Stress Evolution in Solid-State Li-ion Battery Materials
Annual Report November 2012

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Summary of Annual Progress

ZnS powders were synthesized using the solvothermal approach. The powders were characterized using secondary electron microscopy (SEM), transmission electron microscopy (TEM), x-ray powder diffraction (XRD), and energy dispersive x-ray spectroscopy (EDX). The Zn_xCu_yS powders are manufactured as cathodes in coin cells to test their viability in Li-ion batteries. The initial comparison is between cathodes prepared at Planar Energy using the streaming protocol for electroless electrochemical deposition (SPEED) with and without solid state electrolyte and tape-cast cathodes using polyvinylidene (PVDF) and carboxymethyl cellulose sodium salt (Na-CMC) as a binder. Results show a beneficial effect of the solid state electrolyte on the SPEED cathodes and improved cyclability of the Na-CMC cathodes over PVDF.

Annual Progress Report

ZnS powders have been fabricated by solvothermal synthesis in a Teflon lined pressure vessel. Precursors to the synthesis include zinc nitrate, copper nitrate, thiourea, ammonium hydroxide, ethanol, and water. The solution is heated in the pressure vessel for 3 hours at 160 °C. After being collected through the use of a centrifuge, the resulting powder is then rinsed and dried in air at 110 °C. The ZnS powder contains particles that range from 10 nm to a few micrometers in size, although morphologies differ as seen by SEM in figure 1. Powder XRD and selected area electron diffraction (SAD) were utilized to identify the structure of the sulfide particles. The Williamson-Hall method of determining particle size from peak broadening suggests that particle size is on the order of 20 nm. The fine particle and grain sizes were confirmed by TEM shown in figure 2.

The ZnS powders were then used to form a cathode for a lithium ion battery. The theoretical capacitance of ZnS is 550 mAhr/g based on the complete conversion of ZnS into Li_2S. The sulfide batteries were discharged to 0.5 V and charged to 2.5 V. The cathode was prepared by adding together 75 wt% ZnS, 15 wt% carbon, and 10 wt% polyvinylidene fluoride (PVDF). The product was then ball-milled for 2 hours. After ball-milling, the product was added to 1-methyl-2-pyrrolidone, which acts as a solvent to form a slurry. The slurry was tape-cast onto a Cu substrate. The tape-cast slurry was then dried in air at 110 °C overnight. The cathode and Cu current collector were placed into a pouch cell opposite of Li metal with a Celgard polypropylene separator between. The electrolyte used is a solution of 1 M $LiPF_6$ in 1:1 ethylene carbonate (EC):dimethyl carbonate (DMC) solvents. An alternate water-based slurry was made by replacing the PVDF with a 300,000 kDa carboxymethyl cellulose sodium salt (Na-CMC) binder at the same weight ratio.

Slurries were also created at Planar Energy using the same solvothermal powders. The Planar slurry was spray deposited onto a stainless steel substrate and annealed in a sulfur ambient atmosphere of 325 °C for 5 min. Afterwards, sections were cut out and made into pouch cells. Planar Energy also provided solid state electrolyte coatings of $LiAlGaSPO_4$.

ZnS cathodes made with PVDF and Na-CMC were compared. A ZnS-PVDF type cathode was tested at a current of C/20 with an initial discharge capacity of 335 mAhr/g discharged to 0.5 V. The cyclability of the cathode is very poor in the liquid electrolyte as seen in figure 3. A similarly tested A similarly tested ZnS cathode with a Na-CMC binder had an initial discharge capacity of 320 mAhr/g when discharged to 0.5 V. Unlike the case with the PVDF, the Na-CMC binder cathode retained some cyclability as seen in

figure 4. Ongoing research is being done to determine the role of the Na-CMC and improve the binding of ZnS cathodes to a substrate.

To determine the effectiveness of a solid state electrolyte in a hybrid cell configuration, ZnS cathodes prepared through the SPEED technique were tested. The ZnS-SPEED cathodes were tested at a discharge rate of C/10 and showed an initial discharge capacity of 360 mAhr/g at 0.5 V. The ZnS-SPEED cathodes had varying performance between each sample, but on average, the discharge capacity would reach 200 mAhr/g by the 3rd cycle and 100 mAhr/g by the 5th cycle. With the addition of a $LiAlGaSPO_4$ layer, the ZnS-SPEED cathodes displayed some consistency in performance between the samples. The capacity retention is also improved with the additional solid state electrolyte layer since the discharge capacity would not reach 200 mAhr/g until the 7th cycle and 100 mAhr/g at >25 cycles. A summary of the results is shown in figure 5.

The $LiAlGaSPO_4$ solid state electrolyte was also tested with the Na-CMC cathode, however, the cathode lost integrity in the annealing process. A similar benefit of the solid electrolyte has not been seen in non-ZnS-SPEED cathodes so far. The expected benefit of the solid state electrolyte is to reduce the Li_2S dissolution during cycling and improve the long term cyclability. However, changes in the electrochemical properties have also appeared between the ZnS-SPEED and ZnS-SPEED with the solid state electrolyte. These electrochemical reactions are still under investigation.

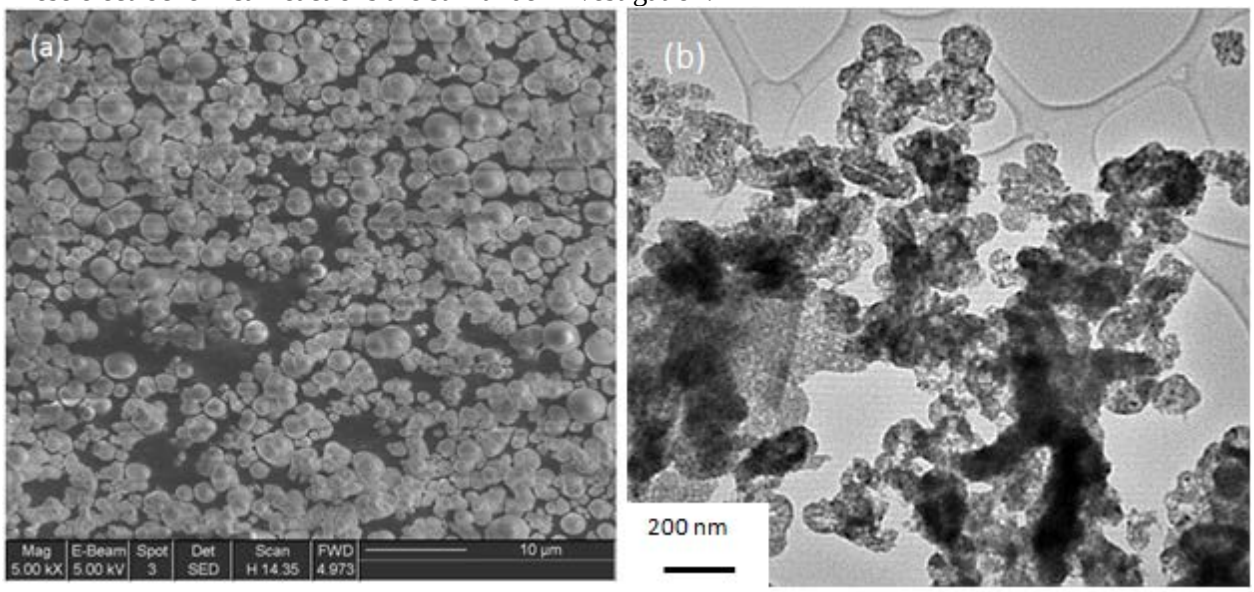

Figure 1. (a) Top-down SEM images of ZnS and (b) bright field TEM image of ZnS

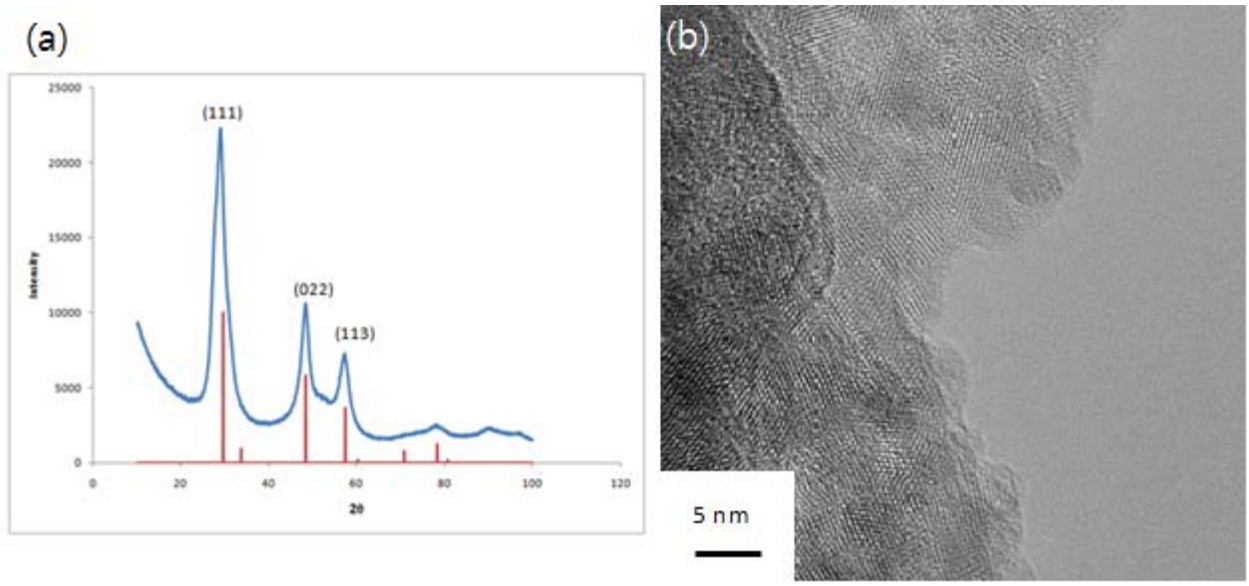

Figure 2. (a) XRD of synthesized ZnS and sphalerite reference pattern, (b) bright field TEM of synthesized ZnS show small crystal size

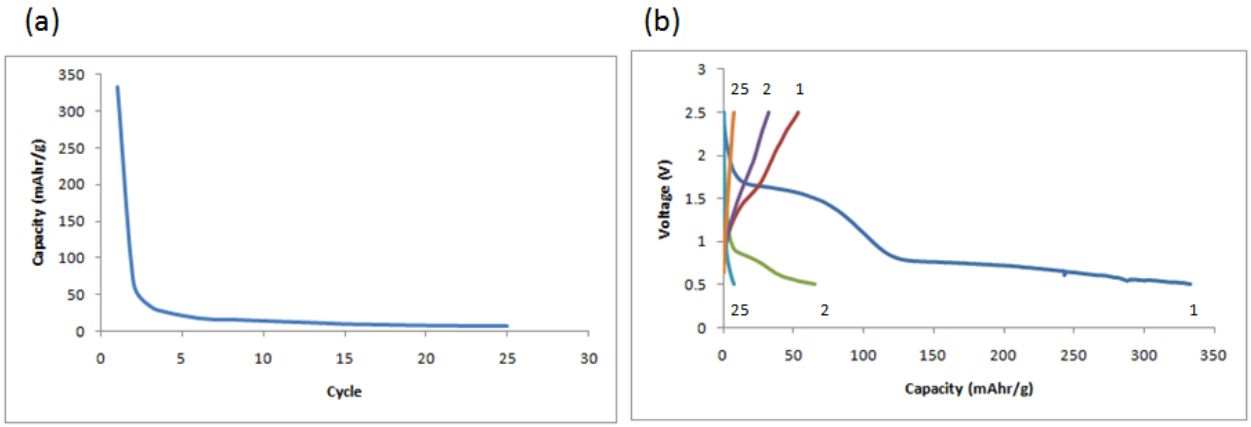

Figure 3. (a) Cycle life of ZnS-PVDF battery, (b) Charge/Discharge profile of ZnS-PVDF battery at C/20

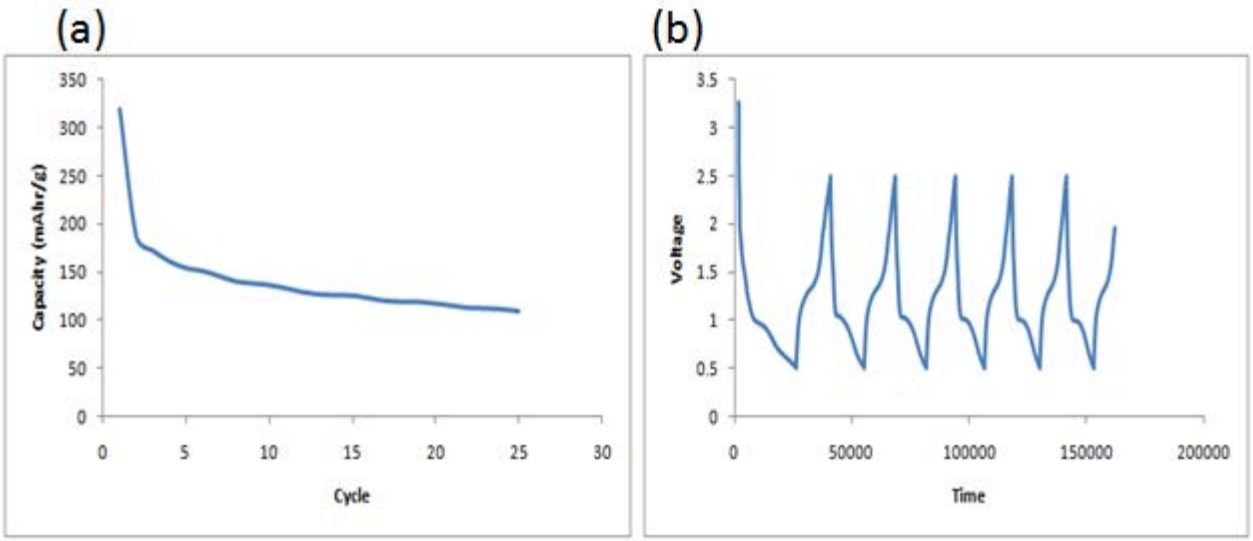

Figure 4. (a) Cycle life of Na-CMC ZnS battery, (b) Charge/Discharge profile of Na-CMC ZnS battery at C/10

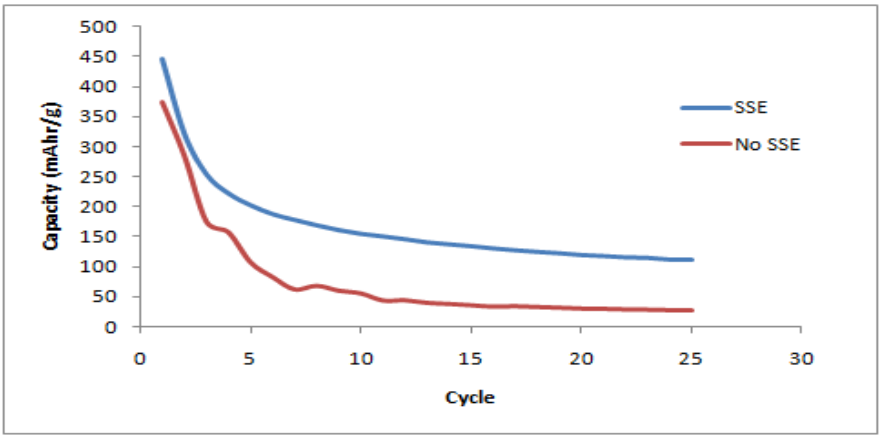

Figure 5. Comparison of ZnS-SPEED with solid state electrolyte and without solid state electrolyte. Results are an average of 4 samples each.