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VTO FY22Q3 Quarterly Report

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Task 1.10 – Three-Dimensional Printing of All-Solid-State Lithium Batteries

(Jianchao Ye, Lawrence Livermore National Laboratory)

Project Objectives. The project has two primary objectives: (1) down select three-dimensional (3D) printing and post-processing approaches for SSE/cathode integration, and (2) understand battery failure mechanisms via *ex situ* and *in situ* characterization.

Impact. The adoption of thin separator layer, thick cathode structure, and metallic lithium anode will lead to EV batteries with > 350 Wh/kg energy density for increased mileage per charge. The higher ionic conductivity with suppression of lithium dendrite growth will allow high CCDs for fast charging applications. The improved electrode/electrolyte contact will increase battery cycle life for long-term service.

Approach. The technical approaches include advanced manufacturing based on 3D printing and related techniques, *ex situ* / *in situ* characterizations, and battery testing. Direct-ink writing (DIW) 3D-printing techniques will be employed to fabricate thin-film SSEs (< 100 μm), gradient SSEs, and 3D interfaces for battery performance evaluation. Three approaches including sintering-free, hybrid, and co-sintering will be investigated. The knowledge obtained from these approaches is transferable and complementary to each technique.

Out-Year Goals. The long-term vision of the team is to 3D-print all components of the ASSLBs to facilitate the scale-up of ASSLB manufacturing. In this project, the team will tackle the issues emerging from integrating SE with electrodes. The project goal is to demonstrate a successful 3D-printing approach to integrate SSE into electrodes and show reasonable capacity retention (that is, > 80%) after 300 cycles at current density ≥ 1 mA/cm^2.

Collaborations. The team will work closely with a computational partner (Task 3.11 led by B. Wood) to better understand battery failure mechanisms and design new battery architectures and chemistries for performance improvement. The team is collaborating with Dr. Sangil Kim and Dr. Gang Cheng from University of Illinois at Chicago on composite polymer electrolyte development.

Milestones

1. Determine the polymer / $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO) interfacial chemistry effects on the total ionic conductivity and Li$^+$ transference number. (Q2, FY 2022; Complete)
2. Improve conductivity and strength of composite polymer electrolytes (CPEs). (Q3, FY 2022; In progress)
3. Obtain porous co-sintered LLZTO-SSE/NMC/C electrolyte/cathode bilayer structure. (Q4, FY 2022; On schedule)

Progress Report

Mechanical properties (Modulus E and hardness H) of PEGDA/PEGMEA/PEO/LiTFSI solid polymer electrolytes (SPEs) were measured using spherical indentation, as shown in Figure 1. The Young's modulus ranges from 290kPa up to 10 MPa, while hardness from 9kPa to 300kPa, depending on the composition of the SPEs. Both E and H increase with higher PEGDA content (Figure 1b and d), which forms 3D crosslink network. Increasing the ratio of PEO/PEGMEA can further improve E (Figure 1a), but shows little effects on H (Figure 1c), likely because the two are both with straight polymer chains. One composition used for further studies (PEGDA:PEGMEA:PEO= 1:8:1) shows E of ~2.58 MPa and H of ~156 kPa, which delivers an ionic conductivity of 10^{-5} S/cm at room temperature. Reducing PEGDA and PEO contents can increase the ionic conductivity up to 6 x 10^{-5} S/cm, however, E reduces to 0.29 MPa, and H to 12 kPa.

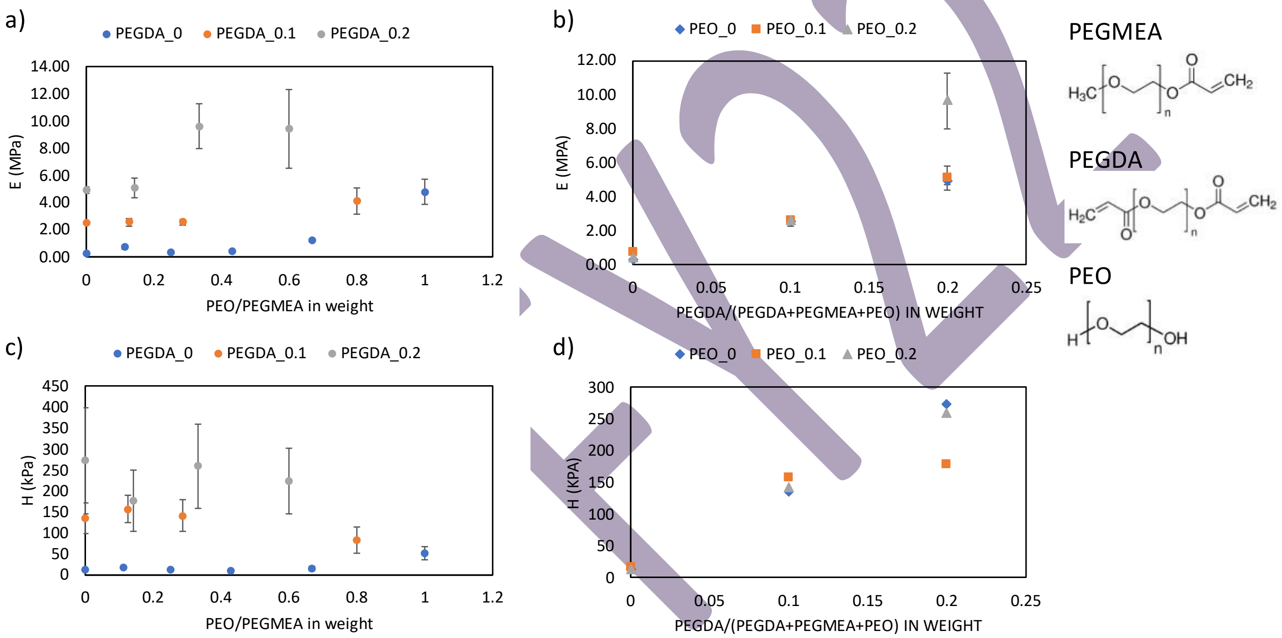

Figure 1. Young's modulus (E) and hardness (H) measured using spherical indentation.

To further improve the ionic conductivity of polymer electrolytes, LLZTO "active" filler nanoparticles were introduced in the 1PEGDA-8PEGMEA-1PEO/LiTFSI matrix. A series of LLZTO contents from 7wt% up to 31wt% were prepared. The highest ionic conductivity of 6.6 x 10^{-5} S/cm was obtained for 7wt% LLZTO (Figure 2a). Further increasing the LLZTO content however leads to the decrease of ionic conductivity. Detailed optimization of the LLZTO content can be conducted in the range below 13wt% to pin down the peak conductivity. The highly conductive LLZTO particles seems to be not involved in the overall Li^+ conduction. The addition of LLZTO particles helps to reduce the crystallinity of PEG polymers and thus improves the conductivity. However, further addition of the particles increases the interfacial area and the impedance between LLZTO and polymer electrolyte could hinder the Li^+ ion transport. Therefore, to improve the conductivity of high-LLZTO-content composite polymer electrolytes, one strategy is to form bicontinuous LLZTO/polymer networks, which is being explored in the sintering-refilling hybrid approach. Another strategy is to improve the Li^+ ion transport between the LLZTO/polymer interface.

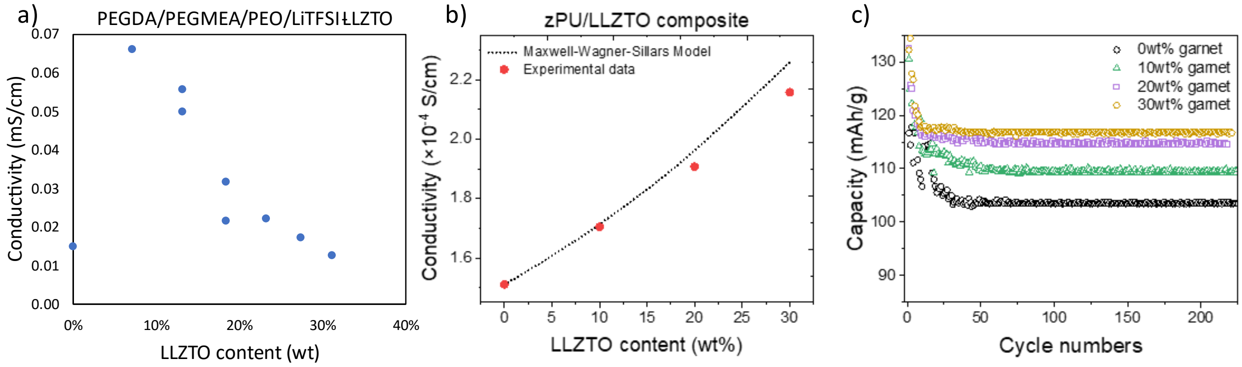

Figure 2. Conductivity of composite polymer electrolytes made from a) PEG/LLZTO and b) zPU/LLZTO recipes. c) Cycling tests of Li|zPU/LLZTO|LFP solid state batteries at 1C rate, room temperature.

To achieve that, the team is collaborating with researchers at University of Illinois at Chicago to develop zwitterionic polyurethane (zPU)/LLZTO composite polymer electrolyte. The high surface energy of the zPU/LiTFSI polymer electrolyte improves the wetting with LLZTO particles. The high LiTFSI content (up to 80wt%) increases the Li$^+$ concentration in polymer matrix and facilitates the ion transport between zPU and LLZTO. As a result, as shown in Figure 2b, the Li$^+$ conductivity of the composite polymer electrolyte (CPE) continuously increases from 1.5 x 10^{-4} S/cm to 2.2 x 10^{-4} S/cm (at RT) with the increase of LLZTO content up to 30wt%. The increasing trend can be fit using a Maxwell-Wagner-Sillars conductivity model. The LFP|zPU-LLZTO CPE|Li full cells also show improved capacity at 1C rate with the increase of LLZTO content (Figure 2c), likely attributed from the higher conductivity. There are significant capacity drops in the first 10-20 cycles for all the zPU cells, though the addition of LLZTO facilitates the stabilization. After ~50 cycles, cell capacity is very stable with little decrease in the next 200 cycles. With such promising results, the team moves forward to introduce 3D printed cathodes to integrate with the zPU/LLZTO CPE. Representative prints are shown in Figure 3. Liquid cells are currently under testing.

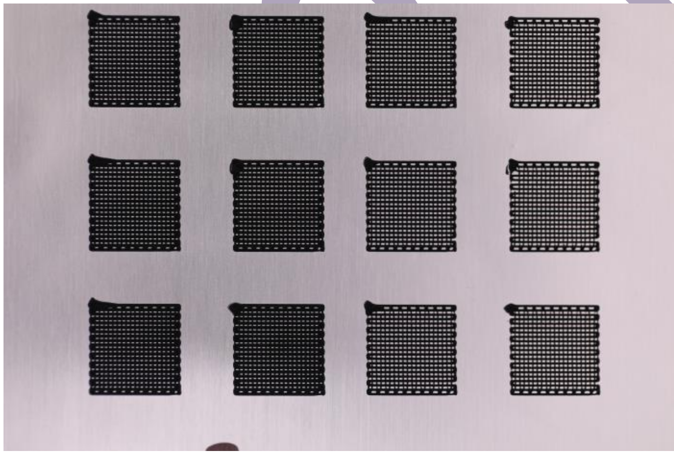

Figure 3. Direct ink writing printed single-crystal NMC811 cathode. Nozzle diameter is 200 μm, hatch spacing is 400 μm, and mass loading is ~ 10 mg/cm².

Patents/Publications/Presentations

Presentations

- Marissa Wood, Liwen Wan, Anirudda Dive, Jianchao Ye. Co-sintered solid electrolyte/cathode interfaces in solid-state batteries. 2022 MRS Spring Meeting & Exhibit, Honolulu, Hawai'I, USA