



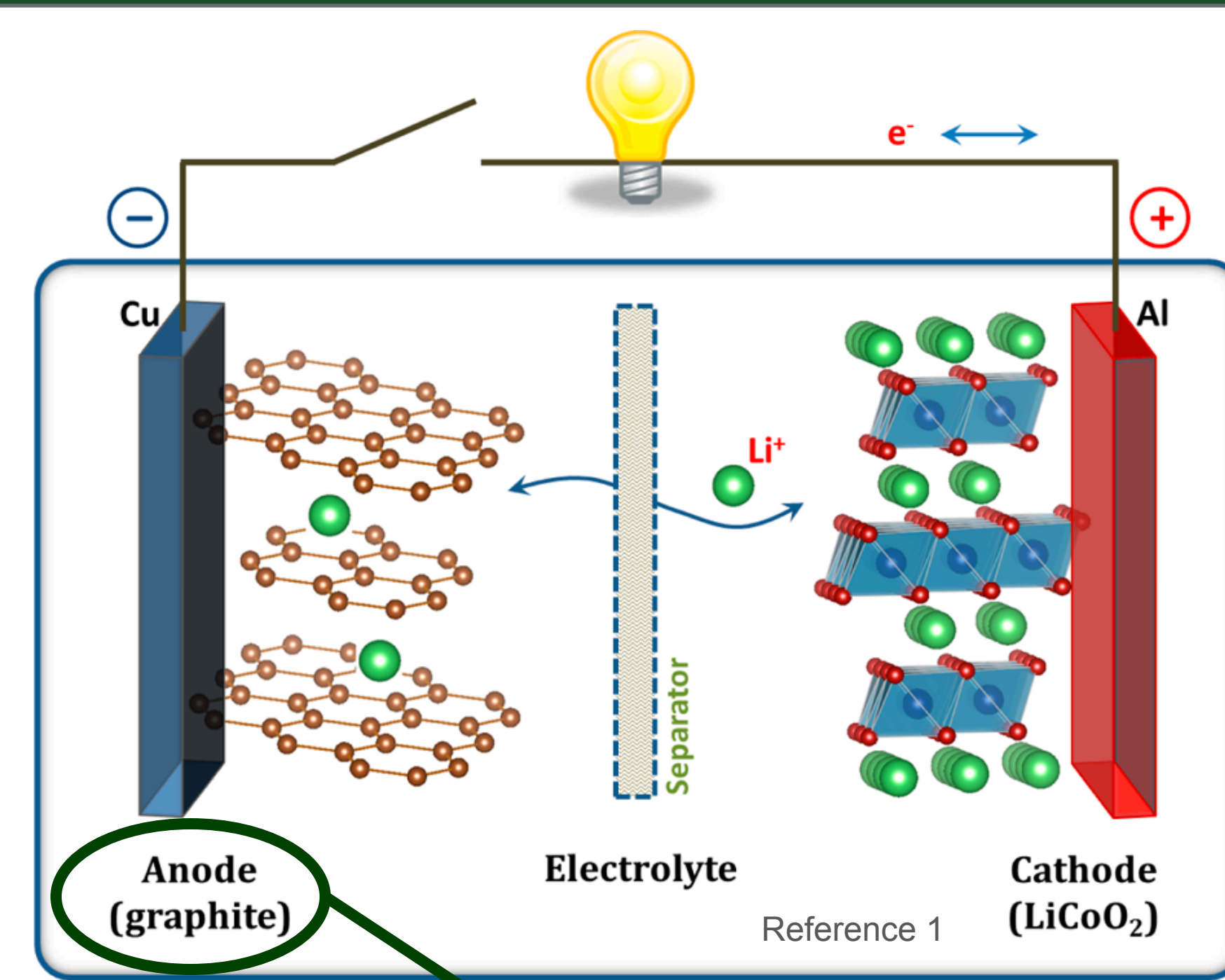
Exploring and mitigating failure modes in anodes for Li-ion batteries

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How can batteries store more energy?

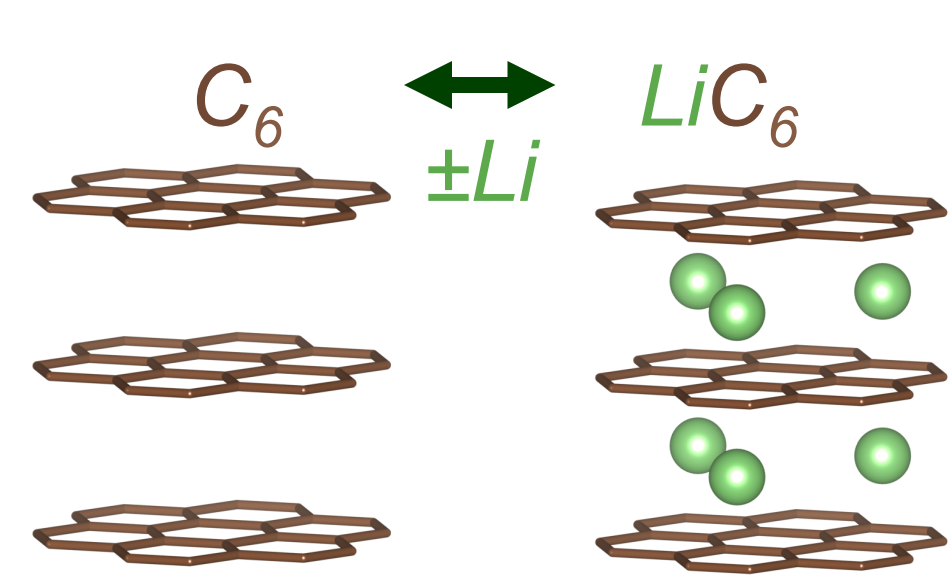


Rechargeable Li-ion batteries store energy by reversibly storing Li-ions (Li^+) at different electrochemical potentials in negative (**anode**) and positive (**cathode**) electrodes. The cell voltage (difference in potential between electrodes) and the **capacity** (amount of Li^+ in each electrode) determine the energy the cell can store.

Thus, one way to increase the energy that a battery stores is to use an electrode material with greater capacity per unit mass (mAh/g) or per unit volume (mAh/cm^3). Many new materials exist that have capacities greater than graphite, the anode used in today's Li-ion batteries. However, many of the new materials exhibit limited useful lifetimes due to failure modes that we aim to understand and mitigate to produce high capacity batteries that are commercially viable.

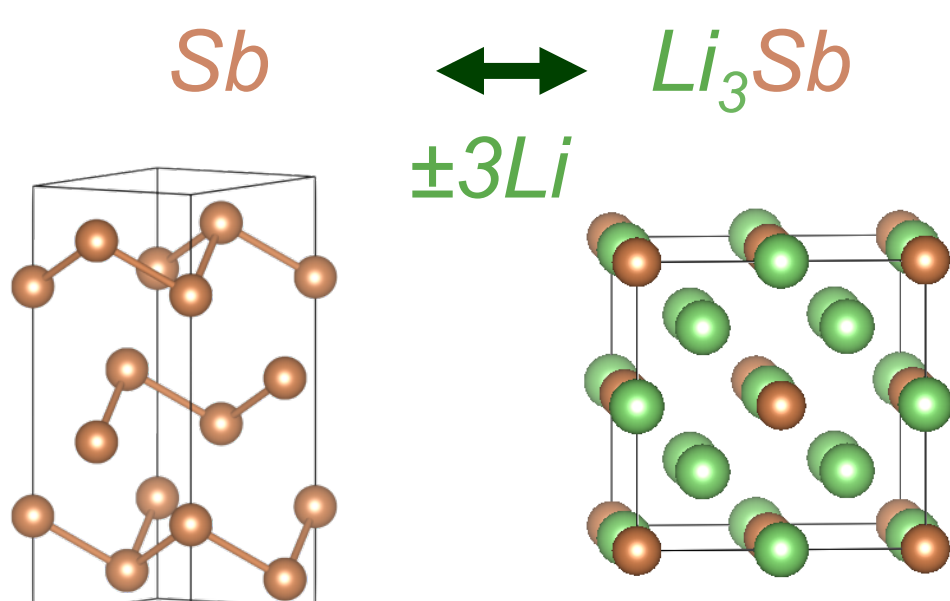
Next generation anode materials

Intercalation material: graphite



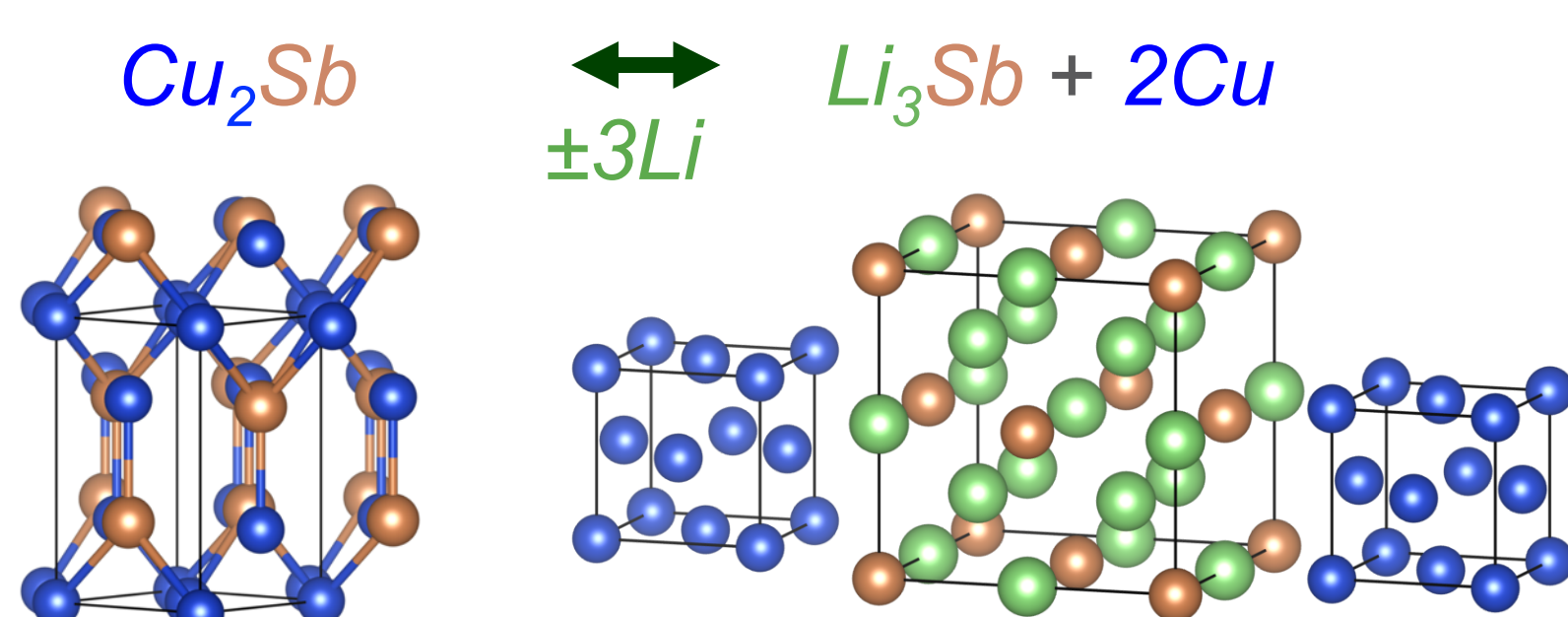
372 mAh/g
800 mAh/cm³
good conductivity
10% volume change

Alloying material: antimony



660 mAh/g
4418 mAh/cm³
poor conductivity
129% volume change

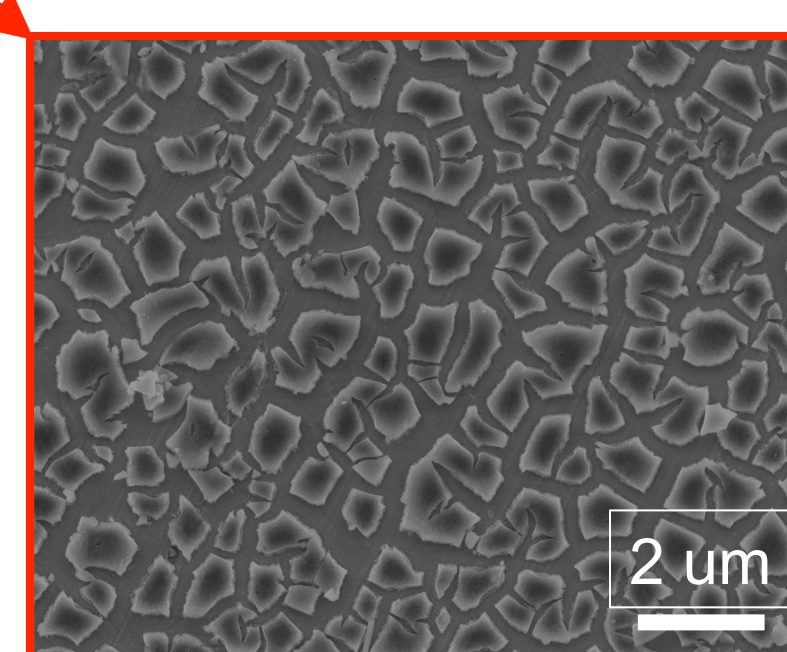
Conversion material: copper antimonide



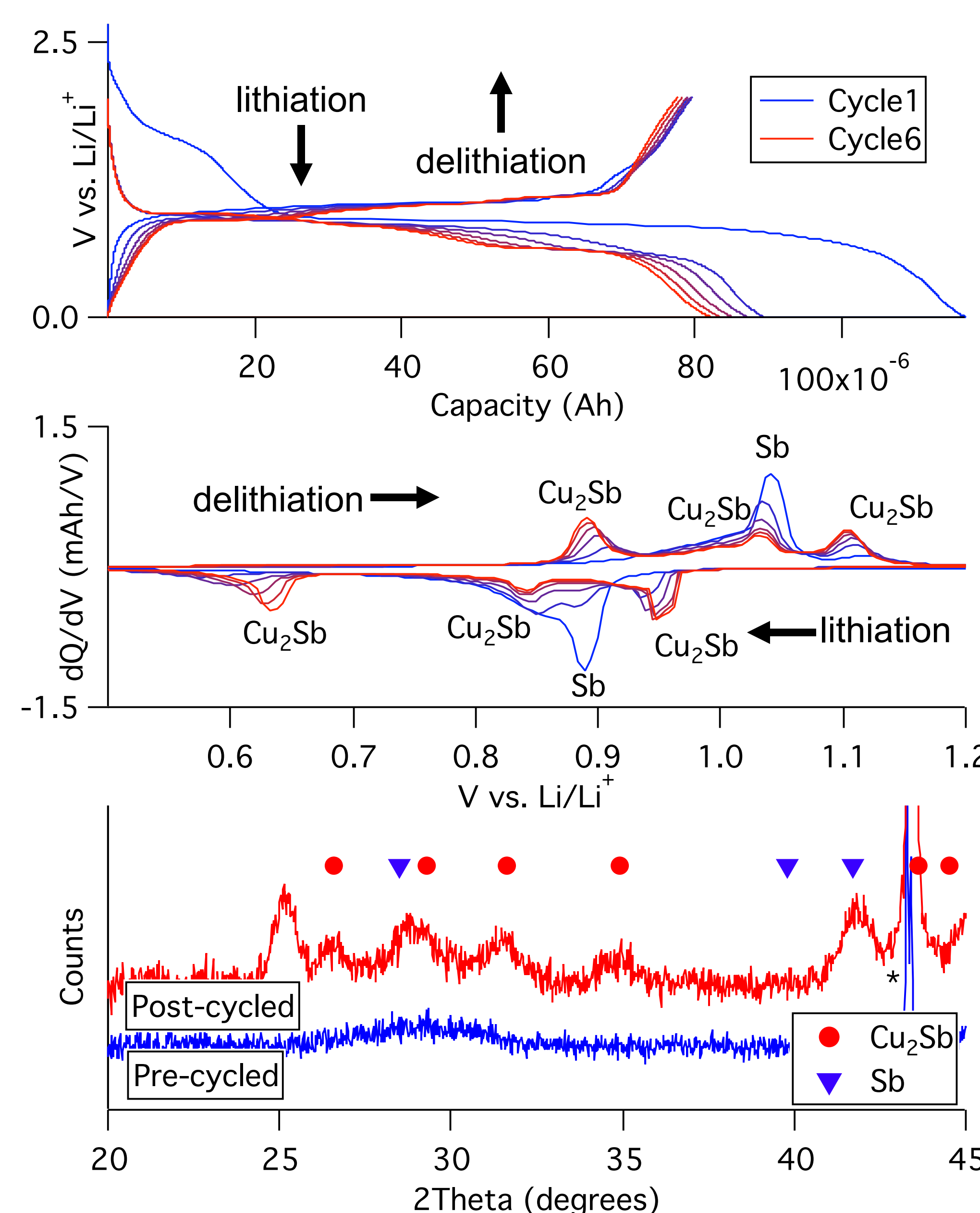
323 mAh/g
2730 mAh/cm³
improved conductivity
~90% volume change

Failure mode:
volume changes
during cycling
film or particles of
active material

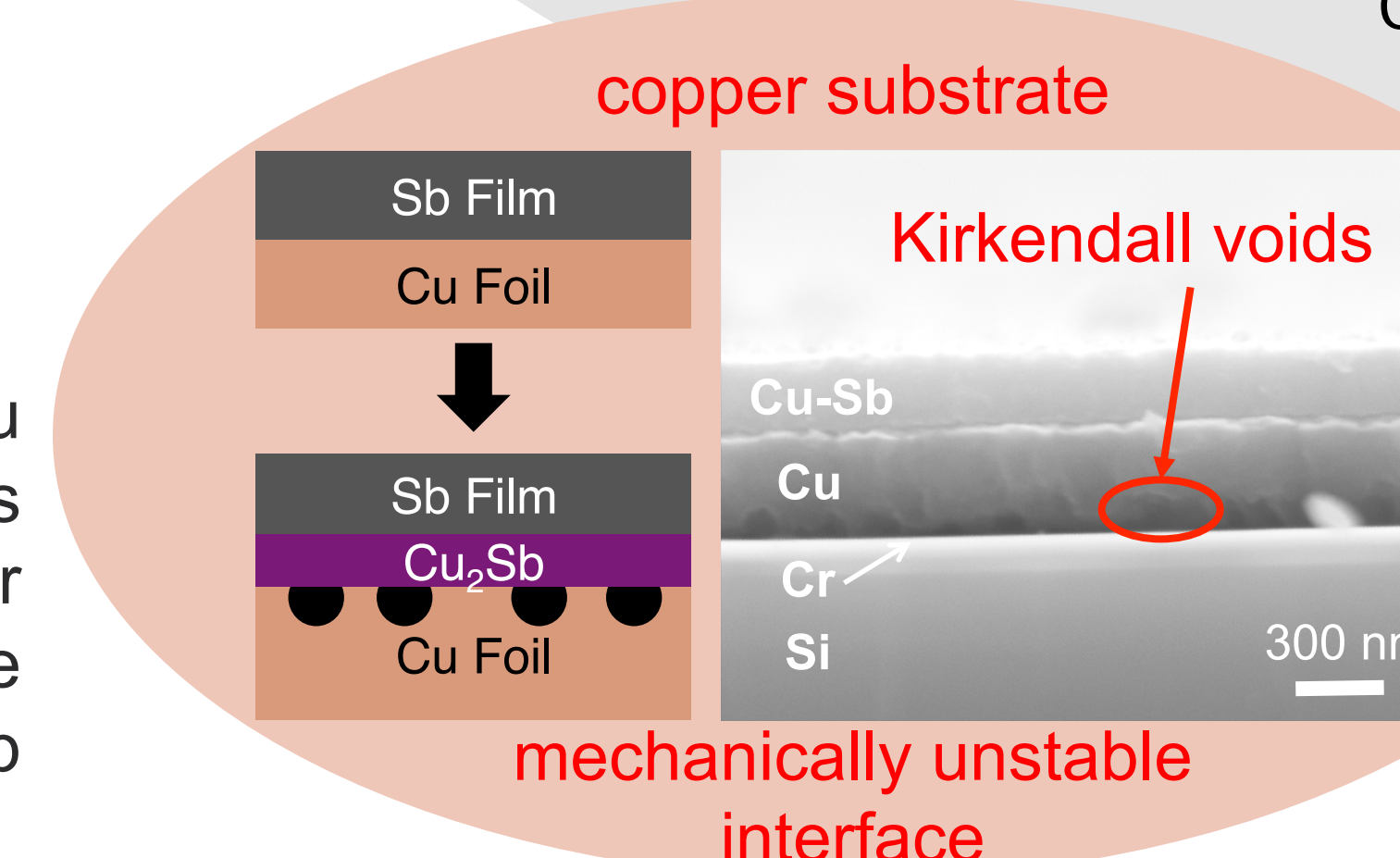
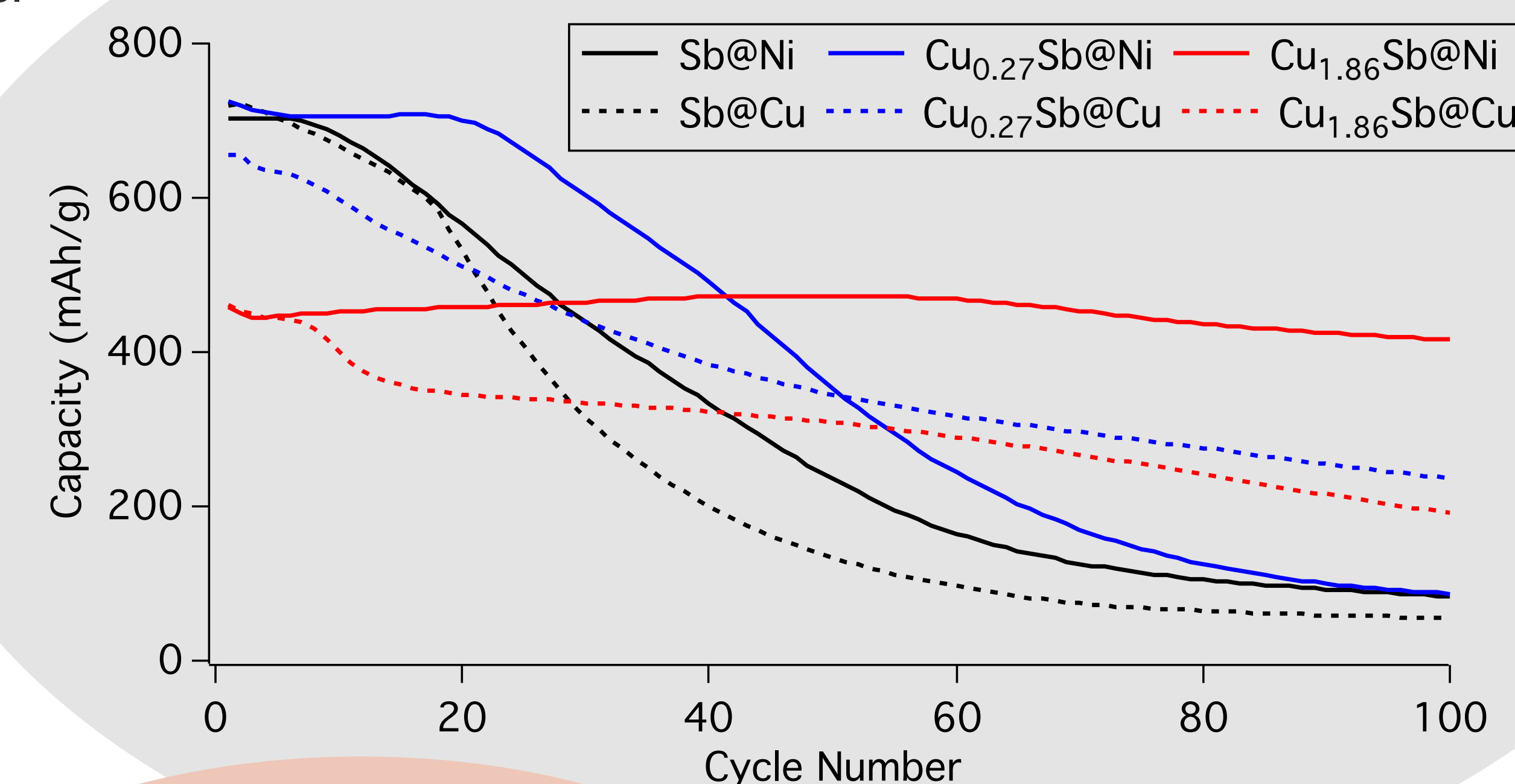
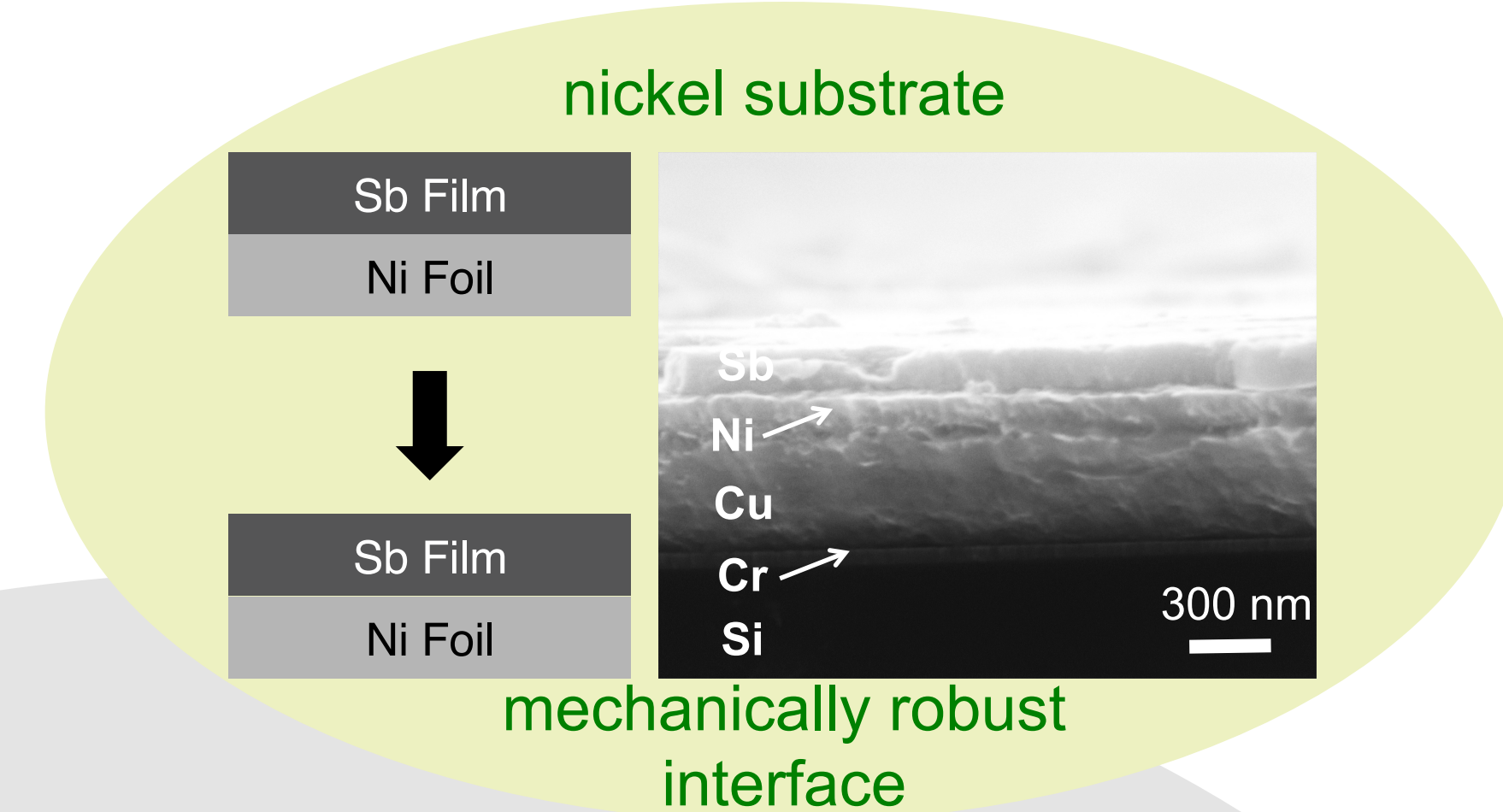
cracking,
pulverization, and
delamination



Electrochemical performance of Cu-Sb anodes is substrate dependent

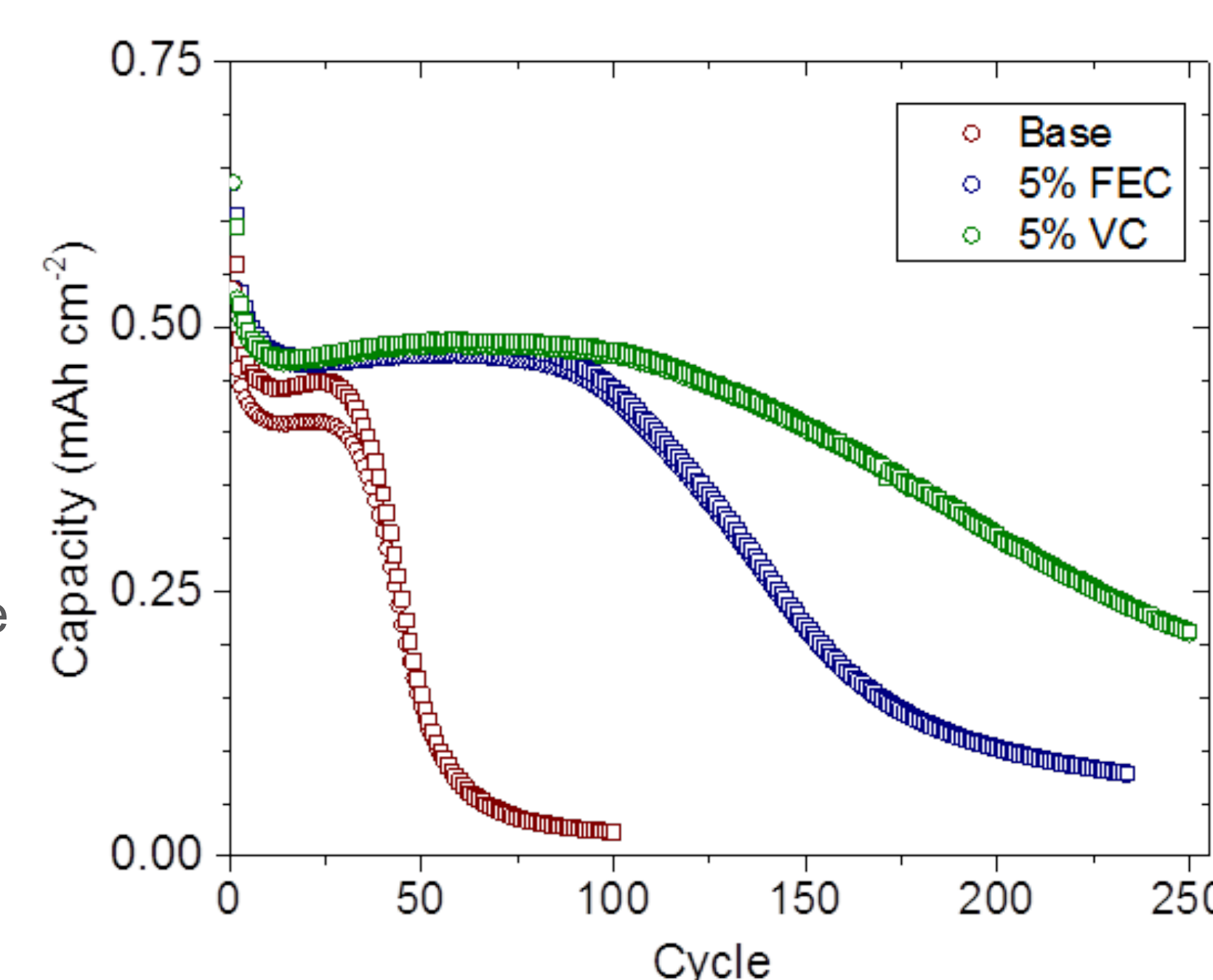


The lack of interdiffusion between Sb-containing thin films and Ni substrates results in a film-substrate interface that is resilient to the volume changes of the Sb as it alloys and dealloys with Li^+ . This strong interface results in Cu-Sb thin film anodes of any Cu-Sb composition to have cycle lifetimes superior to those on Cu substrates.

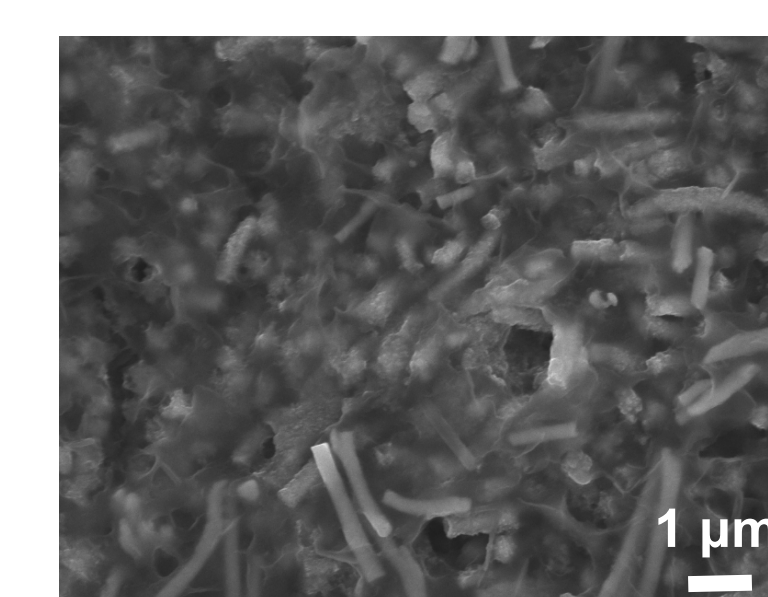
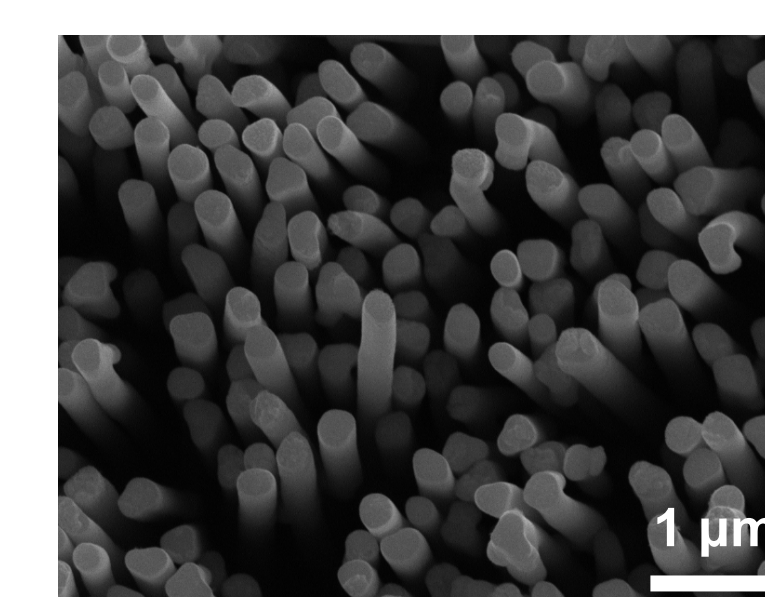


The interdiffusion between Sb-containing thin films and Cu substrates to form Cu_2Sb is confirmed by XRD. The process of interdiffusion creates Kirkendall voids that mechanically weaken the film-substrate interface and exacerbate film delamination. This weak interface results in Cu-Sb thin film anodes of any Cu-Sb composition to have cycle lifetimes inferior to those on Ni substrates.

What is still needed to make these anodes commercially viable?



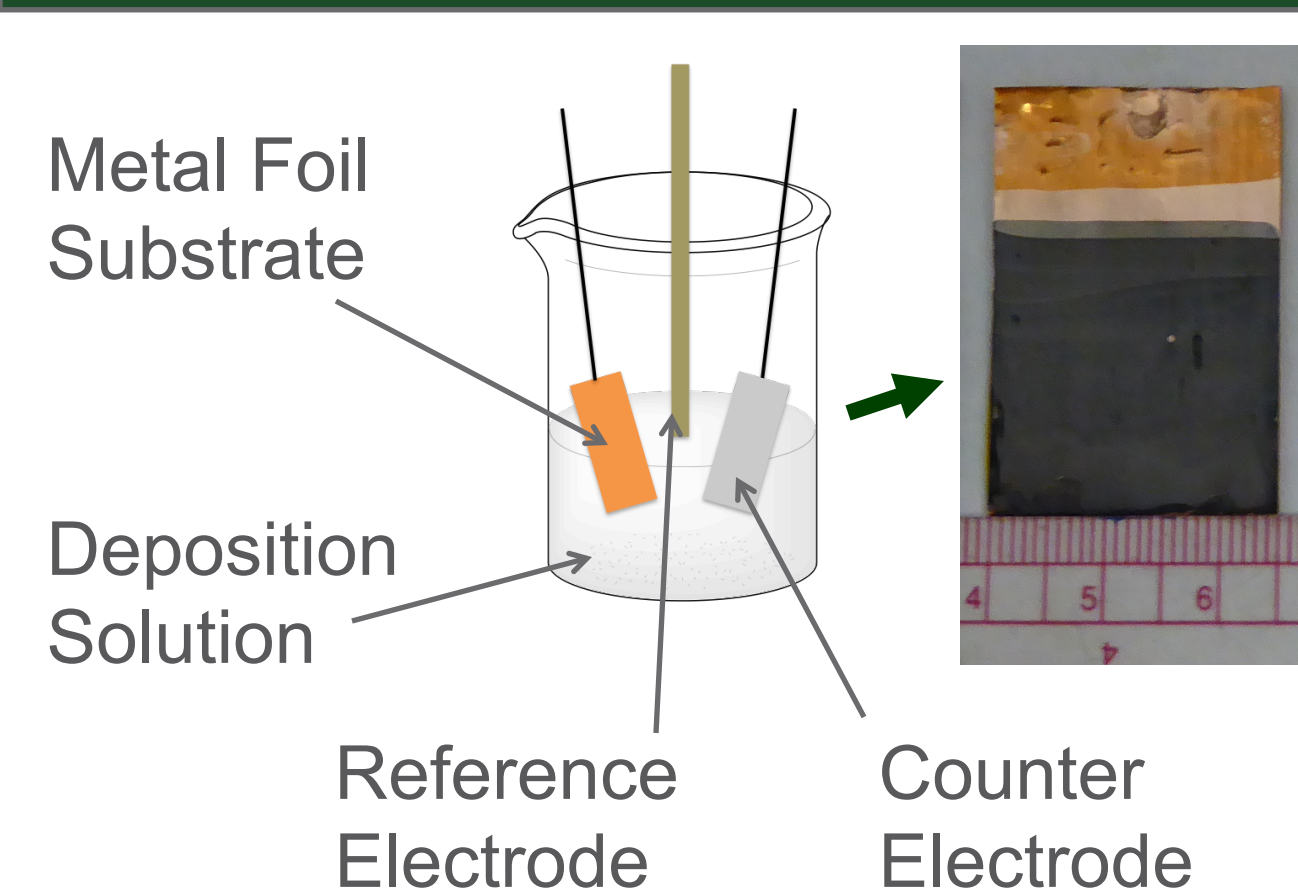
Nanowires of Cu_2Sb resist mechanical degradation during cycling



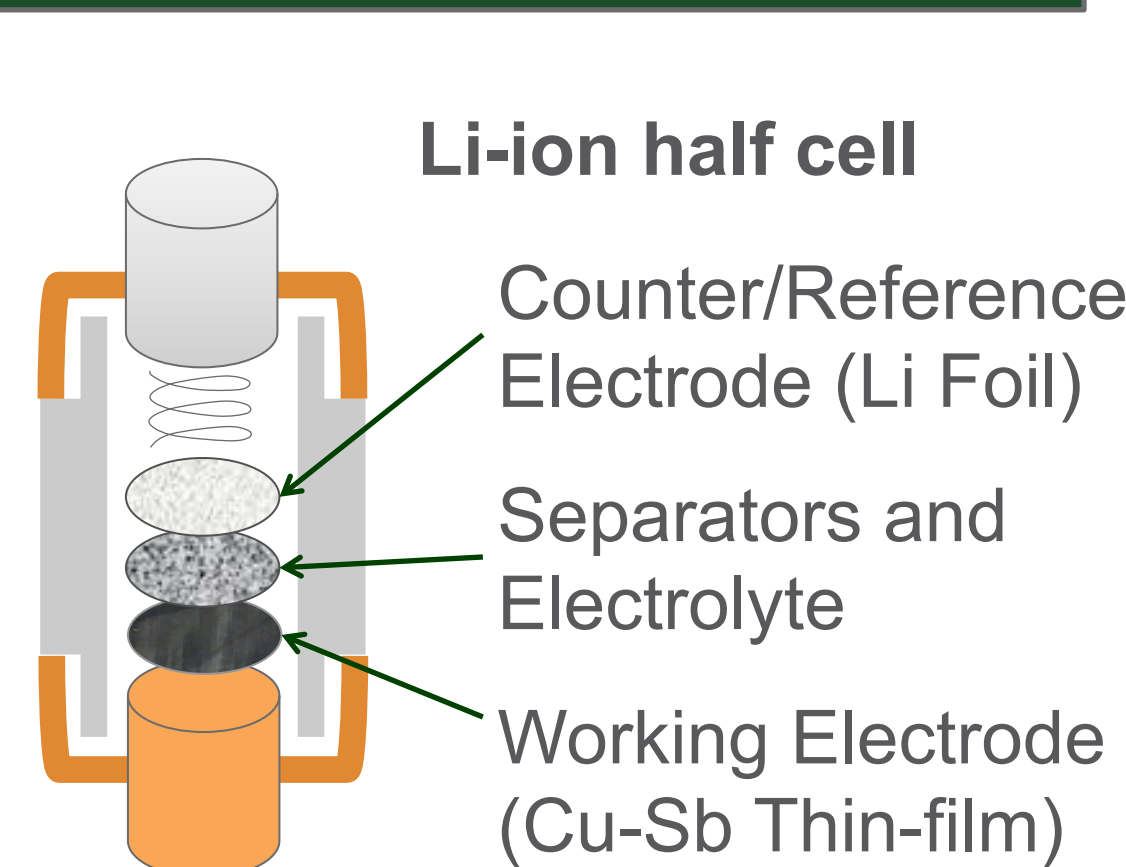
High surface area results in excessive growth of SEI layer

Mechanical degradation still plagues the cycle lifetimes of alloy and conversion anodes. Nano-structuring of these materials has been shown to help alleviate such degradation by providing space for active material to expand and contract. However, another battery failure mode can be exacerbated by nano-structuring: excessive growth of the solid-electrolyte-interface (SEI) layer as seen above as a residue coating a nanowire array anode after cycling in a Li-ion battery. Strategies to mitigate this failure mode include the use of electrolyte additives to passivate SEI layer growth and extend cycle lifetimes (shown left).⁴ Ultimately, the design of commercially viable batteries with increased energy density needs to address all failure modes concurrently.

Electrodeposition of thin film Cu-Sb anodes



We use electrodeposition to produce Cu-Sb anode materials we are interested in studying. By careful selection of the deposition solution composition and the potential applied between the counter and reference electrodes, we produced thin films of our desired material directly on metal foil substrates (left).³ The films are characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) both before and after cycling them in Li-ion half cells (right) to gain understanding about how the materials fail during cycling.



1) J. B. Goodenough and K.-S. Park, The Li-Ion Rechargeable Battery: A Perspective, *J. Am. Chem. Soc.*, 2013, **135**, 1167–1176.

2) L. Fransson, J. T. Vaughney, R. Benedek, K. Edström, J. O. Thomas and M. M. Thackeray, Phase transitions in lithiated Cu_2Sb anodes for lithium batteries: an in situ X-ray diffraction study, *Electrochem. Comm.*, 2001, **3**, 317–323.

3) J. M. Mosby and A. L. Prieto, Direct Electrodeposition of Cu_2Sb for Lithium-Ion Battery Anodes, *J. Am. Chem. Soc.*, 2008, **130**, 10656–10661.

4) E. D. Jackson and A. L. Prieto, Copper Antimonide Nanowire Array Lithium Ion Anodes Stabilized by Electrolyte Additives, *ACS Appl. Mater. Interfaces*, 2016, **8**, 30379–30386.

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