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VTO FY23Q3 Quarterly Report on 3D Printing of All-Solid-State Lithium batteries

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Disclaimer

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Task 1.6 – Three-Dimensional Printing of All-Solid-State Lithium Batteries
(Jianchao Ye, Lawrence Livermore National Laboratory)

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

Project Impact. The adoption of a thin separator layer, thick cathode structure, and metallic lithium anode will lead to electric vehicle 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 critical current densities 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 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 all-solid-state lithium battery (ASSLB) to facilitate the scale-up of ASSLB manufacturing. In this project, the team will tackle the issues emerging from integrating solid electrolyte 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 3.8 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 S. Kim and G. Cheng from University of Illinois, Chicago, on composite polymer electrolyte (CPE) development.

Milestones

1. Demonstrate that SSE has > 10^{-4} S/cm conductivity and that full battery can charge/discharge with > 80% capacity. (Q1 FY 2023; Completed)
2. Determine the relationship of ionic conductivity and mechanical properties with $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) content in CPEs. (Q2, FY 2023; Completed)
3. Improve conductivity and stability of catholytes against cathode. (Q3, FY 2023; Complete)
4. Improve performance of co-sintered electrolyte/cathode bilayer. (Q4, FY 2023; In progress)

Progress Report

In the previous report, the team found rapid capacity drop in assembled LFP/Li cells using PEGDA/PEGMEA/PEO-LLZTO based composite polymer electrolyte (CPE). To understand the degradation mechanisms and improve the cycling stability, the team assembled tens of coin cells including Li/CPE/SS, Li/CPE/Li, LFP/CPE/Li, Graphite/CPE/Li for comprehensive comparison. Adjustments such as electrode calendering and introducing FEC additive were found to enhance the mechanical and electrochemical stabilities.

Cathode calendering improves the conductivity and mechanical stability.

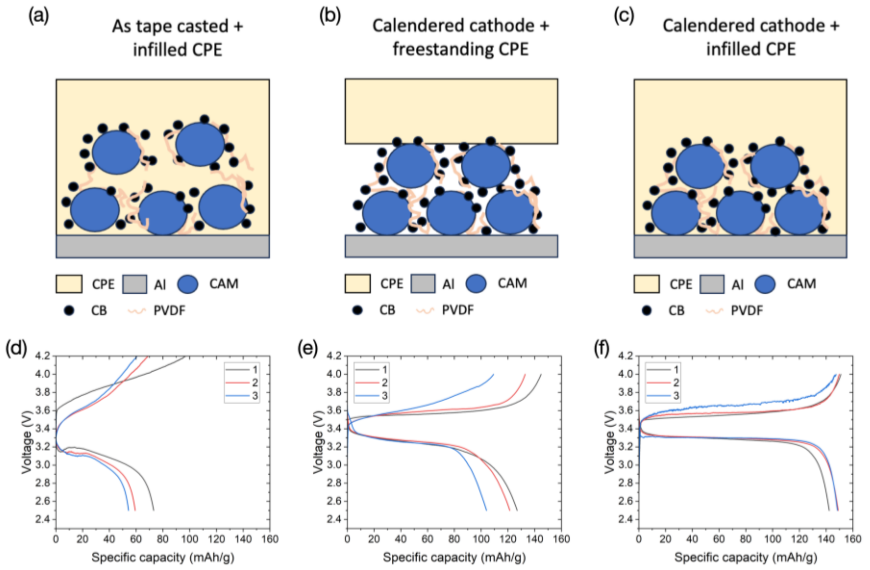

Figure 1. Illustration of the three integration methods for LFP/CPE/Li cell assembly. (a) As-tape casted LFP cathode film infilled with CPE. (b) Calendered LFP cathode film stacked with freestanding CPE. (c) Calendered LFP cathode film infilled with CPE. (d), (e), and (f) are the corresponding charge/discharge curves at C/10 rate.

To improve physical contact in the cathode, the as tape casted cathode was calendered using a hot roller press. CPE was infilled into calendered cathodes to compare with the previously reported as-casted cathode. Free-standing CPE film was stacked onto calendered cathode to make another cell without catholyte infilling for performance comparison. Figure 1 illustrates the three configurations and shows the corresponding charge/discharge curves at room temperature at C/10 rate. Generally calendered cells show higher capacity than as casted cell, suggesting some active materials in the as casted cathode are not in good contact with the current collector or adjacent carbon black particles after CPE infilling. Upon cycling, volume change may further weaken the particle-particle contact and therefore leads to continuous material loss. Using freestanding CPE in the calendered cell with LFP mass loading of 5 mg/cm^2, the team demonstrated a cell with high initial capacity of 145 mAh/g at RT, but the value dropped quickly to 110 mAh/g in the third cycle. It is likely that insufficient ion transport pathway in this case led to fast capacity decay. By infilling the CPE into calendered cathode to provide ion transport medium, the capacity reaches 150 mAh/g, and maintains that value in the following two cycles. Compared with as casted electrodes, the IR drop decreased from 168 mV to 48 mV after calendering. EIS (Figure 2) also shows the reduction of interfacial resistance by adopting infilled calendered cathode, suggesting the gain of electrochemical surface area. Calendering strengthens the bonding between active materials and therefore can maintain good electrical contact during processes including CPE infilling, vacuum drying, and UV cure. The above results reveal the importance of maintaining cathode integrity in a functioning solid-state battery.

To be noted, the calendered cathode plus infilled CPE cell gradually showed noisy charging voltage signal and increased charging overpotential (Figure 1f), suggesting dendritic growth is still a problem in the LFP/Li cell with soft CPE separator. The impedance after three formation cycles increased to 2000 ohm, also suggesting an interfacial instability problem.

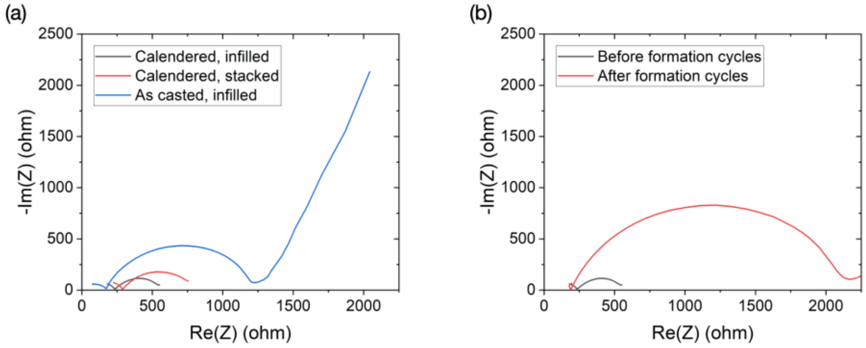

Figure 2. EIS shows reduced interfacial resistance after calendering.

FEC additive improves the mechanical properties of PEG based CPEs and shows higher cycling stability.

FEC has been found to improve the SEI quality in liquid electrolyte based LIBs and was recently found to be beneficial for polymer electrolytes (Lin, et al. Nat. Nanotechnol. 2022, 17, 768-776). Here, the team added 1wt% of FEC in the CPE and studied its effects in the mechanical, electrochemical properties and cell performance.

AFM nanoindentation reveals the improvement of Young's modulus, from 1 MPa to 5 MPa, making the casted film easy to peel off from the glass slide substrate. This improved mechanical property could be beneficial to mitigate dendrite penetration and reduce the chance of short circuit during cell assembly. With the increase of mechanical properties, trade-off was observed with ionic conductivity reduced to 2~5 x 10^{-5} S/cm at room temperature. However, heating it up to 60 °C gives a 10 times higher conductivity (4 x 10^{-4} S/cm).

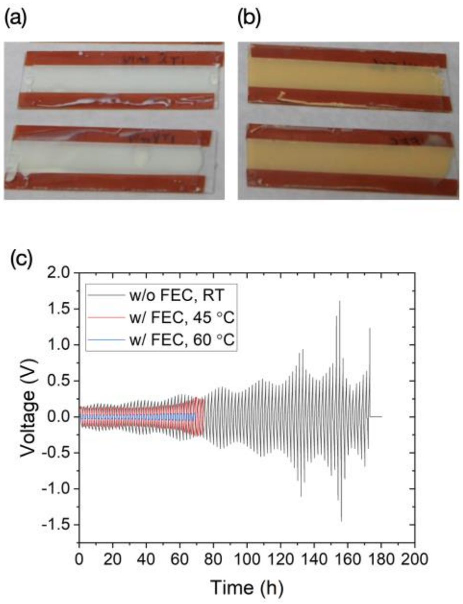

Figure 3. Casted CPE films without (a) and with FEC additives (b). (c) The Li plating/stripping cycling stability test. 0.1 mA/cm^2 current density, 1h plating/ 1h stripping.

Li symmetric cell showed Li plating/stripping overpotentials gradually increased from 24 mV to 50 mV at 0.1 mA/cm^2 after 33 cycles. Lower the temperature to 45 °C led to an increase of overpotential to 140 mV and gradual increase to 270 mV after 35 cycles. The overpotential is close to the Li-CPE7-Li cell run at room temperature, as shown in Figure 3. However, the cycling stability of the LFP cell improved significantly with the FEC addition.

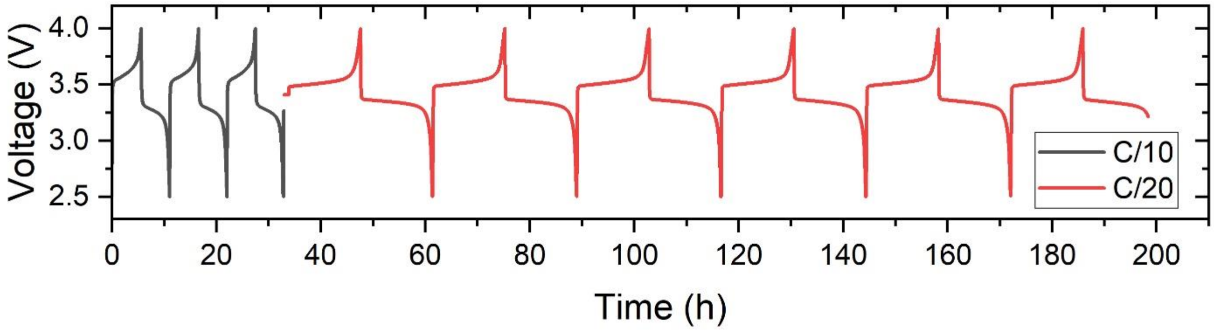

Figure 4. Cycling of an LFP-CPE7F-Li cell with FEC added CPE, infilled into as-casted LFP film, at 45 °C.

The LFP-CPE7F-Li Cell run at 45 °C shows stable cycling with capacity of 115 mAh/g at C/20, and ~ 90 mAh/g at C/10, as shown in Figure 4. Stable charging/discharging with no overpotential increase or microshorts was observed in the current 13 cycles at C/10 and C/20 rates. Further increasing the temperature to 60 °C led to a capacity of 135 mAh/g at C/20. EIS (Figure 5) shows that both the bulk and interfacial impedance decreased 10 times with increasing temperature to 45 °C, which is in contrast to the CPE without FEC that showed interfacial resistance decrease of only 22 % with increase temperature to 60 °C. This strongly indicates that FEC stabilizes the SEI layer with metallic Li anode. Noted that the absolute capacity is not as high as the calendered LFP at RT without FEC (Figure 1c), which might be affected by connectivity of active materials in the infilled cathode. Using a calendered LFP for the CEP7F cell could lead to further enhancement of the cell performance and will be tested in the near future.

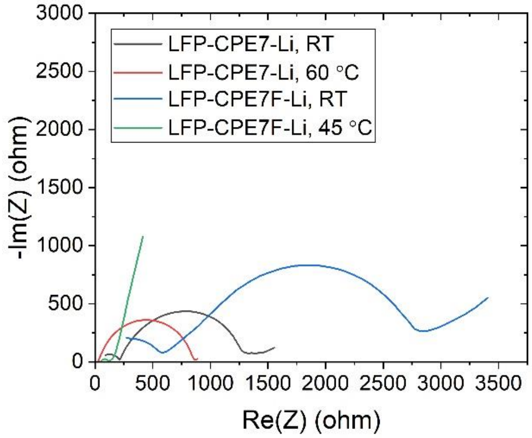

Figure 5. EIS comparison of LFP cells using CPEs with or without FEC additives, tested at different temperatures.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.