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And The 2019 Nobel Prize in Chemistry Goes To...

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It was the week after the announcement of the winners of the 2019 Nobel Prize in Chemistry, and we were gathered together in Atlanta for the 236th meeting of the Electrochemical Society. Given that the prize was given to three scientists who performed seminal work leading to the development of the lithium-ion battery, John Goodenough, Stan Whittingham, and Akira Yoshino, and the Atlanta Hilton was buzzing with excitement. After all, ECS meetings have been and still are the best settings for hearing about and discussing all things “battery”. One of the winners of the award, Stan Whittingham, was attending the meeting, and was stopped in his tracks constantly by people wanting to shake his hand and offer congratulations or to take selfies with him. That got me to thinking (after taking my own selfie with Professor Whittingham) about the long journey from these initial discoveries, made in the 1970s and ‘80s, to where we are today.

The Lithium-Ion Battery Market Today

Lithium-ion batteries enabled the revolution in consumer electronics starting in the late 20th century; there is no doubt that cell phones, tablets, and laptop computers are great conveniences that have made a positive impact on how we conduct our lives and do business in the 21st century. Lithium-ion batteries are now widely used in power tools, cameras, toys, and medical devices as well. The lithium-ion battery market was estimated to be about 37.4 billion USD in 2018, and is projected to grow to 92.2 billion USD in 2024, as demand for electric vehicles (EVs) and hybrid electric vehicles (HEVs)

increases.¹ The stellar performance and decreasing cost of lithium-ion batteries have transformed EVs from a niche market only for enthusiasts to products attractive to the average driver. Automobiles like the Tesla Model 3, the Nissan Leaf, and the Chevrolet Bolt are readily available to the public for purchase at affordable prices, and nearly every large automaker has EVs or HEVs for sale or under development. Lithium-ion batteries are also being used for behind-the-meter storage (e.g., Tesla's PowerWall). Another application where lithium ion batteries will make an impact is grid storage, although they not only have to compete with other types of batteries such as redox flow systems, but other types of energy storage such as pumped hydro. Still, the ever-dropping price of lithium-ion batteries and their excellent reliability make them a natural choice for society's energy storage needs.

Initial Discoveries that Led to Lithium-Ion Batteries

Whittingham's insight that intercalation chemistry (specifically, lithium insertion into TiS_2) could be exploited for use in batteries with lithium metal anodes set the stage. Goodenough discovered LiCoO_2 , another classical intercalation compound, which undergoes reversible insertion/de-insertion of lithium ions at higher potentials vs. Li^+/Li than TiS_2 , improving energy density. However, as Goodenough described it, "battery manufacturers at that time could not conceive of assembling a cell with a discharged cathode."² The lithium metal anode was, however, unreliable, to say the least. Upon repeated cycling, highly reactive mossy deposits or dendrites of the metal formed, leading to sudden shorts or, worse yet, explosions. When Yoshino revealed that carbons with certain physical characteristics could function as anodes without the drawbacks of lithium metal, the modern version of the lithium-ion battery was born. The system could be

cycled much more reliably than lithium metal batteries, and using a pre-lithiated cathode like LiCoO_2 was actually an advantage, because cells could be easily assembled in the discharged state and then charged before use.

The Journey from Initial Discoveries to Lithium-Ion Batteries Today

In 1991, Sony commercialized the first lithium-ion batteries.³ These cells, made with petroleum coke as the anode and LiCoO_2 as the cathode, had practical energy densities of about 200 Wh/L and specific energies of about 80 Wh/Kg, less than half that of state-of-the-art lithium-ion batteries today. Researchers from many different scientific disciplines and countries, in industry, national labs, and academia, worked to advance lithium-ion battery technology, ultimately resulting in a more than doubling of practical energy density as well as a dramatic drop in cost (from more than \$1000/kWh a decade ago to about \$175/kWh today).⁴ While LiCoO_2 is still the cathode of choice for small batteries, low or no-cobalt alternatives such as LiFePO_4 , variants of LiMn_2O_4 spinels, and layered transition metal oxides containing multiple metals such as NMCs ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$) and NCA ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) are preferred in devices intended for automotive applications or large-scale energy storage because of cost and sustainability concerns. The original petroleum coke anodes have been replaced with graphite or graphite/silicon composites, which offer higher capacities and better first cycle efficiencies. Optimization of electrolytic solutions resulted in improved performance, as did work on binders and separators, and advances in design of electrodes, cells, and battery packs. While improvement and better understanding of these devices and the materials within them are still high priorities today, research has expanded to include “beyond lithium-ion batteries”, many of which are based on the intercalation concept, but

with ions like Mg^{2+} or Na^+ . Most of these next-generation systems are still in their infancy, but the remarkable success story of lithium-ion batteries provides a roadmap for their development as well. In short, the pioneering work of Goodenough, Whittingham, and Yoshino so many years ago, will continue to have positive repercussions for years to come.



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² John Goodenough, **Acc. Chem. Res.** 46, 1053 (2013).

³ See **Interface**, “Lithium-Ion Batteries: The 25th Anniversary of Commercialization” Vol. 25, 2016.

⁴ Bloomberg New Energy Finance Report <https://about.bnef.com/electric-vehicle-outlook/#toc-viewreport>