Lithium Dendrite Growth through Solid Electrolytes

Investigated using Thin-Film Batteries with Tunable Artificial Grain Boundaries

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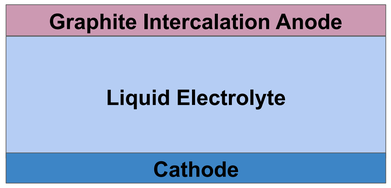
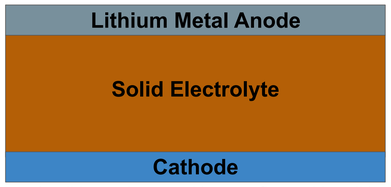
Motivation

- Solid electrolytes enable lithium metal anodes in lithium batteries
  Benefits: Improved safety Higher energy density

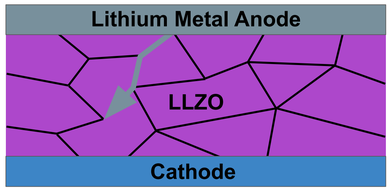


A conventional lithium-ion battery uses flammable liquid electrolyte and a graphite intercalation anode

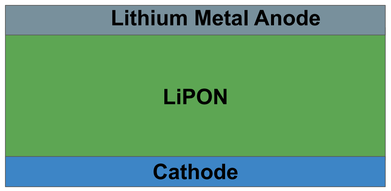


A solid-state battery with a non-flammable solid electrolyte can use a metallic lithium anode

- The relatively low ionic conductivity of solid electrolytes (10^{-2} – 10^{-7} S/cm) is a barrier to device performance
- But lithium dendrites grow along grain boundaries in many solid electrolytes that have high ionic conductivity, causing short circuits and cell failure



Sintered LLZO permits lithium dendrite growth[1]



Amorphous LiPON inhibits lithium dendrite growth

Goals

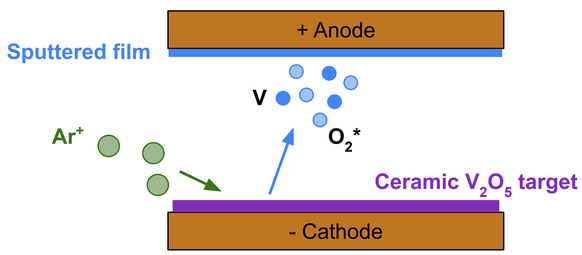
1) **Investigate dendrite growth as a function of grain boundary properties**
   - Mechanical weakness makes dendrite growth energetically favorable
   - Electrical conductivity enables reduction of lithium deep in solid electrolyte
2) **Develop thin-film solid state batteries as a platform for further experiments**

   Require: a) Sufficient capacity to grow dendrites
   b) Well understood deposition processes for reproducibility

   Enable: a) Dendrite growth under pressure applied by a nanoindenter
   b) Vertical grain boundaries

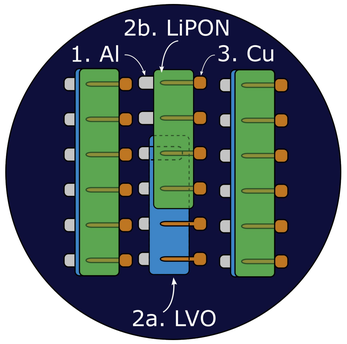
Reactive Sputter Deposition

- Argon ions are accelerated towards target and eject (sputter) material onto the substrate
- A magnetic field confines the plasma and increases the deposition rate
- Reactive working gases enable the deposition of complex chemistries

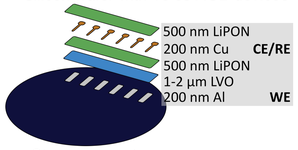


Solid-State AGB Devices

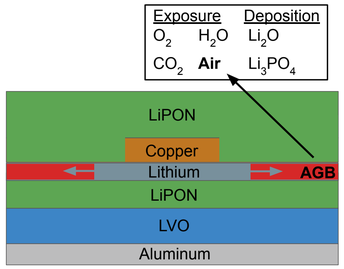
- Air exposure of the first layer of lithium phosphorus oxynitride (Li_2PO_2N) introduces a tunable grain boundary
- Anode-free design relies on lithium from the cathode being plated on the copper current collector upon charging



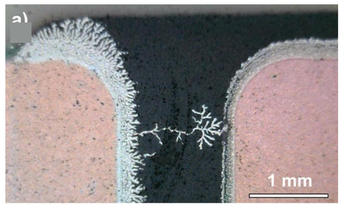
Silicon wafer with 18 ss-AGB devices



Stack blow-out

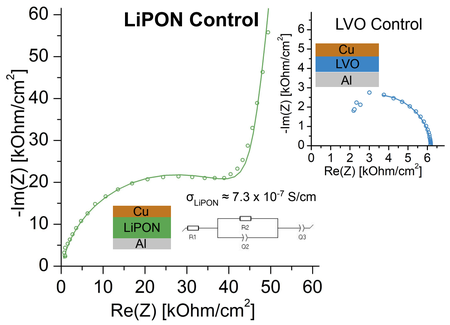


ss-AGB cross section

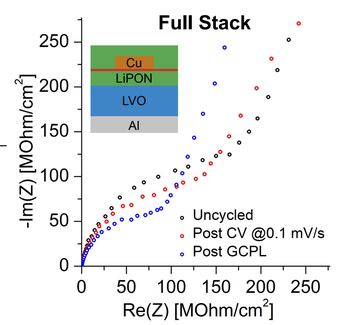


Dendrite growth in a horizontal AGB between LiPON layers reported by Westover et al.[2]

Result: Electrochemical impedance spectroscopy (EIS) indicates that high full-stack impedance originates in LVO/LiPON interface



LVO- and LiPON-only control devices indicate reasonable impedance of Al/LVO and LiPON/AGB/Cu interfaces

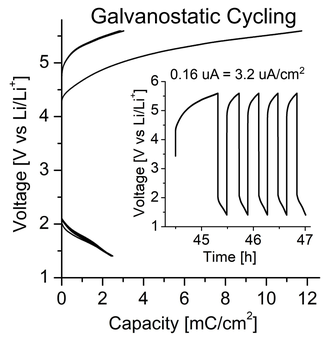


Full stack ss-AGB devices have unacceptable impedance from LVO/LiPON interface

Result: High impedance leads to low capacity and impaired ability to plate lithium

30 mC/cm²
Needed to plate 40 nm of Li
1 mC for 4 mm²

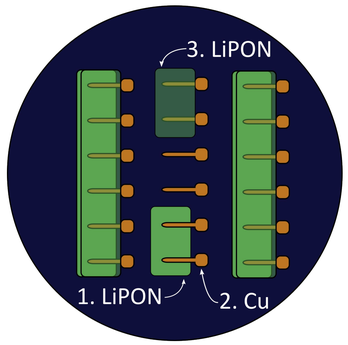
89 mC/cm²
Expected from 500 nm of $Li_1V_2O_5$
3.6 mC from 4 mm²



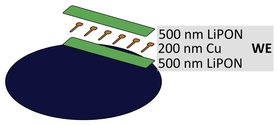
Galvanostatic cycling moves only ~10% of the expected capacity

Beaker-Cell AGB Devices

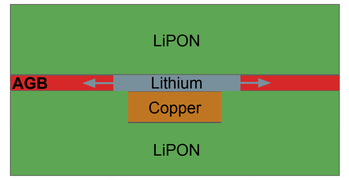
- Lithium foil counter electrode in a liquid cell ensures adequate capacity to plate lithium onto copper
- Samples retain artificial grain boundary between LiPON layers
- Aim to plate lithium in beaker cell (1 M $LiClO_4$, lithium foil as CE)



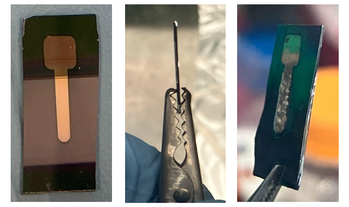
Silicon wafer with 18 b-AGB devices



Stack blow-out

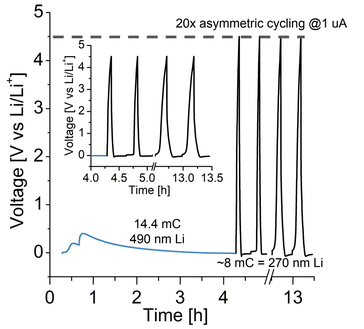


b-AGB device cross section

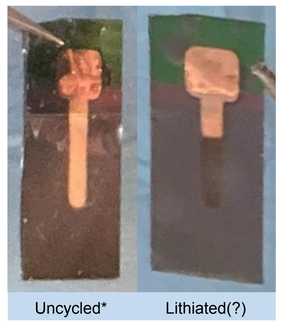


Uncycled b-AGB sample *Sample mounted on alligator clip* *Lithiated Cu-only control device*

Result: Copper under LiPON can be lithiated



Plating step and asymmetric cycling leads to lithiation of copper finger



Visual evidence of lithiation is supported by circumstantial evidence from Raman spectroscopy (not shown)

Future Work

1) Grow dendrites in b-AGB by cycling devices at high currents (~100 uA/cm²)
2) Repeat experiment with AGB-free devices (no air exposure) to confirm that the AGB interphase is required for dendrite growth

Acknowledgments

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1. Ren *et al.* **2015**. "Direct observation of lithium dendrites inside garnet-type lithium-ion solid electrolyte." *Electrochem. Comm.* 57
2. Westover et al. **2019**. "Deposition and Confinement of Li Metal along an Artificial Lipon–Lipon Interface." *ACS Energy Lett.* 4 (3)