All Solid State Battery with Glass Electrolyte and High Energy Density

William Rauch, Adrian Grant and Lazbourne Allie

Johnson Energy Storage
275 Decatur Street, Atlanta, GA, 30312 USA
brauch@johnsonenergystorage.com

Abstract

Solid state batteries hold the promise of higher energy density and increased safety over today's lithium ion batteries and many companies are competing to define the technology. High energy is achieved by enabling a lithium metal anode in lieu of graphite, decreasing the weight and volume at a cell level. A process has been developed at a lab scale which has the ability to create high surface contact between a glass electrolyte and the active cathode material. Further, this process allows the simultaneous creation of the separator layer integral to the electrolyte in the cathode structure. Glasses are being optimized for the desired battery profiles and process compatibility. They are in a family of glasses best characterized as Oxy-Sulfides. These glasses limit the instabilities known with Argyrodite and similar sulfide electrolytes while maintaining conductivities in the 10^{-3} S/cm range. Further, the process completes the cell structure as a continuous glass with no porosity or grain boundaries for dendrite path formation. The surface is conducive to long cycle life of the lithium anode.

Keywords

Battery: Solid State: Solid Electrolyte: Glass: Lithium Metal: Safety

Introduction

Lithium ion batteries have become ubiquitous throughout society due to their ever increasing energy density, cycle life and performance. It is noted however, that lithium ion is quickly approaching theoretical limits that do not fully satisfy the needs of the future. With concerns of global warming driving the need to limit the use of fossil fuels, batteries have come to the forefront for solving issues with mobility and energy storage for grid stability. Solid state batteries offer a new generation of batteries that can increase safety, enhance energy density and provide a durable solution to today's energy needs.

Current lithium ion batteries have three shortcomings that need addressing in order to meet expectations of the future. One of the largest issues is safety. Lithium ion batteries use an electrolyte that is highly flammable. This is what is required to provide sufficient conductivity of lithium ions while being stable over a wide voltage range. The flammability is exaggerated by the low boiling point and volatility of these liquids. As batteries increase in size, the concern over this hazard grows as well.

Secondly, the demand for more energy in applications, the size and weight of the batteries must grow. Lithium ion batteries are fast approaching theoretical limits of volumetric and gravimetric efficiency. The desire for automobiles with longer range between charges meets space limitations. This is even more pronounced when one envisions electrification of aircraft where energy per weight is critical. This limitation in lithium ion may prevent viable electric aviation.

And finally, there is cost. While lithium ion batteries have dropped more than 10 fold in cost to manufacture in the past decade, they are displacing fossil fuel engines that have a century of engineering to bring costs under control. Of note here in particular is that while batteries are now reaching cost competitive levels for displacement of fossil fuels, any enhancements in safety and energy density cannot raise the price relative to the energy stored.

Most in the research community agree that a non-flammable electrolyte is a starting point for all advanced batteries. As batteries join the automotive environment, actuaries are summing the cost of the electric vehicle with the risk they may pose if a vehicle bursts into flames or is the cause of injury. Long efforts too eliminate flammability from liquid electrolytes have led to compromises in performance, particularly at lower temperatures, and battery life. Solid electrolytes can limit safety hazards in two ways. Firstly, by providing a solid barrier to short circuiting between the anode and cathode which produces local heating and secondly by limiting the potential to boil the electrolyte into a flammable vapor.

Many researchers and several start-up companies are investigating a range of solid electrolyte options to add safety to batteries while maintaining general performance metrics of batteries made with liquid electrolytes. Development parameters of interest often focus around the rate at which lithium can move through the electrolyte as that is its primary purpose. Lithium ion batteries typically use a liquid electrolyte that ranges for 5 to 20 milli-siemens. This can be a challenging value to achieve in solids as the mechanism for ionic motion is much more constrained. But with careful engineering of materials, some polymers, ceramics, and glasses can approach these values.

The solution to the second issue of energy density follows directly behind the use of a solid electrolyte. Early batteries (ca 1980) relying on lithium ions for charge

transport directly used lithium metal as the anode. This led to an early generation of batteries in personal electronics that were prone to electrical shorting. The direct use of lithium metal can allow the growth of lithium on the anode in poor structure. Lithium would plate to the anode current collector in non-dense structure and in particular could form growths, known as dendrites, that could cross from the anode to the cathode, shoring the cells. These dendrites led to the use of intercalation anodes such as graphite to give the lithium a home on the anode side of the cell and limit dendrites. The upside was safety, but the downside was a substantial loss of energy density.

With the advent of solid electrolytes, it is believed that lithium metal anodes will again be employed to gain back lost energy density. Plated lithium metal as an anode, stores almost 10 times the energy in the same space as graphite. This can lead to cells that have twice the specific energy (Wh/l) and also twice the energy density (Wh/kg) as today's lithium ion batteries. Solid electrolytes are seen to prevent dendrite growth as they are a solid barrier to lithium metal within the cell.

Polymer electrolytes have been practically used for many years in various forms. Many polymer batteries struggle with performance at low temperatures and scientists often create polymer gels to enhance the conductivity to counter this effect. Polymers will likely move towards the market first due to the ease of using polymers in manufacturing. Polymers can both create a solid separator film and integrate into the cathode structure where the lithium ions are stored. But polymer electrolytes may not fully address safety concerns as their strength may not be able to withstand the driving force of dendrite growth.

Ceramic electrolytes offer another potential for a solid electrolyte. The ceramics (defined here as crystalline metal oxides) discovered thus far require high temperature processing to produce and has that "grandma's china" tendency to fracture. Given that solid electrolytes are in reality, performing two functions, the transport of lithium within the cell and the electrical separation of the anode from the cathode, they must be integrated into a cell for both purposes. Most work to integrate ceramic solid electrolytes into battery structures has limited the ceramic to a solid thin film between the cell halves and must then use a more flexible electrolyte to reach into the depths of the cathode for general transport. The use of ceramic powders within the cathode structure has generally failed due to the poor pathways provided between pressed hard particles.

Sulfide electrolytes, typified by the Argyrodite materials with the base formula Li_6PS_5Cl have been developed due to their high conductivity that approaches that of liquid electrolytes. Known issues with this chemistry is the instability of these compounds in moisture and their reactivity within the battery cell environment. Cells are constructed using the material as a powder and pressing

together to create contacts between the particles. The softer nature of the material can make for some compelling results. This does not produce a solid barrier layer and the lack of electrochemical stability means that it cannot at this time be readily used with a lithium metal anode. In this case, the larger safety picture is addressed because the material possesses lower flammability than liquid electrolytes, but the potential for shorting may still exist in that it does not prevent dendrite propagation. Finally, without the ability to utilize a lithium anode, the gains in energy density promised are not realized.

Finally, we get to glass electrolytes. Conduction of various ions through glass has been studied for more than 50 years. Glass in this case is defined as an inorganic, amorphous material that transitions from an immobile solid, to a flowable glass phase and finally to a molten liquid with increasing temperature. Glasses most typically studied are oxide glasses where the network is formed with specific metal oxides such as SiO_2, B_2O_3 and P_2O_5. The literature through the years shows a maximum limitation in oxide glasses to about 0.01 milli-siemens in conductivity, or about 4 orders of magnitude lower than liquid electrolytes. Recently, glasses have been discovered which replace some of the Oxygen with Sulfur within the structure. With full replacement, the materials fall into the Sulfide class of materials with the Argyrodites. With sulfide glasses high levels of conductivity are achieved but suffer the same issues of electrochemical instability with lithium. Being that we are now working with glasses, structures are more fluid and the potential to mix Oxides and Sulfides into the same glass network becomes possible. These glasses, termed "oxy-sulfides".

Glass electrolytes allow flexibility in designing chemistry to make engineering trade offs in various properties. As noted, sulfide networks are characterized by high conductivity but low electrochemical stability relative to oxides. Johnson Energy Storage has been working alongside Professor Steve Martin of Iowa State University who has been exploring ion conducting glasses for over 40 years. To this unique area of chemistry, we bring in a new dimension in processing that does not limit the material to a sheet of separator or to packed particles. We have discovered that glass offers flexibility in battery construction that allows a single glass electrolyte to be formed as part of the separator as well as integrated into the interparticle space between the active cathode material making for continuous ion pathways throughout the cell.

Methodology
Johnson Energy Storage produces and investigates its own proprietary glass formulations, and the results here focus on glasses which are best termed as oxy-sulfide glasses. Batch materials suitable for production of the desired chemistry are heated to melt point in a controlled atmosphere environment. These melts are then subsequently quenched to form solid sheets for basic electrochemical testing.

Samples of the glass are then utilized in cell construction in combination with a porous cathode structure to form full battery cells. The cells produced have a seed layer of lithium metal evaporated onto the surface to complete the desired cell configuration for testing (Figure 1). Cells are charged and discharged using a Maccor battery cycler to evaluate various aspects of the battery performance.

Figure 1: Illustration of the cell configuration utilized by Johnson Energy Storage.

Battery performance is compared and correlated to the specific microstructure as determined through Scanning Electron Microscope imaging. Primary details of interest include thickness of the separator layer, relative ratio of cathode active material to electrolyte within the cathode region and the depth of fill of the glass into the cathode structure. Many of these features are linked to primary glass properties such as glass transition temperature (Tg), and crystallization temperature (Tc)

Results

Within this program, numerous compositions of oxide and oxy-sulfide glass have been produced to investigate critical properties relevant to solid state battery applications. Figure 2 illustrates the conductivity of broad classes of electrolyte materials and includes typical values observed for potential glass electrolytes. Conductivity is inversely proportional to the internal resistance of the cell and controls the ultimate rate of charge and discharge, losses in efficiency and defines at some level, the necessary operational temperature for a battery. The figure indicates the potential for oxy-sulfide glasses to replace liquid electrolyte system. With the superior conductivity of liquid based electrolytes as the benchmark, there is a need to minimize other contributors to resistance during cell construction in order to match the performance of lithium ion batteries.

Herein lies the reason why thoughtful cell construction is critical. Is solids, ions conduct based on their concentration and mobility within the material structure. Discontinuities in the material, such as grain boundaries, particle to particle transfer or passing from one conductive material to another adds substantial resistance that is not part of the scientific

measurement of conductivity. Secondly, the function of the solid electrolyte as a separator is to prevent electronic conduction between the anode and cathode while allowing ions to pass freely. The separator needs only to be thick enough to block electronic leakage and is ideally in the small micron range. This design parameter relies on a difference in lithium ion conduction and electron conduction that is greater than 4 orders of magnitude. With 5 orders of magnitude separation seen in the oxy-sulfide glasses, the separator layer can be as thin as 10 microns.
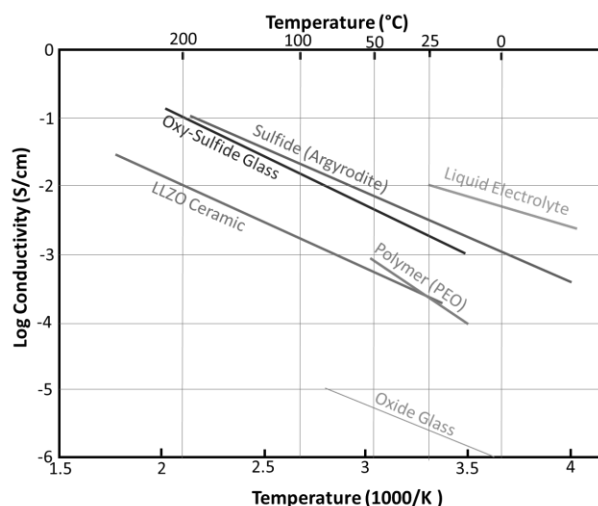

Figure 2: General range of conductivities for the broad classes of potential solid electrolytes.

The image below, Figure 3, shows the structure developed in laboratory sample cells. The layers shown from top to bottom include 2 microns of lithium, 22 microns of glass separator, on a 48 micron cathode. The glass electrolyte penetrates deep into the cathode in the observed structure allowing lithium stored throughout the structure to be accessed and utilized to store energy.
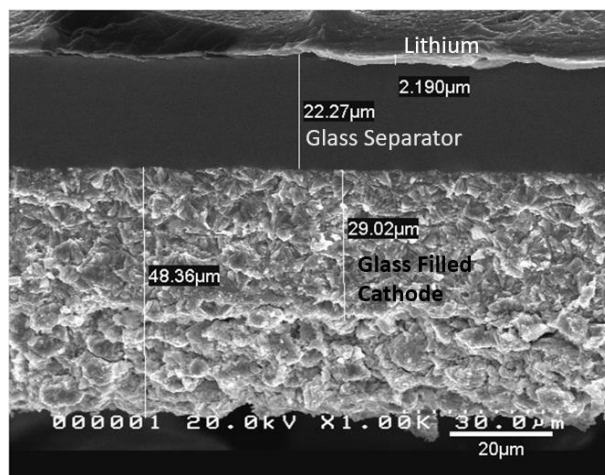

Figure 3: Cross Section image of the cell layers in a glass electrolyte based solid state battery.

The cathode preferred for this solid state battery construction uses Li(NiMnCo)O$_2$ (811) which can be used up to 4.6 volts versus a lithium anode. Below (Figure 4) is a plot from a staircase potential voltammetry test showing the stability of the glass electrolyte with capability of withstanding voltages in excess of the anticipated cell potential.
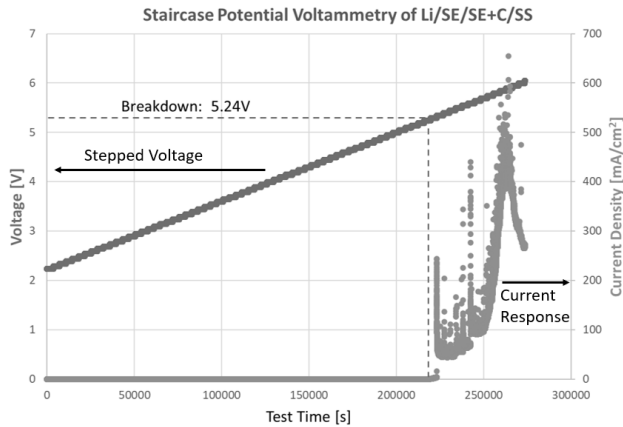

Figure 4: Staircase potential voltammetry for a cell in the configuration Li|OSglass|OSglasss-C|StainlessSteel.

A small laboratory cell constructed using the above mentioned techniques and materials underwent basic battery testing, cycling initially at C/20 rate for 2 cycles and then at a rate of C/4. Battery tests were performed in a glove box at ambient temperature in an unpackaged state. The cycling curves (V and I versus time) and charge-discharge capacity plots are shown in Figures 5 and 6 respectively. While this cell is small and has low capacity it shows the stability of the materials and construction techniques in a true solid state battery. This cell shows 28 stable cycles as of publication and is continuing to cycle with high efficiency.
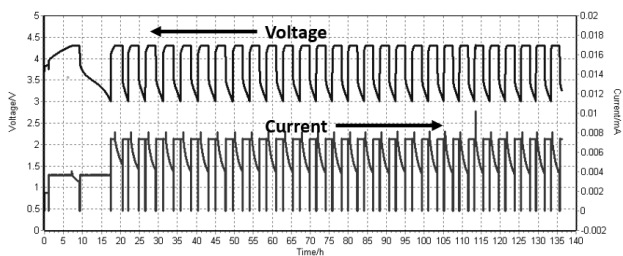

Figure 5: Voltage and Current plots for a solid state cell constructed using an oxy-sulfide glass electrolyte as Aluminum|NMC-OSglass|OSglass|Lithium|Copper.

The potential energy density was calculated based on practical configurations using the current construction techniques. Through the course of experimentation, it has been discovered that full theoretical capacity of the chosen cathode material can be utilized in the battery so long as the glass electrolyte extends throughout the cathode structure. Figure 7 below was generated assuming aluminum cathode current collector of 10 microns, cathode with 60% active material loading at the plotted thickness, a 10 micron glass separator, 2 microns of seed lithium and 10 microns of copper anode current collector. Energy density is compelling at cathode thicknesses above 40 microns.
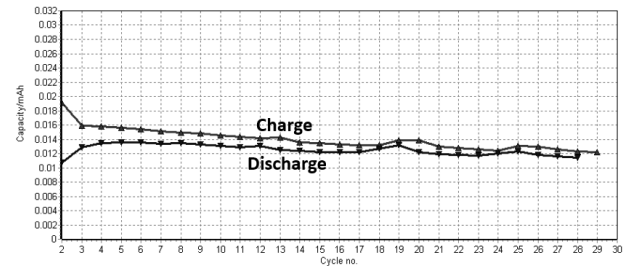

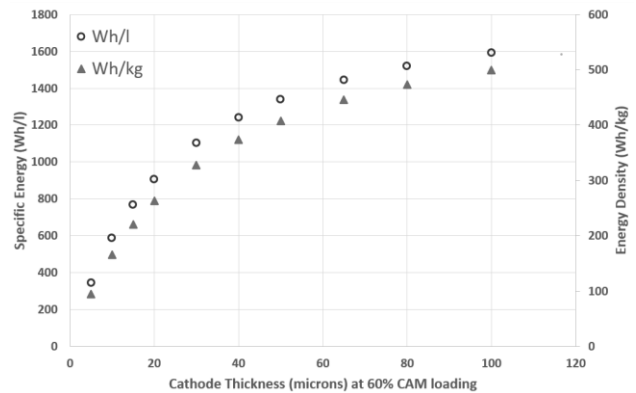**Figure 6:** Charge/Discharge capacity for above cell

Figure 7: Calculated energy density at a cell level for solid state batteries utilizing glass electrolyte and the noted cathode thickness.

Conclusions

Johnson Energy Storage has demonstrated the capability to utilize highly conductive glass electrolytes in the Oxy-Sulfide range to build a solid state lithium battery. This battery has the capability to operate safely in a wide temperature range from -20 °C to over 100 °C. The glass has good voltage stability and can be used with a lithium anode which will enable high energy density. Specific energy in excess of 1400 Wh/l and energy density of over 400 Wh/kg are predicted at the cell level.

Acknowledgements