

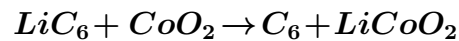
Innovation in Lithium-Ion Battery Technology

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Introduction

Lithium-ion Batteries work on the same premise as most other batteries. That is energy is stored by first using energy to induce an energetically unfavorable state. The example of pumping water uphill has been brought up in class as a simple but efficient method to store energy effectively batteries do the same thing, but instead of working against gravity batteries work against the preferred equilibrium status of a system. Lithium Ion batteries specifically move the below reaction one way or another depending on whether the battery is charging or discharging.



As the reaction is being pushed either way Lithium Ions are being moved from anode to cathode or cathode to anode. We can follow a lithium ion on its journey by looking at Figure 1 below.

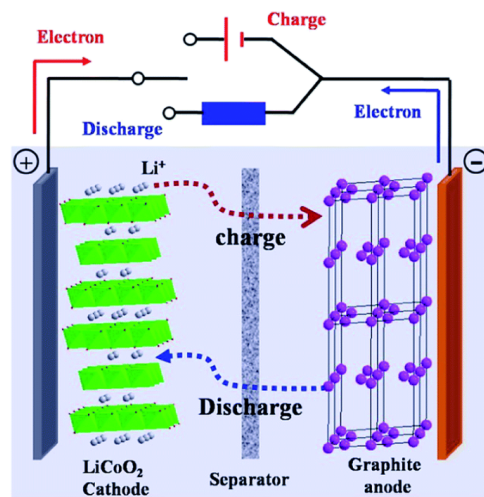


Figure 1: Sun et al 2014

In a charging cycle an external electrical circuit is applied to the battery. The Lithium Ions are originally held in the $LiCoO_2$ matrix attached to the (usually copper) cathode. These

Lithium atoms are oxidized and pop out of this matrix into the electrolyte of the battery. Attracted to the increasingly negative anode and repulsed by the positive cathode these ions partition through a separator and become deposited on the graphite anode matrix. This process essentially pushes these Lithium ions to a place that they are not comfortable so once the battery is done charging and once there is a place for electrons to flow they will reverse their journey moving from anode to cathode and generating a flow of electrons that travels along the circuit powering a device.

Beginning in 1912 under G.N Lewis Lithium has been investigated for the purpose of creating batteries. Low atomic weight and size made the element an attractive prospect in the field of ion batteries. In 1980 there were several major discoveries that made the adoption of Lithium ion batteries possible. First John B. Goodenough, an American chemist, discovers the Lithium oxide cathode, secondly Rachid Yazami developed the graphite, finally a Japanese duo Tokio Tamabe and Shjzukuni Yata discovered a novel nano-carbonacious-PAS (polyacenic semiconductive material). These three developments pushed the efficiency off Lithium-Ion batteries to a point where it was now a major area of research for many labs. This led to further developments in the field such as more efficient Electrolytes, safer anodes, more stable cathodes, and others. These developments culminated in the introduction to the commercial market of Lithium Ion batteries by Sony and Asahi Kasei in 1991. By 2011 Lithium-Ion batteries accounted for 66% of all portable rechargeable batteries used in Japan. As technology has advanced cost has come down, as can be seen in Figure 2 cost of Lithium-Ion batteries has plummeted as energy density has steadily increased.

Li-Ion Pricing and Energy Density, 1991-2005

Adapted from Buchman (2005)

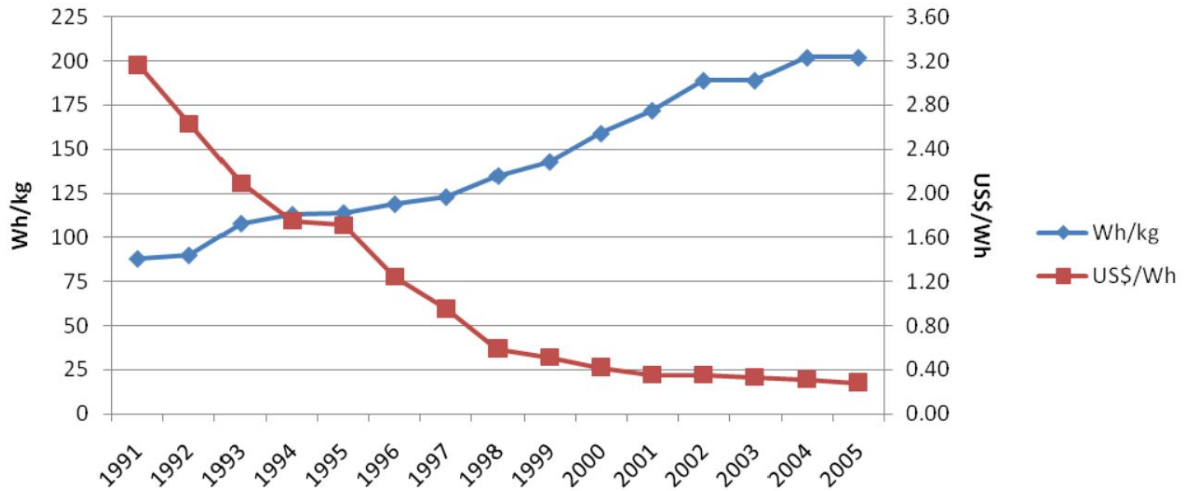


Figure 2: Li Ion battery cost vs efficiency (rameznaam.com 2015)

Lithium-Ion batteries show an advantage over other storage mediums in that they have a high energy per density and per volume. Seen in Figure 3 this allows the batteries to discharge slowly and constantly, and also makes them perfect for portable devices.

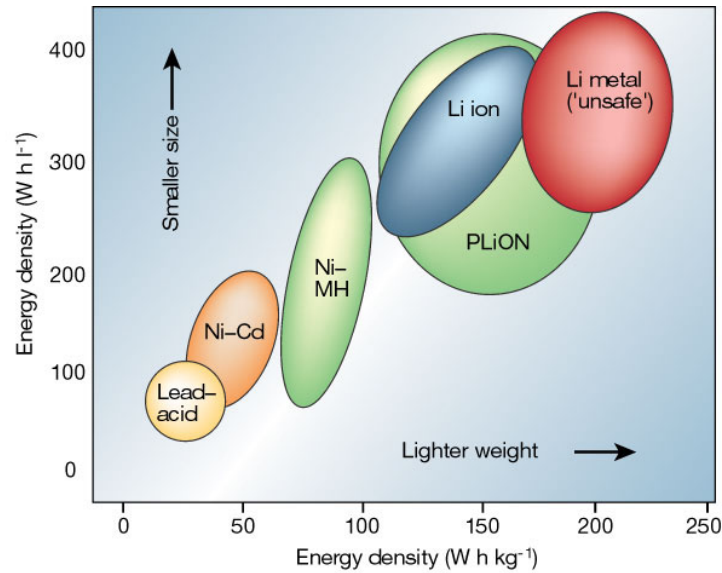


Figure 3: Tarascon & Armand *Nature* November 2001

We can see from this figure that Lithium Ion batteries inhabit a sweet spot with a balance of light weight and smaller size, but looking to super cede this position is the up and coming Lithium Polymer batteries with a wide variety of polymer electrolytes available the resulting batteries can have a wide range of attributes. Also of note are the Lithium-metal batteries that are possible, as noted on the figure they are considered unsafe due to their ability to create metal dendrites that will short circuit a battery upon charging. We can compare the positions on this graph to a more relate-able quantity (gasoline) in Figure 4. This figure also gives us a nice survey of current Lithium Ion technology.

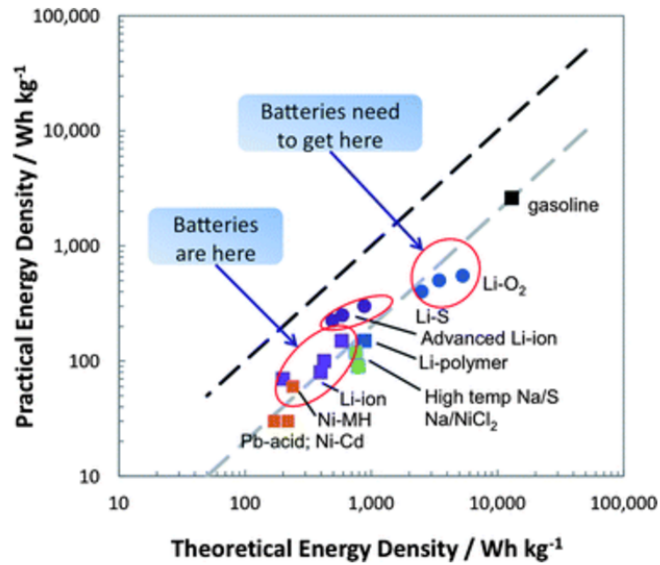


Figure 4: Thackeray, Wolverton, and Isaacs *Energy Environ. Sci.* 2012

Current State of Field

Most of the current research including the article that will be highlighted later in this paper are focused on development of new materials to be used in Lithium Ion batteries. The three main components of interest being the anode, cathode, and electrolyte. Yushin et al simplify the current avenues of research into the six strategies shown in Figure 5 [4].

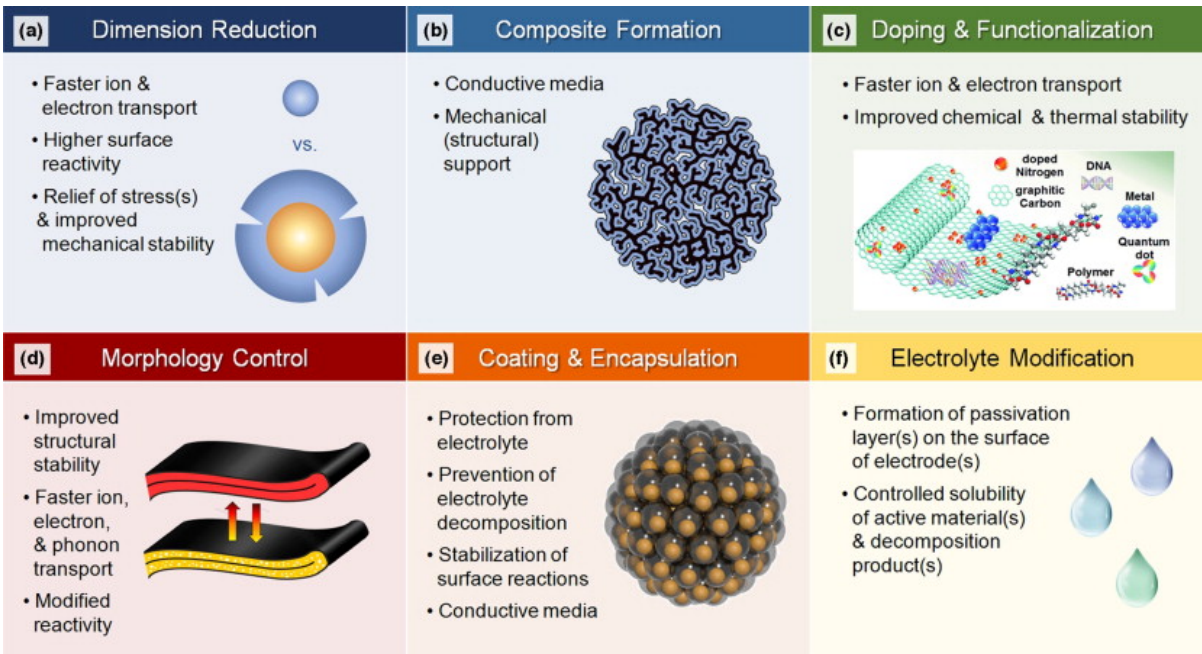
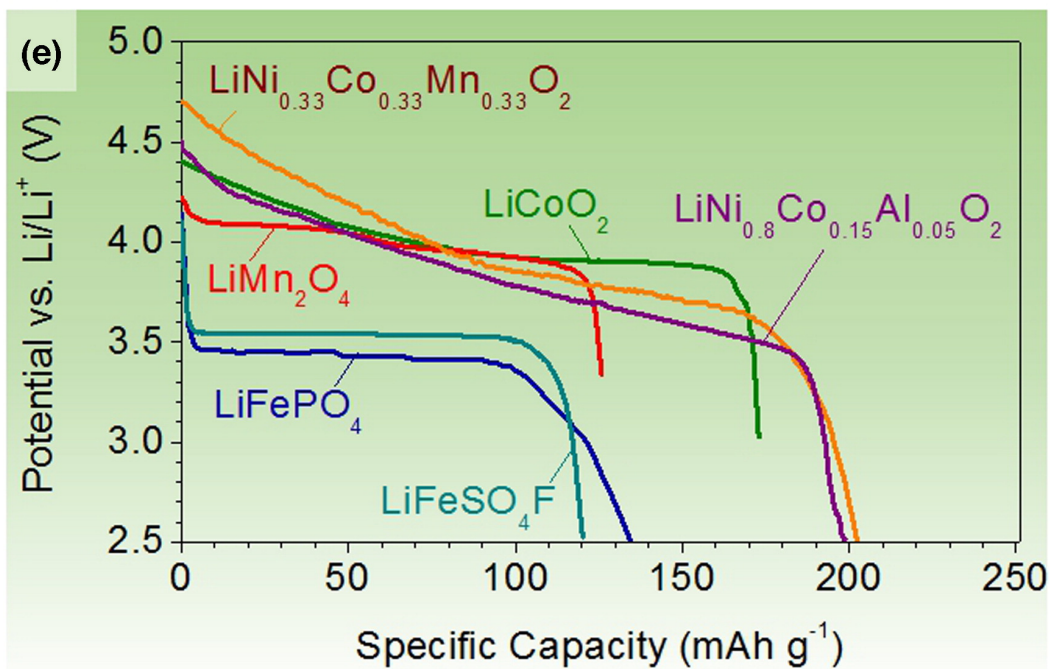
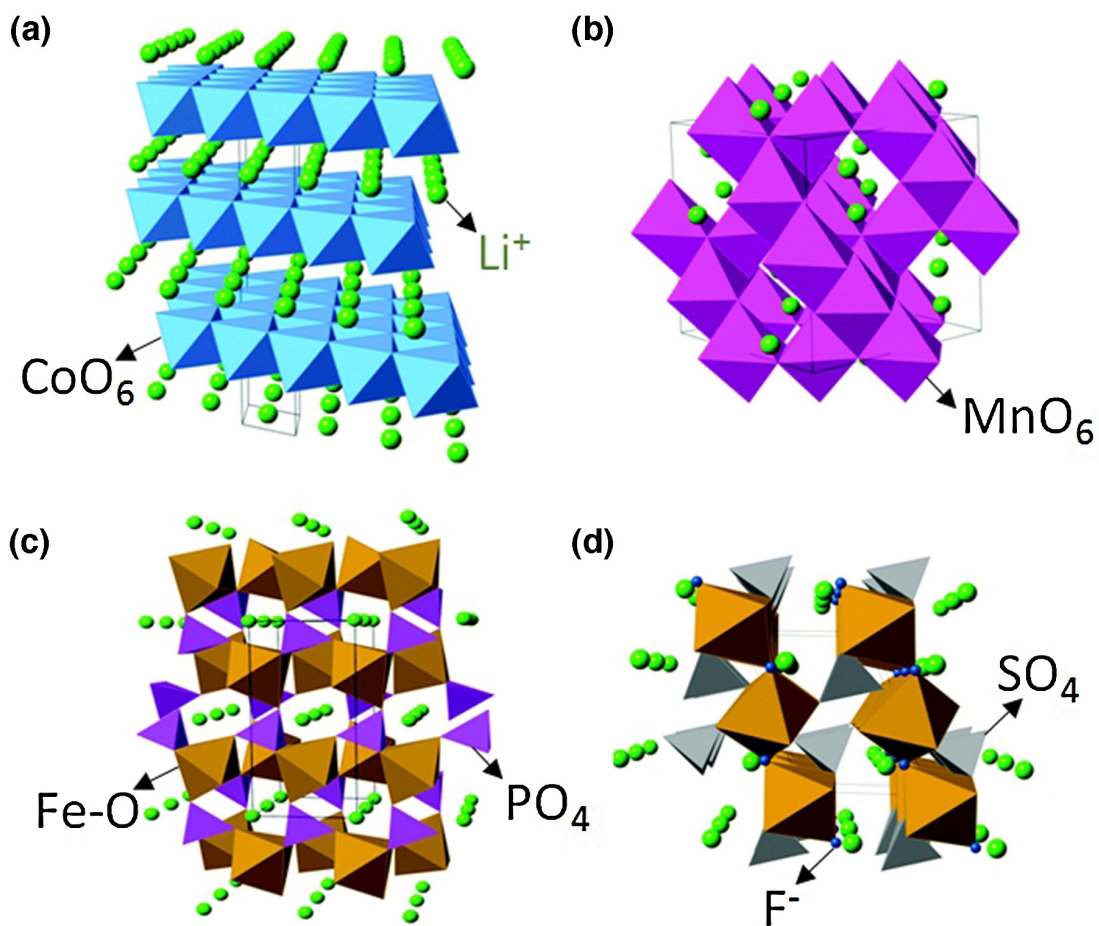


Figure 5: Yushin et al *Materials Today*. 2014

Cathode

Current Cathode research is begin done to eliminate one of the future problems with Lithium Ion batteries, the rising demand and therefore price of rare earth metals. Most modern Lithium Ion batteries use a LiCoO_2 battery where the cobalt would be the deciding factor as to the price of the cathode. Another limitation is the low thermal stability of LiCoO_2 batteries this led to the fires seen in the samsung note 7 cell phones. Current replacements for Cobalt are Iron, Manganese, and Nickel, but they all suffer from various flaws. Iron based cathodes have a smaller Potential vs Lithium (shown in Figure 6) this means that the potential that can be stored in the battery is less. Cathodes containing Manganese show a suitably high potential, but are unable to reach a high specific capacity. Finally batteries using Nickel (and another transition metal Mn or Al) show high potentials vs Lithium, but that potential drops significantly when specific capacity is increased [4].



Anode

Anode research is mainly focused on preserving the battery's potential while eliminating the possibility of several catastrophic problems. The most significant of those problems is the formation of lithium dendrites into the electrolyte that can cause a thermal run-away reaction that can cause the battery to catch fire. The original anode material and still the current material of choice is graphite. Seen in Figure 7. The graphite forms a matrix through which the lithium ions can partition. Depending on the style which the graphite is formed the matrix can be better at forming the solid electrolyte interphase or have a higher capacity for lithium partition. These two styles are called hard carbons or graphitic carbons respectively. Also successfully commercialized is a Lithium Titanium Oxide anode. These cathodes are attractive for their high capacity, thermal stability, and relatively high volumetric capacity. The downsides are higher cost, and the potential for side reactions happening on the anode

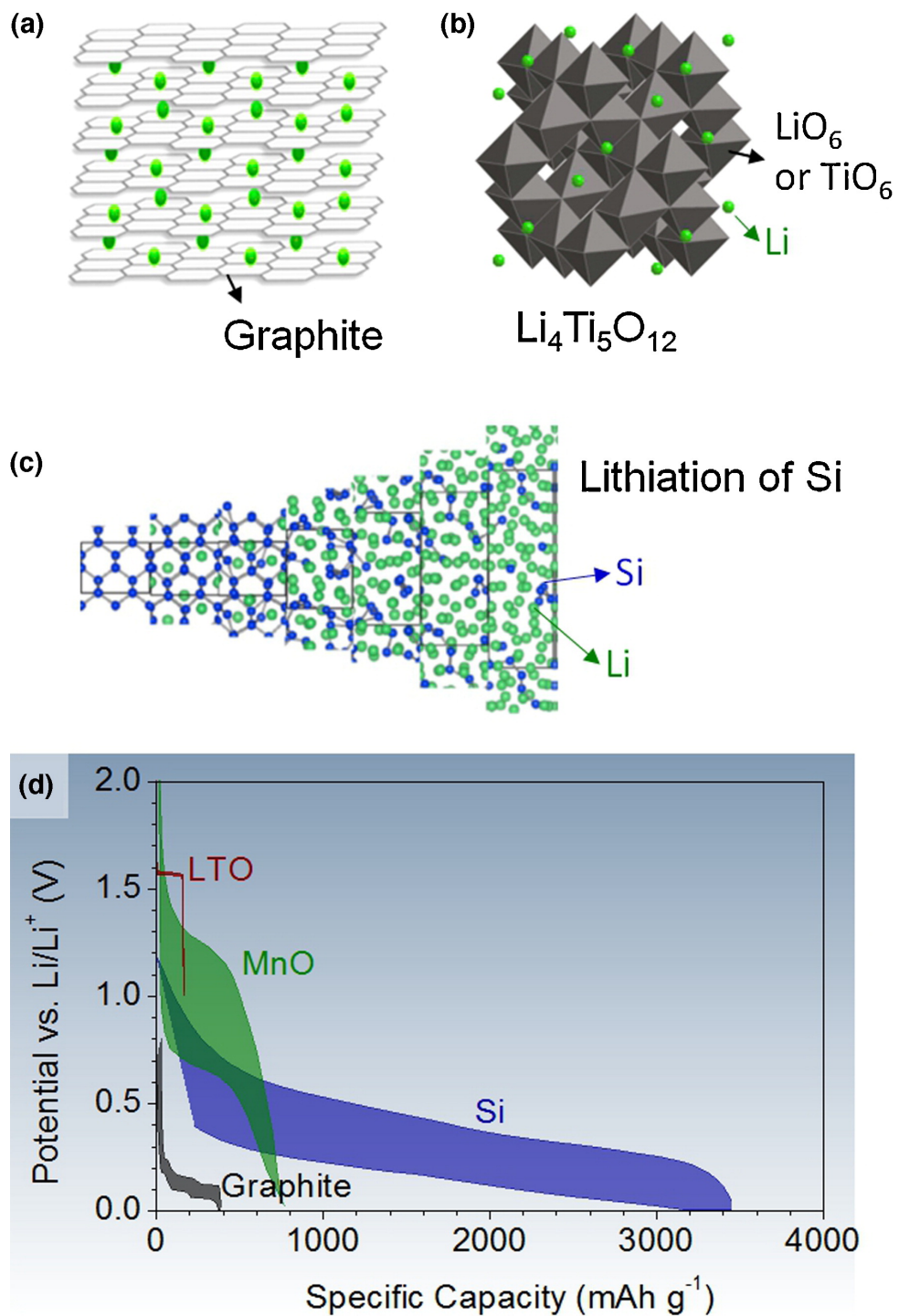


Figure 7: Yushin et al *Materials Today*. 2014

Electrolyte

The electrolyte is the main focus of the article that I have chosen to display, but First I'll give an overview of electrolyte research as I have done for the anode and cathode. The electrolyte is strictly speaking the compounds or group of compounds that solubilize the lithium ions and facilitate transport for anode to cathode or the reverse. The most common composition available today is a mix of Ethylene carbonate, Propylene Carbonate, and a lithium salt (usually PF_6). The Electrolyte works together with the material that makes up the anode to produce the previously mentioned Solid/Electrolyte Interphase (SEI). Pictured in Figure 8 2 competing mechanisms have been proposed that lead to the formation of a SEI.

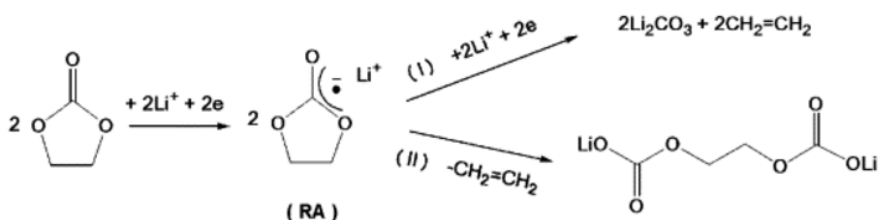


Figure 8: Zhang et al *Journal of Power Sources* 2006

Most current research can be split into two categories. Either focused on discovering additives that can be injected into current electrolytes or new types of electrolytes. The additives discussed by Zhang serve to either promote the creation of a stable SEI, favor the second mechanism in Figure 8 (which produces less gas), enhance the thermal stability of LiPF_6 , protect from overcharge, or improve the deposition of Lithium on the graphite anode. There are many other ways to change the way the electrolyte interacts with the anode and cathode, but in the interest of brevity I'll avoid them and move on to the article of focus.

Solid Electrolyte Lithium-Ion Batteries

The paper of focus is "Alternative strategy for a safe rechargeable battery" written by M. H. Braga, N. S. Grundish, A. J. Murchisona and J. B. Goodenough [3]. The last name may be familiar from the first part of this paper, John B. Goodenough was responsible for the first commercially viable cathode and he's still at it today with potentially another development for the field. This article fits into the larger paper, because it deals with the idea of replacing the conventional electrolyte with something different altogether. The material replacing the electrolyte in this case is a glass/amorphous solid with the chemical makeup.



The Glass is prepared from its precursors LiCl (99%, Merck) or NaCl (99.9%, Merck), Li(OH) (98.0%, Alfa Aesar), or Na(OH) (99%, Merck), and Ba(OH)₂·8H₂O (98.5%, Merck), or CaOH (96.0%, Merck) [2] by heating a mechanical grinding. The Glass is then cooled using HCl evaporation. The cells were constructed by placing an anode metal either lithium or sodium against the glass electrolyte then sandwiching the electrolyte with the cathode disk (made up of Carbon, Sulfur, and glass electrolyte). The current was then funneled to a copper coin collector [1]. This can all be seen in Figure 9.

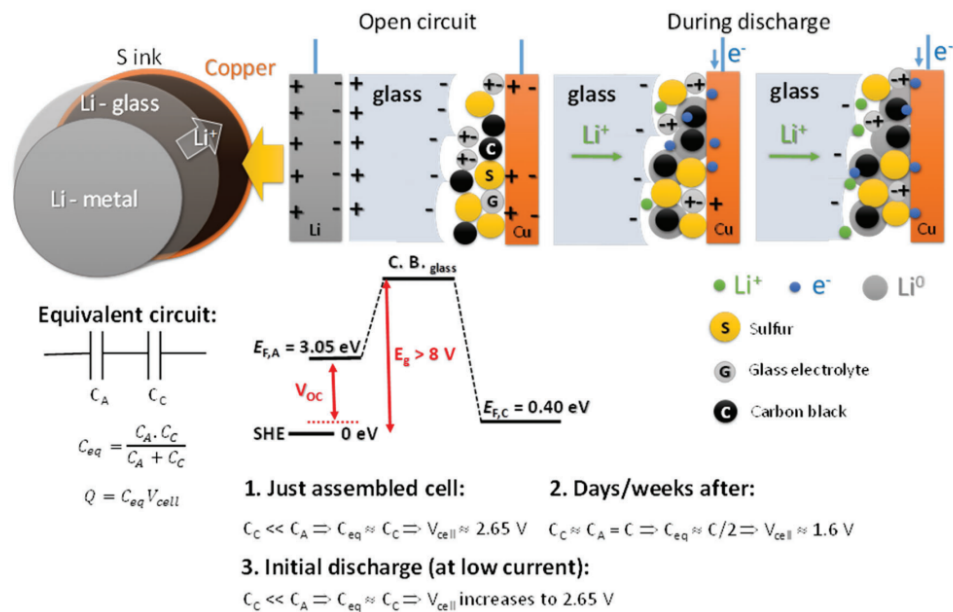


Figure 9: Depiction of experimental cell construction and function[3]

We can trace the path of a Lithium Ion much the same way that we did before. A lithium Ion that begins as a part of the Lithium metal anode will be oxidized during discharge and partition into the Li-Glass Electrolyte. This partitioning will either continue as the Lithium Ion moves through the electrolyte or more likely will promote another lithium ion already in the glass to partition towards the LiS-G cathode. Once to the cathode the ion will associate most strongly with the sulfur atoms, which have been shown to be the reduction sites. These Lithium Ions then receive an electron from the circuit and plate onto the cathode. Shown in the figures below the Discharge Voltage has significant potential (around 2.34 V optimally for recharge), and significant longevity.

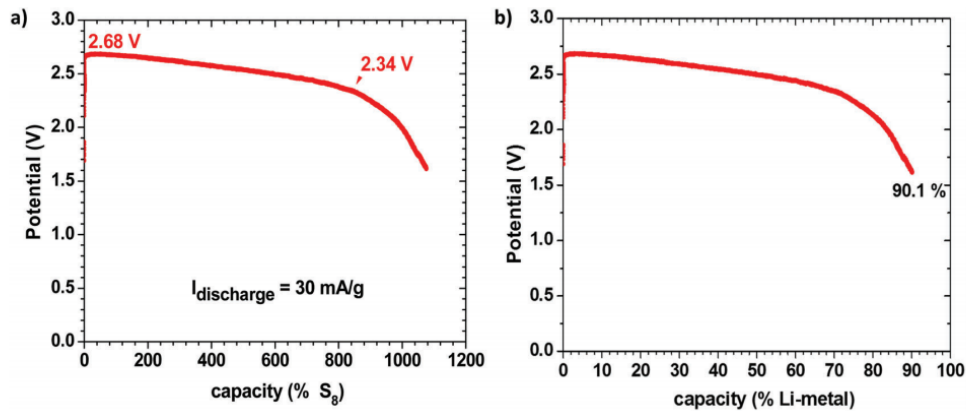


Figure 10: Discharge voltage vs Capacity of Li-S cell [3]

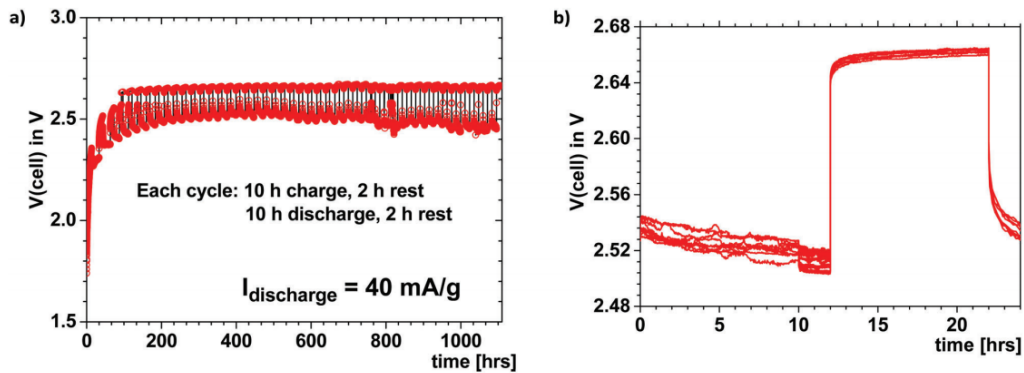


Figure 11: Discharge voltage vs Time of Li-S cell [3]

Significance

The significance of this paper is partly in the demonstration of the potential new electrolyte, but it also showcases another attractive future in Sodium-Ion batteries. With the advent of solid metal anodes higher battery potentials are making it possible for lower capacity metals, like Sodium, that are cheaper than Lithium to become viable ion choices. Sodium in particular was tested using a Na-Ferrocene cell. The results show a voltage near 2 V after the 200th cycle. The replacement of an organic electrolyte with the glass also allows for greater thermal stability.

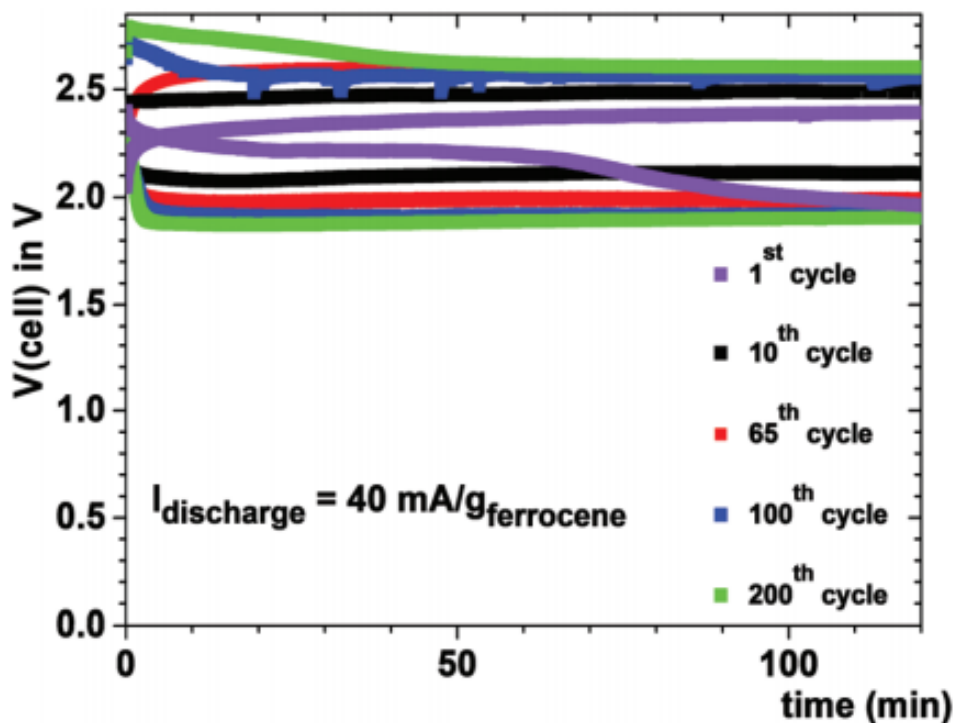


Figure 12: Sodium cell cycling (Voltage vs time) [3]

The ability to use a battery that works by stripping away the anode to plate onto the cathode also allow the creator the tweak the capacity based on the amount of metal used in the anode. Since there is no reduction of the glass electrolyte by the cathode there is also no SEI formed, this eliminates degradation of cell capacity by lithium being trapped by the SEI. Over all this paper paints an attractive future in Ion battery technology. The current drawback of this technology are the complex method of creation of the glass electrolyte and the initial creation of the cathode interface.

References

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