Developing Novel All-Solid-State Li-Ion Batteries

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ABSTRACT

Frontier Electronic Systems (FES) in collaboration with The University of Tulsa (TU), is currently developing viable manufacturing processes to utilize unique nanoscale material properties and fabricate cutting-edge all-solid-state battery products. Applying nanotechnology and replacing the Li metal electrode commonly used in solid state batteries with a more atmospherically inert anode material such as SnO_2, safer and more robust all-solid-state Li ion batteries can be fabricated. The cell design and fabrication methods of this novel all-solid-state Li ion battery will be discussed. FES has successfully demonstrated the development and application of these all-solid-state batteries, through reproducibly lighting blue LEDs.

Keywords: lithium-ion, batteries, nanotechnology, solid-state, safety

2 INTRODUCTION

Technological advances in electronic devices continue to demand a more powerful battery. Li ion batteries are widely used as the energy storage device of choice, but improvements to the technology are needed to keep pace with the growing energy demand of electronics. The safety of a battery is of key importance as well. By removing the traditional liquid electrolyte and replacing it with a ionicly conducting ceramic material, the flammability of the battery will decrease due to the removal of the organic solvent.

Frontier Electronic Systems Corp. (Stillwater, OK, USA) is interesting in developing all-solid-state Li ion batteries with superb safety and energy storage properties. In collaboration with The University of Tulsa, (Tulsa, OK, USA), FES has successfully conducted novel research on ceramic electrolyte based Li ion cells and is currently developing a unique, lithium metal free, all-solid-state battery. The initial cell design and testing results will be discussed.

3 EXPERIMENTAL

A pellet of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) was synthesized using a raw materials mixture with a proprietary recipe. LATP was tape casted and formed into pellets for experimentation. The LATP was used as both the cell substrate and the electrolyte material. The electrolyte pellet seen in Figure 1, can be sputtered upon by the active electrode materials. RF magnetron sputter coating using a Anatech Hummer instrument was utilized to deposited thin films of active material on the electrolyte. $LiCoO_2$ was used as the cathode material and was sputtered in at 150W in UHP argon atmosphere of about 7mTorr. Cathode film thicknesses averaged around 300nm. Similarly, SnO_2 was also deposited but at a forward power of 100W. Upon completion of $LiCoO_2$ deposition, the $LiCoO_2$/LATP system was annealed in a tube furnace under argon gas. A Lindberg furnace with quartz tubing and a firestone valve were used to heat the samples and maintain an inert atmosphere. Samples were annealed at 600°C for one hour. After depositing the $LiCoO_2$ cathode on one side of the LATP pellet, a thin layer of SnO_2 can be deposited for the anode. Both copper and silver layers can be deposited thereafter as anode and cathode current collectors. Removing a supporting substrate material such as Al_2O_3 or SiO_2 from the cell design will decrease the amount of inactive material present resulting in cells with lower overall mass. Using silver paste strips of copper metal, contact electrodes can be easily attached to the cell.

Electrochemical cell cycling was performed at FES using a Keithley 6430 sub-femtoamp source meter, and TU using a MACCOR 2400 battery cycling unit. All-solid-state cell cycling studies were performed in atmospheric conditions while half-cell testing was performed in an atmosphere controlled glovebox using a two-electrode beaker cell configuration. Typical full-cell cycling ranges between (3.7-1.0 V) for single cell studies. SEM images were collected using a Helios Nanolab Scanning Electron Microscope.

A standard 3.4V Blue LED was used for the LED experiments. All-solid-state cells were connected in parallel,

by stacking the 4 individual cells together making common electrode connections with a soft piece of solder wire and Ag paint as a conductive adhesive. Cells were then placed in a ceramic cell holder with common cathode and anode current collector terminals sputtered on opposite sides of the holder (Ag and Cu respectively). These isolated terminals easily allowed connections with the solder wire creating a single testing terminal.

4 RESULTS AND DISCUSSION

Galvanostatic charge/discharge cycling of the all-solid-state cells were performed on a Keithley 6430 sub-femtoamp source meter. The LATP electrolyte pellet with sputtered thin-films of active anode and cathode materials, SnO_2 and $LiCoO_2$ respectively, is seen in Figure 1.

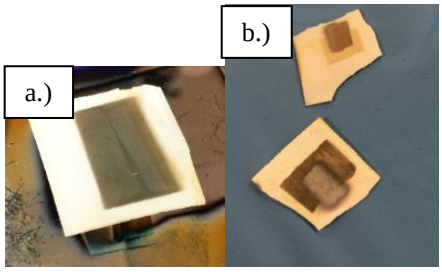

Figure 1: a.) $LiCoO_2$ (dark) sputtered on LATP pellet (white). b.) Samples of SnO_2 with copper current collector deposited on a LATP pellet is seen at the top, and a $LiCoO_2$ cathode with silver current collector on LATP is displayed at the bottom.

A single SnO_2/LATP/$LiCoO_2$ cell was cycled between a voltage range of (3.7-1.0 V) similar to previous cycling ranges for this electrode couple [1]. Figure 2 displays the cycling profile of the single all-solid-state cell. The noticeable inflections upon the discharge display electrochemical events and are classic indicators of battery behavior. This demonstrates the electrochemical energy storage behavior using the electrode chemistry, SnO_2/$LiCoO_2$, with an LATP ceramic electrolyte.

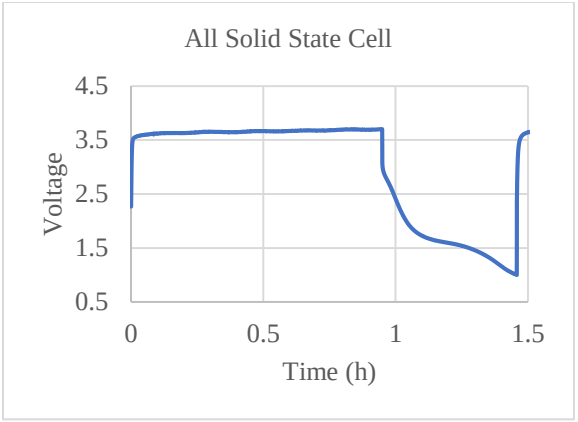

Figure 2: A single cycle of an all-solid-state Li ion cell using a LATP pellet as both the dielectric material and the substrate.

Accepted battery conventions states that two or more cells connected in series or parallel is termed a “battery”. By stacking two all-solid-state cells in the configuration described previously, series connected cells can easily be achieved. Using a silver paint conductive adhesive as a method for making electrical contact between cells, the anode of cell A is connected to the cathode of cell B. The exposed cathode of cell A and anode of cell B are now the series (2S) connected positive and negative terminals, respectively. The operating potentials for this (2S) battery is now doubled from the single cell, notice that the charge voltage cutoff is now 7.4V or double the 3.7V for a single cell. Like the single cell cycling experiments, these data suggest electrochemical behavior of a battery system. It should be noted that the charge and discharge cutoff voltages for this experiment were lowered from the correct (7.4-2.0V) to (5.8-1.2V), to test the effect terminal voltages have on battery performance.

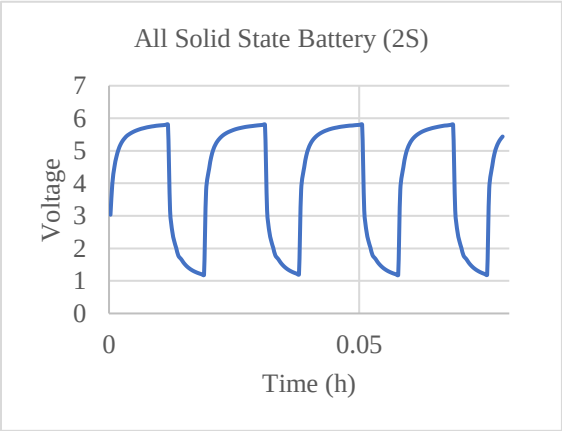

Figure 3: Galvanostatic cycling data displayed above of a two all-solid-state Li ion cells connected in series (2S).

To achieve battery systems with higher capacity (Ah), it is common to make parallel interconnects between cells. This is similar to the series connections described above but instead of connecting cells "head-to-toe," all common cell polarities need to be connected to common terminals. In Figure 4, the stacking mechanism of four individual all-solid-state cells in a ceramic cell holder is shown. The ceramic holder has a thin-film of copper and silver on opposite sides to avoid the electrical contact. The cells with blue color (anode) and red color (cathode) are placed in the holder, alternating which electrode is facing upward. Using silver paint and a small piece of solder wire, electrical contact of the two electrodes can be made to their respective common terminals. This design easily allows for parallel connections to be made. These individual terminals are now the common positive and negative leads for the connected cells.

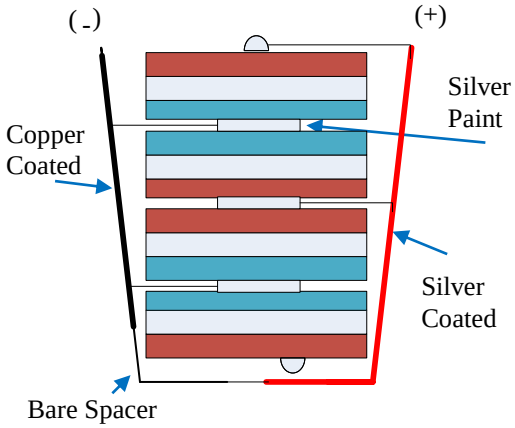

Figure 4: A diagram of the ceramic cell holder and the stacking mechanics needed to fabricate a parallel string of four all-solid-state cells (4P).

The parallel stacking of four all-solid-state Li ion cells in a ceramic cell holder is shown above in Figure 4. Initial stacking experimentation is further described in Figure 5. This figure shows the four individual cells with alternating electrode polarity facing upward. Copper and silver films are present on the cell holder, isolated by uncoated ceramic material in ensure electrical isolation. The four cells are stacked one on top the either in the holder. Please note the removal of solder wire interconnects and silver paint for picture clarity. A completed parallel connected cell holder with solder wire and silver paint can be seen in Figure 7.

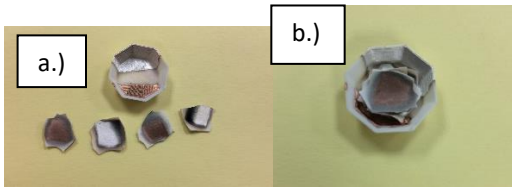

Figure 5: a.) Displays an image of the ceramic cell holder, copper and silver terminals are sputtered on opposite sides of the cell holder to avoid any electrical short. Four all-solid-state cells are present, located below the cell holder. b.) An image of the ceramic cell holder containing all four all-solid-state Li ion cells.

Making interconnects between cell stacks allows for the fabrication of all-solid-state batteries. These connections can easily be achieved and result in variable capacity and voltages. That is, numerous battery properties can readily be achieved. To test this capability, a 3S4P battery was connected in the configuration seen in Figure 6. Where the octagonal shape is the cell holder, and the white, red and silver squares are the LATP electrolyte, $LiCoO_2$ cathode and silver current collector respectively. SnO_2 anode and copper current collector are present under the LATP electrolyte and obscured from vision. The orange and grey portions of the octagons are the common negative and positive terminals.

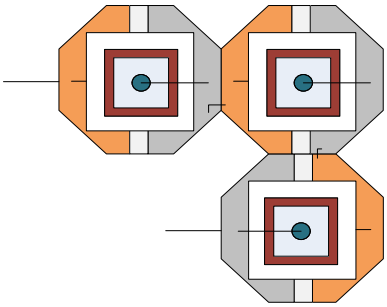

Figure 6: This graphic depicts the layout of a 3S4P configured battery using the three series connected ceramic cell holders containing four parallel connected all-solid-state Li ion cells each.

A prototype 3S4P battery is seen below in Figure 7. The additional solder wires found on each cell holder are present for voltage monitoring capabilities.

TechConnect Briefs 2017, TechConnect.org, ISBN 978-0-9975117-9-6

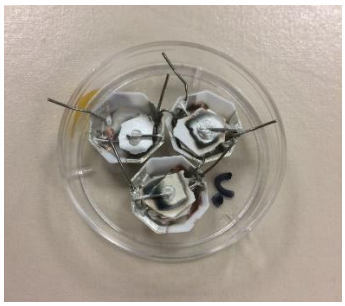

Figure 7: An image of a prototype 3S4P battery, solder wire is used to make interconnection between cells and cell holders.

Three strings of four parallel cells were connected in series and galvanostaticly cycled between an operating potential window of (11.4–3.6 V). The initial charge profile took nearly 0.5h compared to 0.067 and 0.063 hours for the second and third charges respectively. This prolonged charge could be attributed to the initial irreversible reduction of SnO_2 to Sn and Li_2O. This reaction, which has been documented previously [2], can consume Li and as a result, causes a drop in coulombic efficiencies and differences in charge times.

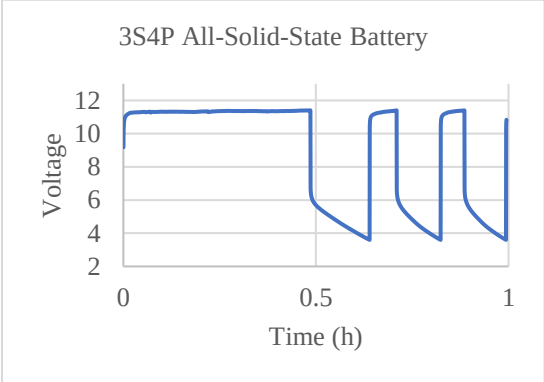

Figure 8: The cycling profile of a 3S4P all-solid-state battery is seen above.

There is a large IR drop that an indication of a resistive system largely impart due to the thickness of the LATP electrolyte pellet. These pellets are near 500µm thick, significantly more than the 300nm active electrode thicknesses. The thicker the electrolyte the further the Li ions must migrate to intercalate into the electrodes. It is plausible that the electrolyte pellets are too thick, causing a drop in ionic conductivity and an over increase in resistance. This resistance is then evident by the large drop in potential upon discharging. However, the presence of an IR potential drop is characteristic of a battery supports the idea that this system is displaying battery-like behavior. Techniques for fabricating thinner LATP electrolyte layers are currently being pursued.

5 CONCLUSION

FES has demonstrated the capability to develop unique all-solid-state Li ion chemistries that can provide improved safety properties including a ceramic electrolyte and a lithium metal free electrode couple. A LATP pellet can serve as both an ionicly conducting electrolyte material as well as a substrate for sputtered thin-films. Sputter coating electrode materials SnO_2 and $LiCoO_2$ on each side of the LATP pellet creates an all-solid-state Li ion cell without the presence or added weight of substrates, separators or packing material. Since the liquid electrolyte and lithium metal used in numerous lithium and Li ion batteries are removed, these all-solid-state systems can be cycled in atmospheric conditions. The ease of handling and manufacturing these cells is thus improved.

Galvanostatic cycling studies performed in atmospheric gas, revealed battery-like behavior for a single cell, 2S and 3S4P systems. A ceramic cell holder can contain cells stacking in either series or parallel configuration with the use of silver paint and solder wire for electrical contacts. Additional experiments on producing thinner LATP electrolyte samples in currently ongoing.

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