



The Origins of the Lithium Battery

Nobel Lecture, December 8, 2019 by
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AS NOTED BY THE ROYAL SWEDISH ACADEMY of Sciences, “Lithium-ion batteries have revolutionized our lives since they first entered the market in 1991. They have laid the foundation of a wireless, fossil fuel-free society, and are of the greatest benefit to humankind.” The idea for rechargeable lithium batteries started in 1972 in the Corporate Labs of Exxon, within a group studying the impact of intercalating electron donors on the superconductivity of the layered disulfides. This breakthrough was based on a fundamental understanding from a solid-state viewpoint of the reactions in solids and particularly of the fast motion of ions within solids. The discovery of fast ion transport in β -alumina, and the need for mixed conducting solids with a wide-stoichiometry range to measure its conductivity played a key role in developing lithium batteries. All of today’s lithium-ion batteries rely on the original intercalation concept used in titanium disulfide. There are still many scientific opportunities to improve the energy density, performance and lifetime of lithium batteries.

INTRODUCTION

Alessandro Volta (1745–1827) built the first electrochemical cell, known as the Volta Pile. Examples of the Pile may be found in the temple built in his memory at the southern end of Lake Como, as shown in Figure 1. He

described these in a presentation to the Royal Society in London in French in 1800.¹ These cells are still made by almost every science student, including those grade students at the British Ambassador's house in Stockholm on December 8th, 2019. In 1859, Plante invented the lead acid battery which still has the largest share of the battery market. In 1966 Leclanche described the original C-MnO₂ cell, which was improved by Urry into today's alkaline cell. In 1899 Jungner described the Ni/Cd cell, which had an active life in portable devices, but has now been mostly phased out because of its toxicity.

The origins of the lithium-ion battery are intimately associated with the discovery and development of fast ion transport of ions in solids. Whereas, Volta originated the study of batteries, it was Michael Faraday (1791–1867) who built the foundation of the science of electrochemistry. It was also he who first reported the discovery of ionic conductors in the early 19th century in silver sulfide, and predicted that many others would be found:²

“432. The effect of heat in increasing the conducting power of many substances, especially of electricity of high tension, is well known. I have lately met with an extraordinary case of this kind, for electricity of low tension, or that of the voltaic pile, and which is in direct contrast with the influence of heat upon metallic bodies, as observed and described by Sir Humphry Davy (2).”

“433. The substance presenting this affect is sulfuret of silver.”

“434. There is no other body with which I am acquainted that, like sulphuret of silver, can compare with metals in conducting power for electricity of low tension when hot, but which unlike them, during cooling, loses in power, whilst they, on the contrary gain. Probably however, many others may, when sought be found.”

It was half a century later that Nernst (1864–1941; Chemistry Nobel Prize, 1920) used the high oxygen ion conductivity of yttria stabilized zirconia, 0.85ZrO₂:0.15Y₂O₃, as a light source³. When a current is passed through the ceramic in air, it heats up until it becomes white hot and glows. It also was the first case of potential thermal runaway. The conductivity of ionic conductors increases with increasing temperature, so a simple current cannot be used, and the control system was sufficiently complex that it was only commercialized by Westinghouse for a short period at the beginning of the 20th century, 1900–1913.



Figure 1. Volta's Temple in Como, Italy.

THE TUNGSTEN BRONZES, 1964–1972

The tungsten bronzes, $M_x\text{WO}_3$, where M is typically an alkali metal or protons, were first described by Wohler in 1824,⁴ and reviewed by our Oxford group in 1968.⁵ They have been of great interest ever since because of their brilliant colors, which are a function of the value of x ⁶ as shown in Figure 2; it is this change of color which allowed their use in electrochromic displays, such as in the 787 aircraft. As x can vary from 0 to 1, and the free electron concentration is directly proportional to x , they represented an excellent opportunity to study the impact of the relative importance of electronic vs geometric factors in heterogeneous catalysis.⁷ The electronic properties were of greater importance, but subsequent studies of their reduction by hydrogen showed how important the structure was in determining the route by which they were reduced.⁸ This reduction was enhanced by the rapid transport of the alkali ions in the lattice, and was the first indication that these materials were mixed conductors, that is showing both high electronic conductivity and high ionic conductivity. Na_xWO_3 forms a range of crystalline structures. At the highest sodium contents the structure is cubic and the same as perovskite, as shown in Figure 3 (left); the sodium ions diffuse in four sided tunnels. As the sodium content is reduced, the structure becomes more complex and tetragonal, and there are three different possible alkali sites; the sodium ions are shown in the larger five-sided channels. At the lowest sodium levels, distorted perovskite structures are observed. For the larger potassium ions, a third structure with hexagonal tunnels is found⁵. Large single crystals of these bronzes can be formed by electrolysis of molten tungstates and the thermodynamics of this process has been determined⁹.

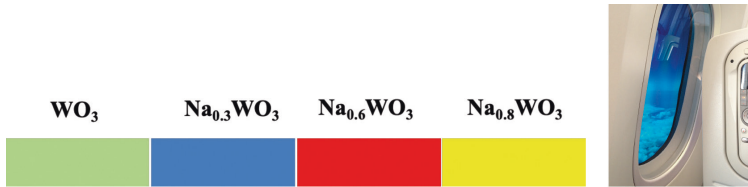


Figure 2. Schematic of the colors of the tungsten bronzes, and right an electrochromic window in the 787 aircraft.

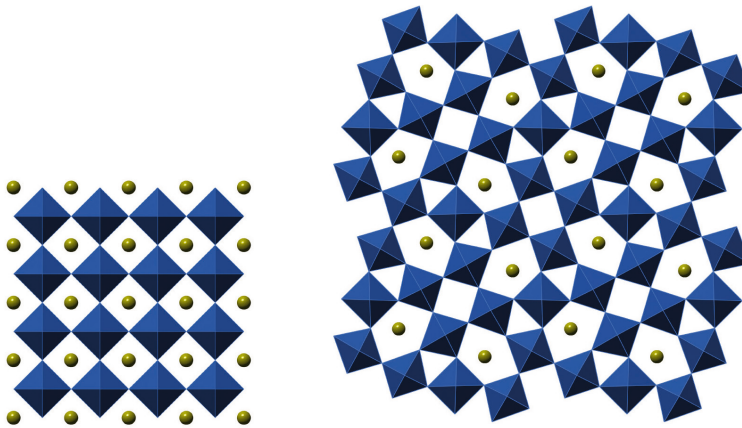


Figure 3. The cubic and tetragonal structures of Na_xWO_3 . The gold circles represent the sodium ions, and the blue octahedra represent WO_6 cornered shared units.

β -ALUMINA, 1968–1972

Sodium β -alumina was initially thought to be just another form of Al_2O_3 , but Pauling showed that it had a layered structure, comprising γ - Al_2O_3 blocks separated by Al-O-Al pillars, as shown in Figure 4 (top). Its nominal composition is $\text{NaAl}_{11}\text{O}_{17}$. The publication of its fast sodium ion conductivity by Yao and Kummer in 1967,¹⁰ represented a major breakthrough and kicked-off the whole new field of Solid State Ionics. As Huggins and Whittingham predicted¹¹ in 1972 “ β -alumina – Prelude to a Revolution in Solid State Electrochemistry”, the field took off exponentially.

The mobile sodium ions reside midway between three pillars as shown in Figure 4 (bottom); there is typically a 15% excess of these ions. The excess ions reside between three other sodium ions as shown. These defects are critical to the conductivity, and the diffusion mechanism is an interstitially knock-on process, so no defects need to be created for a cation to diffuse through the lattice, which results in their low enthalpy of motion.

The ionic conductivity of sodium β -alumina is so high that it cannot be measured using the traditional metal electrodes, like platinum. Electrodes had to be found that were reversible to both electrons and ions. The solution

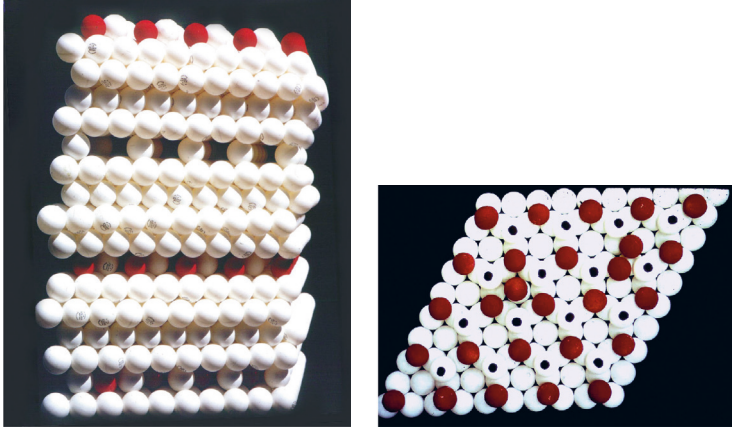


Figure 4. The structure of sodium β -alumina showing (top) the 4 layer γ - Al_2O_3 sheets separated by the Al-O-Al pillars, and (bottom) the diffusion plane of β -alumina showing the mobile cations (red), and the Al-O-Al pillars (oxygen – white spheres, aluminum – black circles). The two defect options for the excess cations are shown; the dumb-bell defect is observed for silver and the interstitial one for sodium.

was the mixed conductor Na_xWO_3 and specifically the larger tunnel structure $\text{Na}_{0.4}\text{WO}_3$, rather than the denser perovskite structure. Figure 5 (left) shows the schematic of the cell used; the sodium β -alumina single crystal was extracted from a brick used to line glass tanks. The resulting ionic conductivity is shown in Figure 5 (right). The sodium β -alumina has a single interstitialcy mechanism from 800°C to liquid nitrogen temperatures¹². The conductivity of sodium in β -alumina is higher than that of sodium in solid sodium metal. The equivalent lithium vanadium oxides, were also used as electrodes for measuring the lithium ion conductivity of Li- β -alumina.

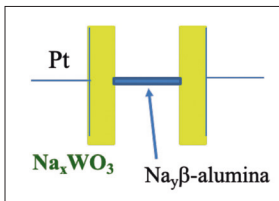
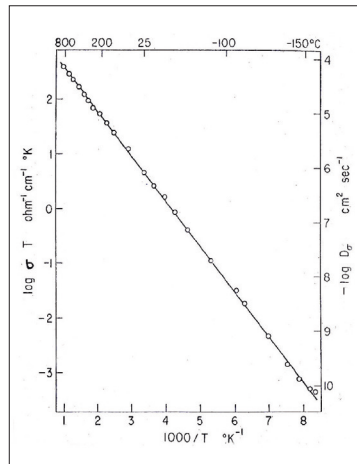


Figure 5. (Left) Schematic of the measurement cell, and (right) ionic conductivity of sodium β -alumina. Reprinted with permission from ref.¹² Copyright 1971, The American Institute of Physics.



The Ford Motor Company had proposed using β -alumina in a battery comprising a molten sodium anode and a molten sulfur cathode. It operates in the temperature range of 300–350°C. The Zebra version of the cell, which also uses a molten sodium anode but a NiCl₂ cathode has also been extensively researched¹³. It has the advantage that it can be built in the discharged state, Ni metal + NaCl, and so does not require dry rooms. Essentially all work stopped in 2016 due to the much lower cost and flexibility of lithium-ion cells and their ability to operate under ambient conditions.

STATUS OF BATTERY CHEMISTRY IN 1972, TITANIUM DISULFIDE AND WHAT IS INTERCALATION

In 1972, battery scientists did not recognize ternary phases and non-stoichiometry, so that the reaction of V₂O₅ with lithium was expressed as:



and for the common dry cell as



However, both of these reactions are now known to occur by insertion respectively of lithium and sodium ions into the lattice to form Li_xV₂O₅ and MnOOH.¹⁴

In 1972 the layered dichalcogenides were of interest because of their superconducting behavior. They were able to intercalate a range of electron donors such as alkyl amines and other organic and organometallic species. It was found by this author that the K_xTaS₂ superconductor could be synthesized by immersion of TaS₂ crystals in an aqueous KOH solution, indicating that the free energy of this reaction was sufficiently high to prevent the evolution of hydrogen gas in the presence of water. This suggested that the layered dichalcogenides could be used to store energy. Of the dichalcogenides, titanium disulfide was found to be particularly preferred because not only is it the lightest in weight but is also a metallic conductor.¹⁵ Titanium disulfide was found to be an almost ideal cathode because:

- There is no need for the addition of an electronic conductor, such as carbon black
- Li and TiS₂ form a single solid solution from TiS₂ to LiTiS₂, so no energy expended on forming new phases
- Li lithium was found to diffuse very quickly so that thick electrodes and even single crystals can be used,^{16,17} and

- Other ions, such as Na and Mg can be similarly intercalated to form the basis of secondary batteries.¹⁶

When lithium is inserted into the van der Waals gap of the layered structure of titanium disulfide there is less than a 10% expansion of the lattice, as shown schematically in Figure 6 (left). On removal of the lithium, the lattice reverts back to its initial state. The perfect reversibility of this reaction is known as an intercalation reaction. This reaction is now often used in dictionaries as an example of intercalation. The original definition of intercalation refers to the insertion of February 29th into the calendar every leap year. Intercalation reactions are important in many areas of chemistry and medicine¹⁸. The layered structure of the LiTiS_2 is shown in Figure 6 (right), the sulfur atoms are packed in a hexagonal close-packed stacking, (hcp) and only differs from the layered oxides in the stacking sequence. The LiMO_2 materials are cubic close packed (ccp), but on removal of lithium can convert to hcp, as found for CoO_2 . This is detrimental to the long-term reversibility of the reaction.

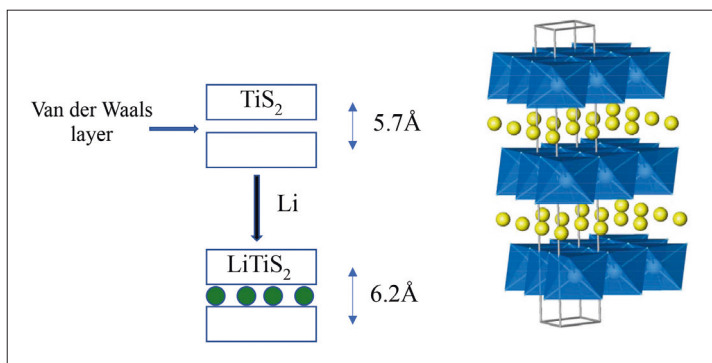


Figure 6. (Left) schematic of lithium intercalation into TiS_2 , and (right) layered structure of LiTiS_2 .

The initial studies of titanium disulfide were made using a lithium anode, and ether based electrolytes, in particular dioxolane.^{16,17,19} The almost perfect characteristics of the Li/TiS_2 couple allowed for high rate systems for hundreds of cycles as shown in Figure 7.²⁰ The difference between the charge and discharge curves is just due to the resistance losses in the electrolyte. The reduction in the cell voltage as the lithium content increases is due to the conduction band being steadily filled as shown schematically in Figure 7 right. Although the discharge curve appears smooth, the lithium ions do tend to order as identified by Thompson using the then new electrochemical potential spectroscopy technique.^{21,22} At the high rates used here the jump time is shorter than the ordering

time, hence the ordering is minimized. This has been observed more recently in the Li/FePO_4 system, where at higher rates the system behaves as a single phase reaction, Li_xFePO_4 , but at low rates phase separation occurs and a mix of FePO_4 and LiFePO_4 is observed.²³ The first operando studies of the reactions in batteries were performed on the Li/TiS_2 system by Chianelli *et al.* at Exxon in the late 1970s.^{24–26}

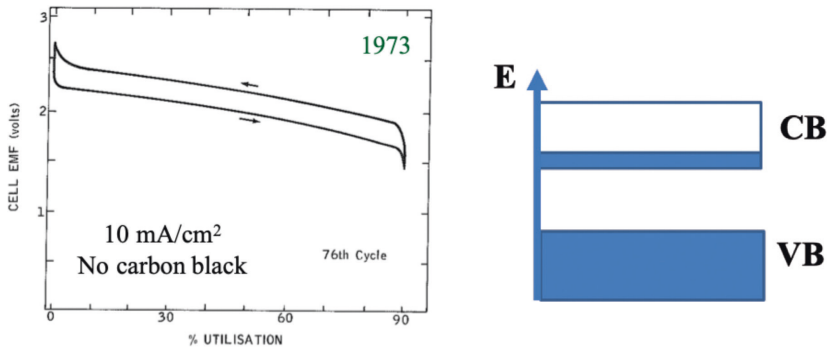


Figure 7. (Left) Discharge/charge curve of Li/TiS_2 at $10 \text{ mA}/\text{cm}^2$ (reprinted with permission from ref.20 copyright 1978 Elsevier); (Right) Schematic of the TiS_2 band structure.

Exxon Enterprises, the new venture arm of Exxon, built a range of lithium batteries in the 1970s and early 1980s. Figure 8 (left) shows a paper-weight used as a demonstration of lithium batteries; besides the battery it contains a solar cell that keeps the battery charged and a clock. This one was built in 1977 and is still operable today, indicating the long cycle life of well-constructed cells. Some of these cells are now in the Nobel Prize Museum in Stockholm. Several of these cells were tested by Rutgers University in 2015 and were found to still have more than 50% of their original capacity.²⁷ In addition, cells as large as $6'' \times 4'' \times 1''$ were constructed and exhibited at the Chicago 1977 EV show and turned a motorcycle battery on and off throughout the meeting (see Figure 8). The morphology of the TiS_2 used in the cells consisted of large platelets as shown in the Figure; these were produced by the reaction of titanium sponge with sulfur. When formed from the commercially viable route of TiCl_4 and H_2S , the platelet appear more star-like. Because of the tendency of lithium metal to form dendrites and/or finely divided lithium, pure lithium anode cells tend to be unstable. Thus, in the commercial cells Exxon used the safer LiAl alloy as anode.²⁸ This was formed in-situ when the electrolyte was added to cells containing sheets of aluminum and lithium. In addition, cells could be built lithium metal free, using a pre-intercalated cathode, i.e. LiTiS_2 .¹⁶

Titanium disulfide can be formed either as the layered structure or in the spinel form. The two differ in the stacking of the sulfur layers, the for-

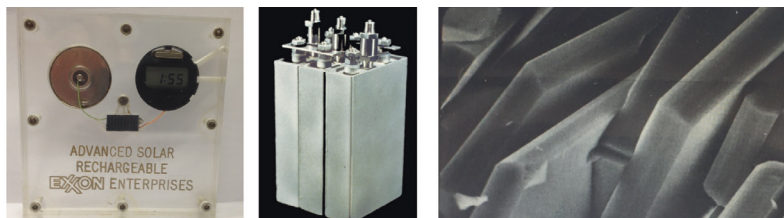


Figure 8. (left) Paper weight utilizing a Li/TiS₂ cell from 1977 and operating in the author's office in 2019; (middle) large TiS₂ cells exhibited at the 1977 EV show in Chicago, and (right) morphology of the TiS₂ crystals.

mer is hexagonal close packed and the spinel is cubic close packed, and as a result diffusion of the lithium ions is two dimensional and in the latter three dimensional. The spinel is formed by removal of the copper from CuTi₂S₄. The lithium diffusion is comparable in both phases.²⁹ Both titanium disulfide phases can also readily intercalate the magnesium ion, which has a comparable ionic size to lithium. Van der Ven's team showed that the potentials for the layered Mg/TiS₂ couple and the spinel Mg/Ti₂S₄ couple for magnesium contents from 0 to 0.5 Mg/Ti, are about 0.8–1.0 volts lower than those of the corresponding Li cells.³⁰ Nazar's team in 2016 published experimental data on the same systems with almost identical voltage characteristics.^{31,32} The spinel phase showed excellent reversibility at 60°C. However, the resulting energy densities are less than half of those of the corresponding Li/TiS₂ couples, indicating that it is unlikely that Mg intercalation cells are a viable alternative to Li cells.

THE DEVELOPMENTS OF LITHIUM-ION BATTERIES POST DISULFIDES

In the late 1970s research accelerated to provide higher energy density and/or lower cost replacements for Li/TiS₂. All the subsequent rechargeable Li-ion batteries use intercalation reactions for both electrodes. The key cell components and history are shown in Figure 9 and Table 1. MoliEnergy in Vancouver used British Columbia's naturally occurring molybdenite ore to develop a Li/MoS₂ battery; Dahn had done his PhD studying the Li/TiS₂ system. Goodenough, who was studying the magnetic behavior of LiCoO₂, recognized that it had a similar structure to LiTiS₂ and studied it in lithium cells.³³ It can provide for cells around 4 volts, and thus loses a lower percentage of its energy density when coupled with a safe intercalation anode, such as those based on carbon. It was the carbon-based anode developed by Yoshino at Asahi Kasei that made the Li-ion battery safe and enabled SONY to market a viable commercial product in 1991.

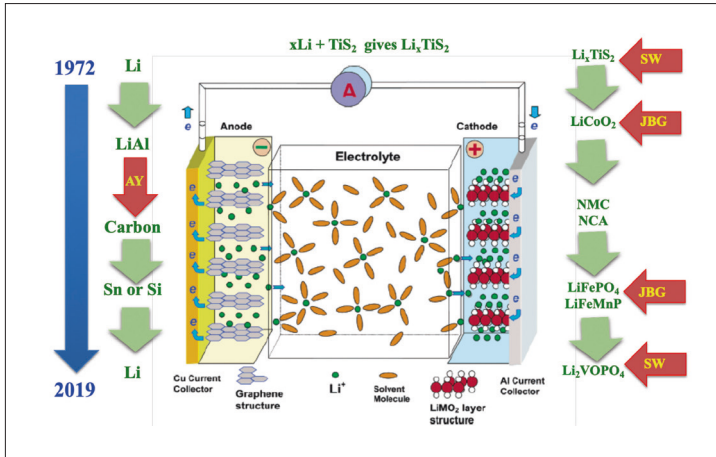


Figure 9. The components of a Li-ion battery showing the layered sulfide/oxide cathode and a layered graphite anode. These are shown as a function of time with the key contributions of the three laureates listed (AY=Yoshino; SW=Whittingham; JBG=Goodenough).

Table 1. Intercalation Reactions are the Basis of all Li-Ion Batteries

- 1970s Exxon (**Whittingham**)
 - LiAl/TiS₂
- 1980s Moli Energy (**Dahn**)
 - Li/MoS₂
- 1980s Oxford (**Goodenough**)
 - LiCoO₂
- 1980s Asahi Kasei (**Yoshino**)
 - C (coke)
- 1991 SONY
 - C/LiCoO₂

The C/LiCoO₂ cell eventually dominated the portable battery market, displacing the Ni/Cd and Ni/MeH batteries within the last ten years. The LiCoO₂ cathode still dominates applications where volumetric energy density is most important and cost is secondary such as smart phones and computers. However, the high cost of cobalt, its natural low abundance and the use of child labor in Congo demanded that its content be reduced. In addition, the use of materials is very inefficient, as seen in Table 2, which shows that today's cylindrical cells have less than 25 % of their theoretical energy density.

Chemistry	Size	Wh/L theoretical	Wh/L actual	%	Wh/kg theoretical	Wh/kg actual	%
LiFePO ₄	54208	1980	292	14.8	587	156	26.6
LiFePO ₄	16650	1980	223	11.3	587	113	19.3
LiMn ₂ O ₄	26700	2060	296	14.4	500	109	21.8
LiCoO ₂	18650	2950	570	19.3	1000	250	25.0
Si/C/LiMO ₂ SONY VC7	18650	2950	725	24.6	1000	264	26.4

The theoretical values in the table assume only the active components, and no volume or weight for lithium beside that in the cathode.

Table 2. Energy densities of some commercial cells, adapted from ref.³⁴

There are several ways to increase the energy density of these cells:

- The carbon is a major issue; it takes up half the volume of the cell as 72 gm of carbon are needed to hold 7 gm of lithium
- Need to use the full lithium in the cathode, not the 50–60% used today
 - o Need to find cathodes that can intercalate more than one lithium ion
- Need cathodes with higher ionic and electronic conductivities
 - o Will allow thicker electrodes, which will reduce the necessary amount of current collectors and separators

Since the 1970s the energy densities of Li-ion cells have been steadily increasing to over 250 Wh/kg.³⁵ There is no reason why the energy density should not exceed 350–400 Wh/kg for intercalation-based cells within the next five years, with an upper dream of 500 Wh/kg or 1 kWh/liter. This last is just 50% of the theoretical values and is the goal of the US DOE Battery 500 consortium. The first step must be modification of the graphitic carbon anode. This is an ongoing challenge, but additions of 5–10% silicon are showing promise. Below two approaches to “closing the gap” between actual and theoretical are described.

THE 1st CYCLE LOSS OF THE LAYERED OXIDE CATHODE

The LiCoO₂ cathode has been replaced for most applications by the NMCA class of material, where much of the cobalt has been replaced by nickel, manganese and/or aluminum. Two of particular interest are: LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ and LiNi_{0.85}Co_{0.10}Al_{0.05}O₂. The higher the nickel content the higher the energy density for any given charge voltage, but the less thermally stable the material becomes, as shown in Figure 10 (left). The instability is determined predominantly by the Ni content; the charging voltage has much less effect.

All these NMC cathodes lose 10–15% capacity on the first cycle as shown in Figure 10 (right).³⁶ If this could be recovered, then the cell’s

capacity could be increased by 10%, allowing energy densities of over 400 Wh/kg to be attained. It seems probable that a sharp drop-off in the diffusion coefficient of the lithium at lithium contents over around 0.8 in Li_xMO_2 is the reason; this is shown in Figure 11.³⁶

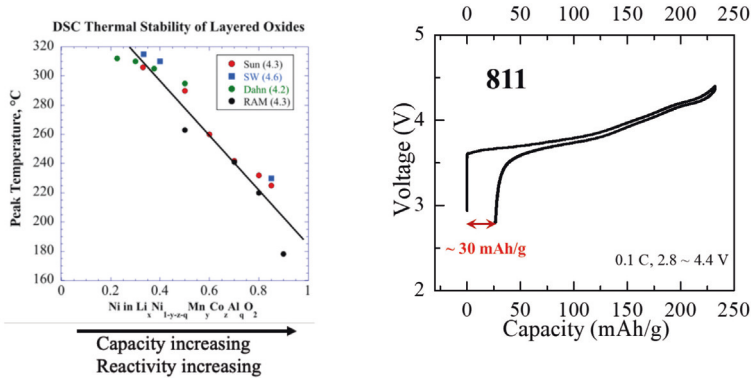


Figure 10. (Left) The thermal stability of several NMC materials charged from 4.2 to 4.6 volts from four different research groups, showing the almost linear behavior of thermal instability to the nickel content; (right) the typical 1st cycle of an 811 NMC material charged to 4.4 volts at a C/10 rate,³⁶ reproduced with the permission of the American Chemical Society.

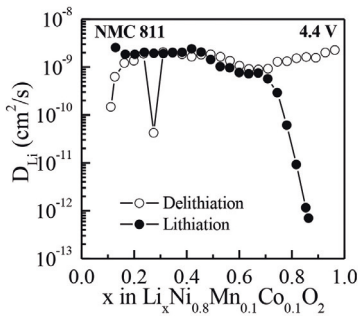


Figure 11. The lithium diffusion coefficient in $\text{Li}_x\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$,³⁶ reproduced with the permission of the American Chemical Society.

However, it appears to be not that simple, as LiCoO_2 (LCO), shows essentially no 1st cycle loss as indicated in Figure 12. This Figure compares 811 with LCO, when both are charged to a depth of 120 mAh/g. The 811 shows a 20% 1st cycle loss, which is reduced to 6% on raising the temperature to 45°C, suggestive of a rate controlling reaction. In contrast, for LCO the loss is less than 3% at 21°C, and reduces to 2% at 45°C. The challenge is to make the 811 and other NMC materials behave in this respect like LCO.

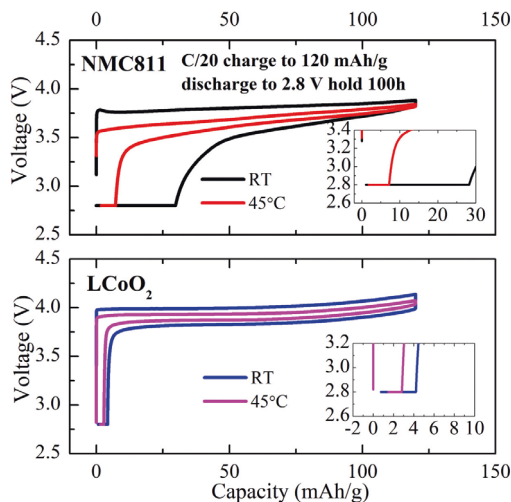


Figure 12. The 1st cycle behavior of NMC811 compared to LCO. Unpublished work at Binghamton (Hui Zhou).

TWO LITHIUM CATHODE MATERIALS, Li_xVOPO_4

An alternative to closing the gap on the layered oxides is to reversibly intercalate more than one lithium ion per redox center. Vanadium is a particularly attractive redox center because the vanadium can readily go between the +5 and +3 oxidation states, and it is the 4th most abundant transition metal. V_2O_5 itself can reversibly cycle 1.5 Li/V, but the structure is not stable and converts to disordered rock salt, $[\text{Li}_3\text{V}_2]\text{O}_5$ with a cell voltage ranging continuously from 3.5 to 1.5 volts.³⁷ The olivine, Li_xFePO_4 , has been extensively used commercially, particularly in China, because of its low cost and enhanced stability, but its capacity is only 170 mAh/g;²³ the science of this cathode material has been recently reviewed.²³ Vanadium forms several phosphates. We have found that one of these, $\epsilon\text{-VOPO}_4$, is particularly attractive as the cathode of a lithium battery. Its structure is shown in Figure 13. It contains VO_4 tetrahedra and highly distorted VO_6 octahedra, with chains of O-V=O-V , where the V-O bonds are alternately short and long along the chain. On lithium intercalation to Li_2VOPO_4 there are no longer any vanadyl groups. When formed by a solvothermal process, cuboid particles of 100–200 nm in size are formed and these give essentially the theoretical capacity of 305 mAh/g at low rates as shown in Figure 13.³⁸ There is no loss in capacity or change in shape of the cycling curves, indicating that the structure is stable to the repeated insertion and removal of two lithium ions. This opens up a new avenue for the exploration of high energy density cathodes.

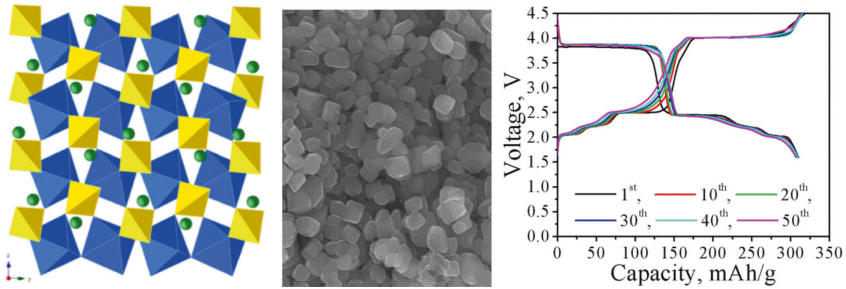


Figure 13. (Left) Structure of ϵ -VOPO₄, with the vanadyl chains coming in/out of the paper. Reprinted with permission from ref.³⁹ Copyright 2005 The Electrochemical Society. (Center) the solvothermally formed cuboid particles, and (right) the electrochemical behavior at a C/20 rate. Reprinted with permission from.³⁸ Copyright 2019 The Royal Society of Chemistry.

CONCLUSIONS

Over the last half century, lithium ion batteries have come from an idea to domination of energy storage for both portable and stationary applications ranging from milliwatt hours to proposed gigawatt grid storage. They enabled the electronics revolution and helped several 3rd world countries to bypass wired phones.

The academy said: ‘They (lithium batteries) have laid the foundation of a wireless, fossil fuel-free society, and are of the greatest benefit to humankind.’. Colleagues we hope that our discoveries will let all of us work together to build a cleaner environment, make our planet more sustainable, and help mitigate global warming, leaving a cleaner legacy to our children and grandchildren.⁴⁰

Many countries and states have mandates for reduction of carbon dioxide emissions, which will drive the growth of electric vehicles of all sizes; some more recent examples that I have personally experienced are shown in Figure 14. There is still much to do to improve batteries for enhanced vehicle penetration into the market. These needs include:

- Higher energy density, so the batteries can be smaller and lighter
- Improved range vs cost, including operating without range penalty in more extreme weather conditions
- Sustainable systems, which must include clean recycling
- Safer batteries, which will require different electrolytes and possibly solid-state systems.



Figure 14. Three examples of electric vehicles. (Left) My wife in one of the first rental electric vehicles on Bermuda that we drove on our 50th anniversary in March 2019 [yes, range anxiety is real]. (Center and right) Two Peterbilt electric vehicles that I drove at their test track north of Seattle in Washington State, October, 2019.

Grid storage is also essential to enable renewable energy storage such as wind and solar; batteries are an essential here as there appear to be severe limits on additional pumped-hydro facilities. I am proud that my own New York State is taking the lead here – having the largest mandate, > 3 GWh, for grid storage. Numerous solar-battery facilities are being constructed around New York State as well as throughout the world. Battery storage load shifting is already economically viable today. Some examples are shown in Figure 15. Grid storage will have several advantages:

- Will allow cleaner sustainable technologies
- o Will enable renewable energy storage
- Will lead to a more efficient grid
- o Will help to eliminate costly peaker plants, which are often the worst polluters
- Will assist in mitigating global warming (messaging)
- Will make communities more self-contained, protecting against calamitous events, such as hurricanes.



Figure 15. (left) A load shifting battery facility at a sub-station south of Saratoga Springs, New York, 2019; (middle) a 16 MWh battery facility in West Virginia, USA to smooth wind power and to shift the load, and (right) a former battery facility in Binghamton, NY.

ACKNOWLEDGEMENTS

I thank Exxon for initiating and supporting our team's work on rechargeable batteries. Those were inspiring days with our great team, and I thank them all: Arthur Thompson, Russ Chianelli, Fred Gamble, Bernie Silber-nagel, John Panella, Robert Hamlen and my boss and mentor for many years Alan Schriesheim. Much of my work at Binghamton has been supported by the U.S. Department of Energy since 1993. The NMC work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy through the Advanced Battery Materials Research (BMR) Program under Award No. DE-EE0006852 and BMR (Battery500 Consortium) under Award No. DE-EE0007765 respectively. The VOPO₄ work was supported as part of NECCES, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0012583. New York State and the University also provided much support for our battery facility, for which I am also very grateful. I would also like to thank the entire worldwide battery research community for their comradeship over the last fifty years; it has been an amazing journey. I would like to thank my two advisors, Peter Dickens at Oxford University and Robert Huggins at Stanford University who guided me for many years. Finally, I would like to thank my wife and family for all their support over the last half century; without them this would not have been possible.

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