41</sup> The latter material is limited by a somewhat lower



potential versus  $\text{Li}^+/\text{Li}$  than  $\text{Li}_x\text{CoO}_2$ , but has high stability and can be used at high charging rates. Several other electrode materials and electrolyte systems have also been discovered, leading to ever-improved energy storage materials for the benefit of society.

### Summary and Outlook

The discoveries of **John B. Goodenough**, **M. Stanley Whittingham**, and **Akira Yoshino** have arguably had a tremendous impact on our world. The lithium-ion battery thus has been an important part of the mobile electronics revolution, as well as the ongoing switch from vehicles powered by fossil fuels to electrically-powered transportation. We have yet to see the overall consequences of this development, but efficient energy storage is a known prerequisite for many of the energy sources used to produce electricity. Over the past decades, this development has progressed rapidly, and we can expect many more important discoveries to come in battery technology. These future breakthroughs will undoubtedly lead to further improvements in our lives, not only for our convenience, but also with respect to global and local environments and, ultimately, the sustainability of our entire planet.

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