

# Lithium-ion Anodes with Aluminum Current Collectors – An Analysis of a Germanium Nanoparticle Composite on an Aluminum Current Collector Tested with a Lower Potential Limit of 0.3 V vs. Li/Li<sup>+</sup> Batteries

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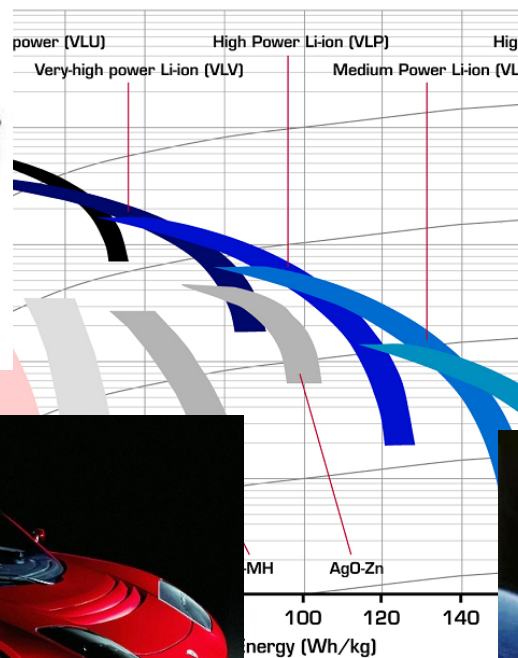


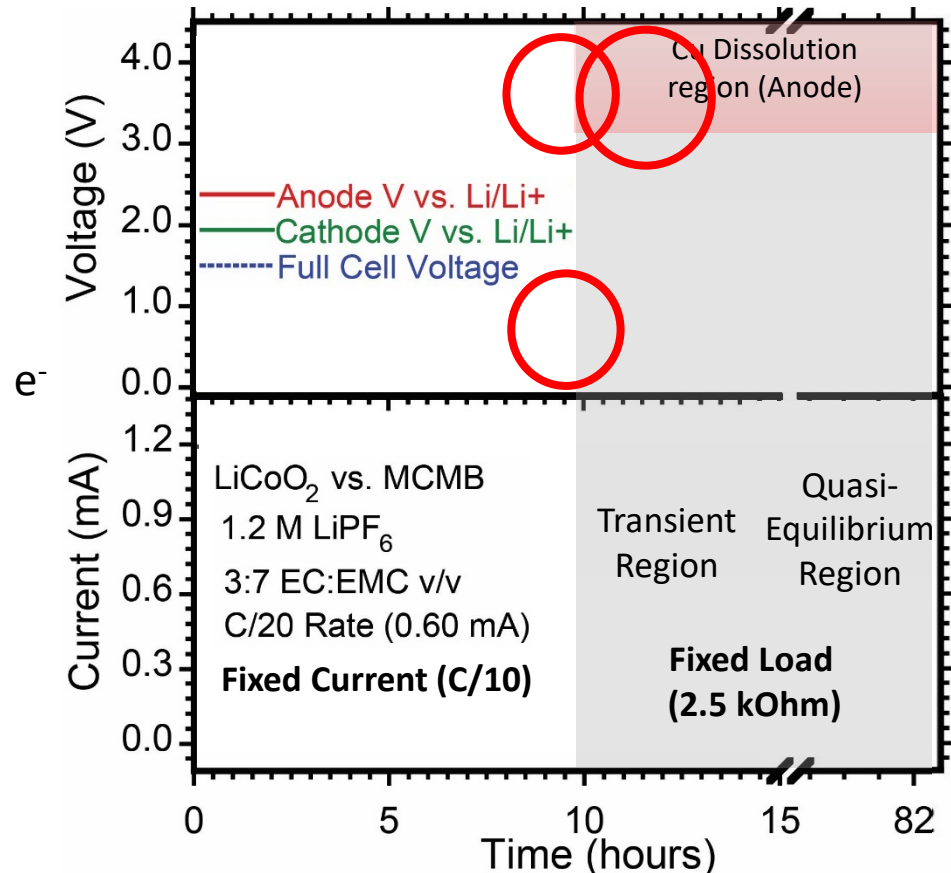
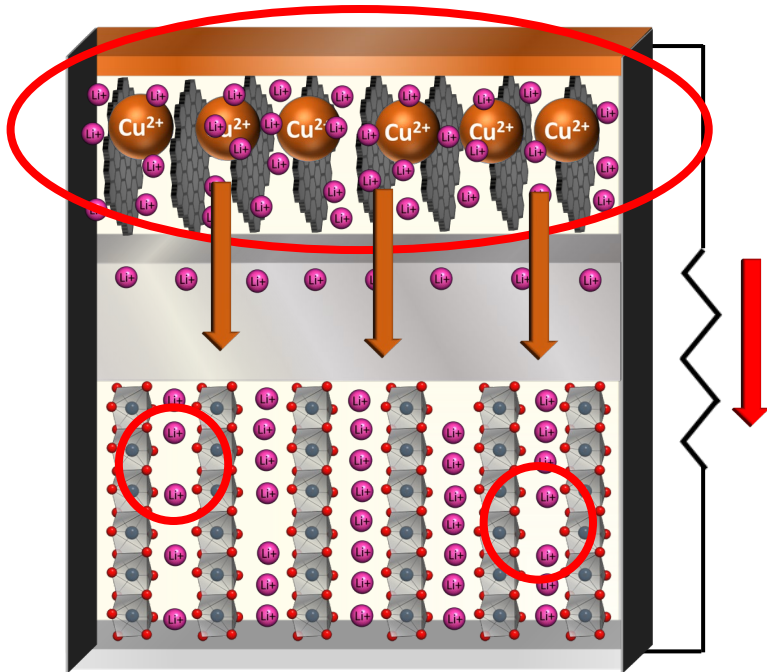
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*Lithium ion batteries have increased energy and power density compared to other chemistries, making them the best choice for many portable electronic applications*



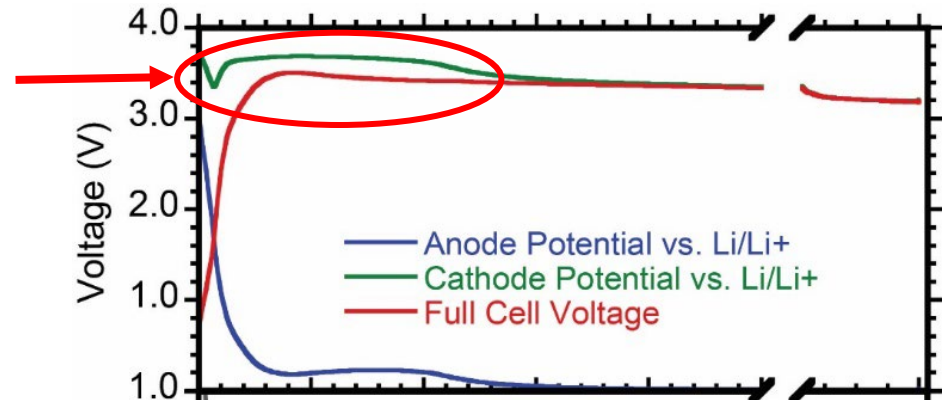


**Conventional lithium-ion cells can't be overdischarged without performance degradation and damage, requires monitoring and BMS protections, need to store in mid-range state of charge**

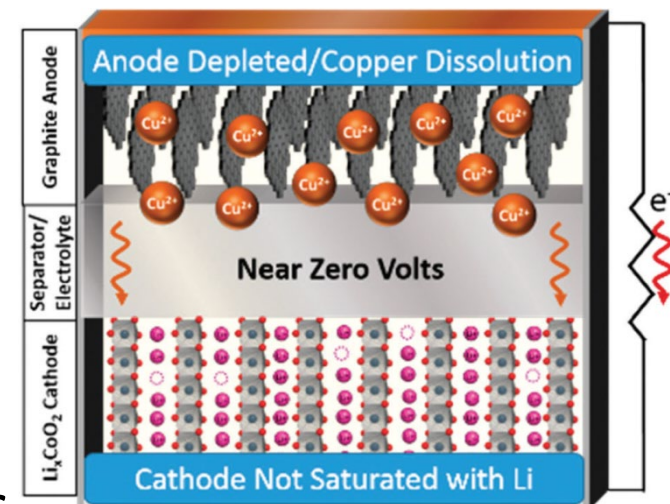




High anode potential resulting in copper dissolution is major degradation mechanism



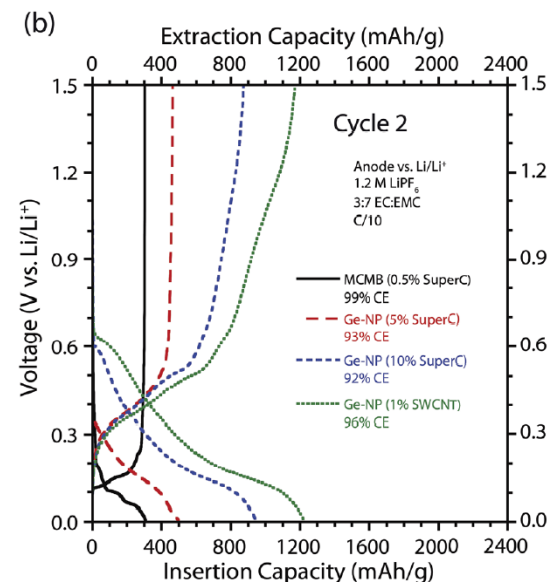
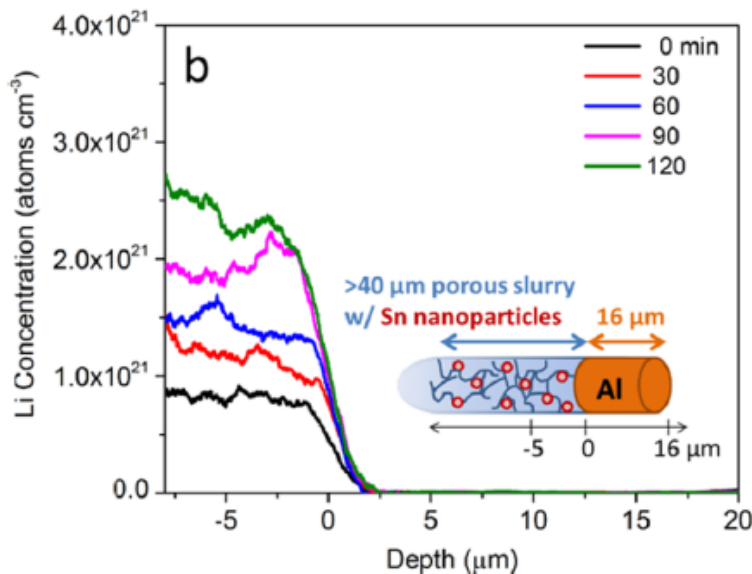
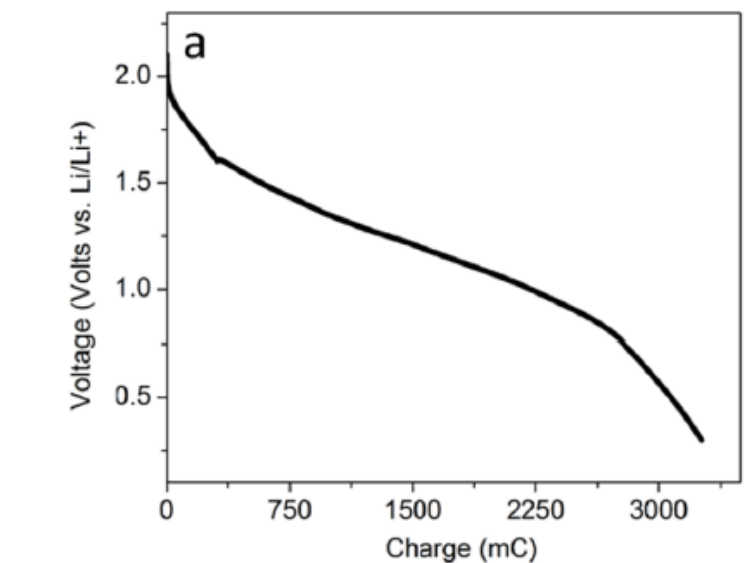
- 2 general approaches for overdischarge tolerance - Can either prevent high anode potential during overdischarge, or make anode tolerant to higher potentials
- Could we use aluminum as the current collector for the anode?
  - Stable to  $>4.5$  V vs. Li/Li<sup>+</sup> in LiPF<sub>6</sub> and LBF containing electrolytes due to Al-F layer formation
  - Alloys with Li at  $<0.3$  V vs. Li/Li<sup>+</sup>
    - **Need anode materials with lithium redox reactions  $>0.3$  V vs. Li/Li<sup>+</sup>**
    - **Lithium titanate is one material that meets this requirement and is in use**



# Potential anode materials with Al CC

- Lithium titanate has drawback of low cell voltage and low achievable energy density
- Tin has an alloying reaction with lithium that occurs in the 0.005-2.0 V vs. Li/Li<sup>+</sup> range
- Prior work by Liu *et al* showed with neutron depth profiling that as long as the potential of an anode stays >0.3 V vs. Li/Li<sup>+</sup>, lithium will not alloy with the aluminum

- Germanium has a portion of its alloying potential above 0.3 V vs. Li/Li<sup>+</sup>
- Has higher specific capacity than Tin and fast lithium diffusion



Danny X Liu, *et al*, Chem Mater (2016), 28, 556-563

Michael Forney, *et al*, J. Mater. Chem. A (2014), 2, 14525-14535

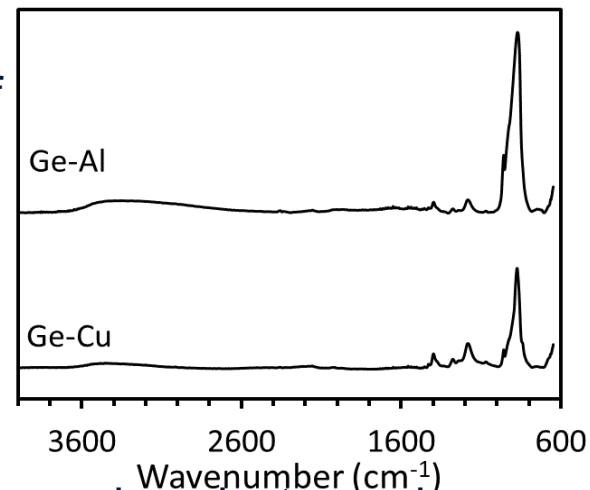


- A lower potential cutoff of 0.3 V vs. Li/Li<sup>+</sup> necessary to avoid lithium-aluminum alloying is *much higher than the conventional lower potential cutoff of 0.005-0.02 V vs. Li/Li<sup>+</sup> that has been used to study germanium as an anode material for Li-ion batteries*
- This study takes a comparative approach for performance, analyzing a germanium anode with an aluminum current collector with a 0.3 V vs. Li/Li<sup>+</sup> lower potential cutoff and comparing results to a germanium anode with a more conventional copper current collector with a 0.005 V vs Li/Li<sup>+</sup> lower potential cutoff
- The high potential material and cycling stability is assessed as well

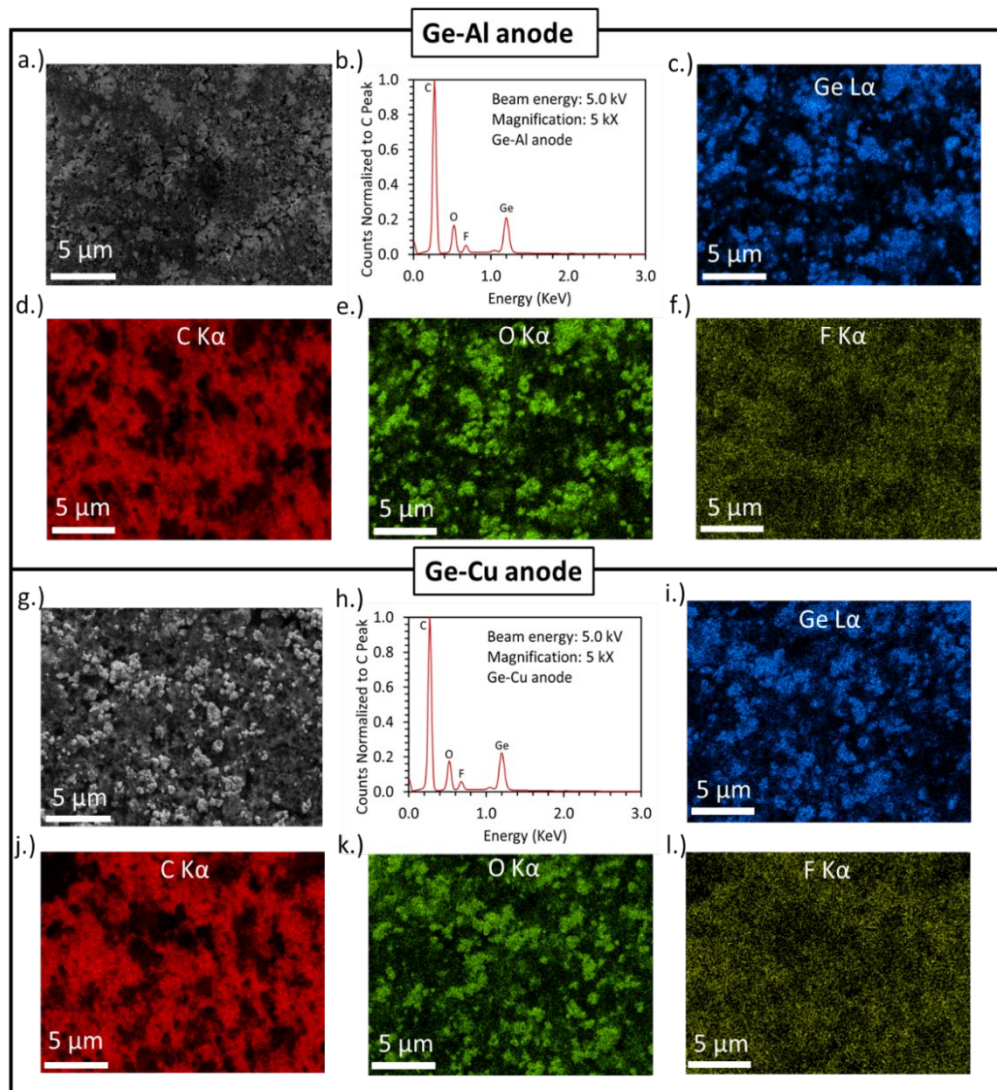


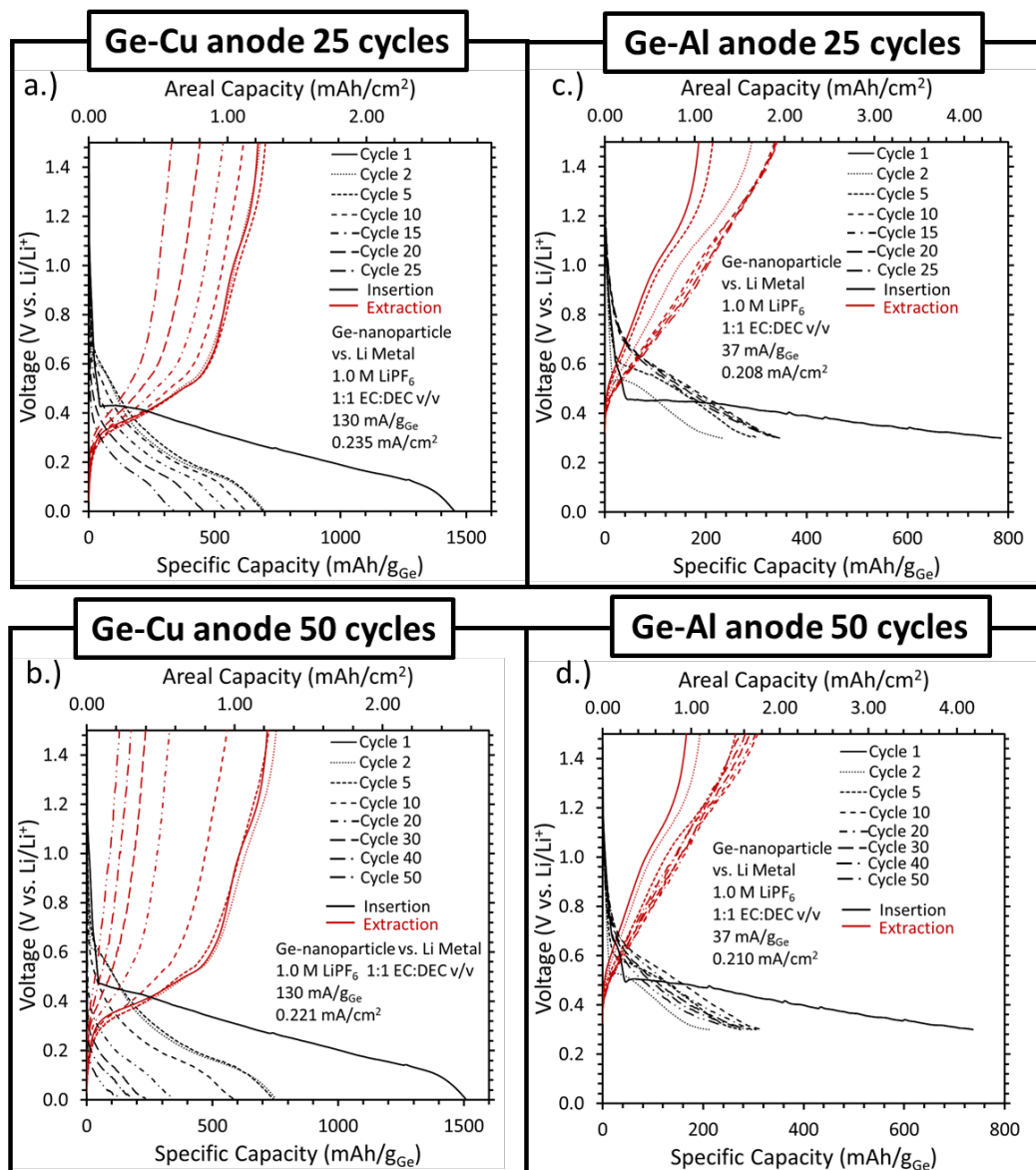


- Ge-Al and Ge-Cu electrode fabricated at 2 mAh/cm<sup>2</sup> targeted areal capacity – Ge-Al thicker due to higher lower potential cutoff



- After fabrication, scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (SEM/EDS) shows 1-2  $\mu\text{m}$  clusters of germanium nanoparticles
  - Also shows co-location of germanium and oxygen
  - Carbon and fluorine corresponding the conductive additive and binder are dispersed around the germanium
- Fourier Transform Infrared Spectroscopy (FTIR) confirms the presence of germanium oxide
- Both Ge-Cu and Ge-Al electrodes similar despite different thickness



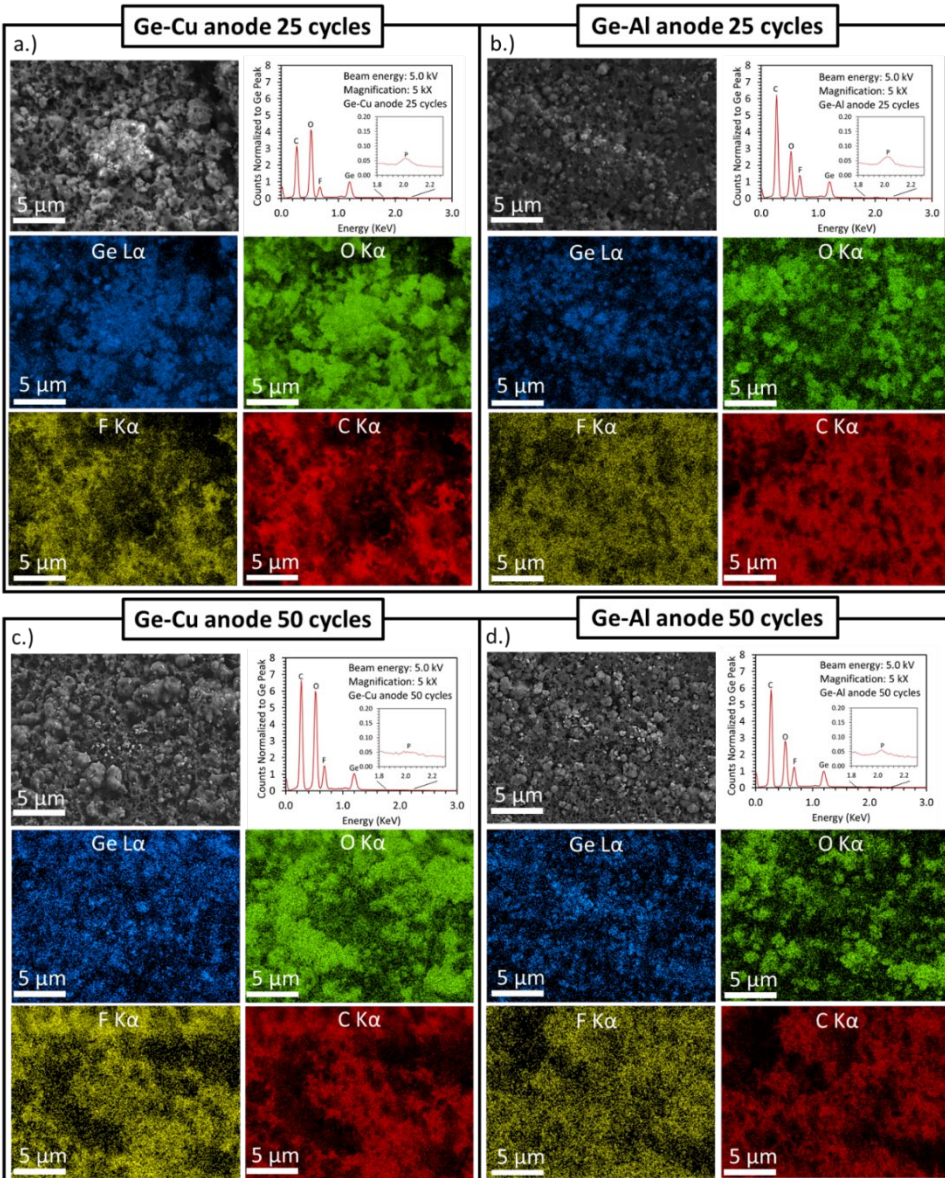


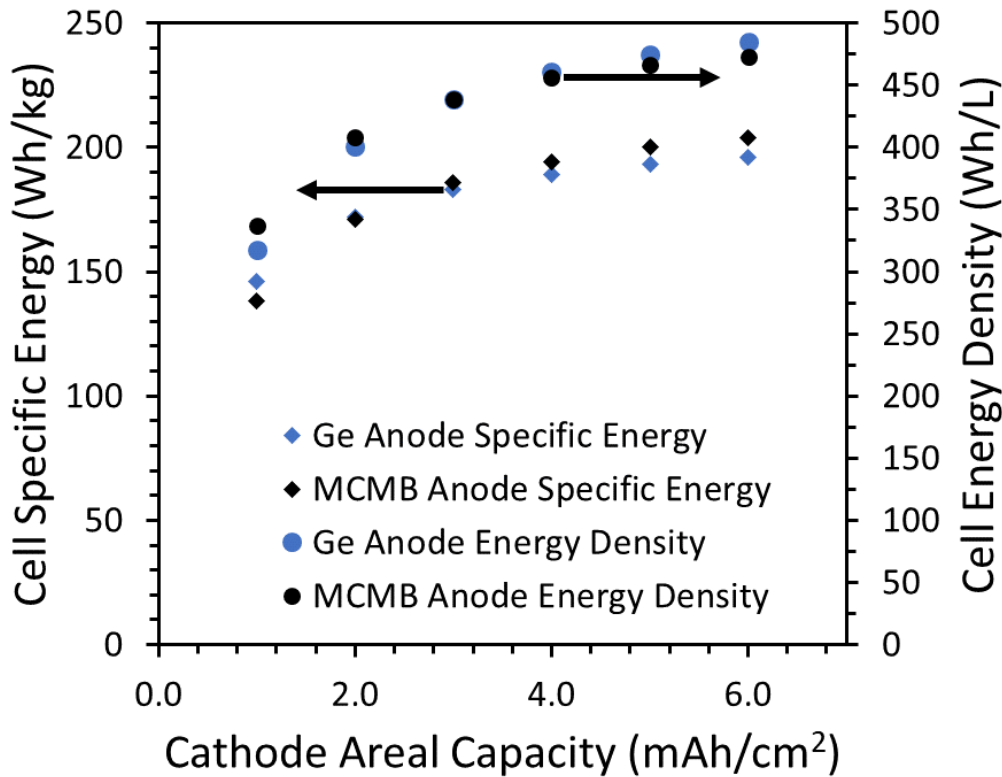
- Electrodes are tested versus lithium metal in a coin cell (like a watch battery)
  - Standard cycle-performance screening method for new materials and electrodes
- Electrodes were cycled at a targeted C/10 current rate based on literature reported capacities of similar germanium nanoparticles
  - 10 hour charge, 10 hour discharge
- Ge-Al electrode has lower specific capacity (mAh/g<sub>Ge</sub>) than Ge-Cu electrode as expected, and also has a higher average extraction potential
  - Will lower full cell voltage
- *However also has much higher capacity stability through 50 cycles*





- SEM/EDS shows less oxygen on the Ge-Al electrode compared to the Ge-Cu electrode
- Relative amounts of O, F, P and C compared to Ge are also stable from 25 to 50 cycles for the Ge-Al electrode but not for the Ge-Cu electrode
- Ge-H bonds in Ge-Al electrode indicated in FTIR
- LiOH presence indicated by FTIR, germanium oxide has also changed
  - May indicate a  $\text{LiOH} \leftrightarrow \text{LiH} + \text{Li}_2\text{O}$  mechanism
- XPS showed that the Ge-Al electrode develops less  $\text{Li}_2\text{O}$ , retains more metallic germanium, and develops germanium carbide compared to the Ge-Cu electrode
- Raman spectroscopy confirmed less amorphization of germanium for Ge-Al electrode compared to Ge-Cu electrode.
- EIS study indicated more stable SEI during cycling in Ge-Al electrode compared to Ge-Cu



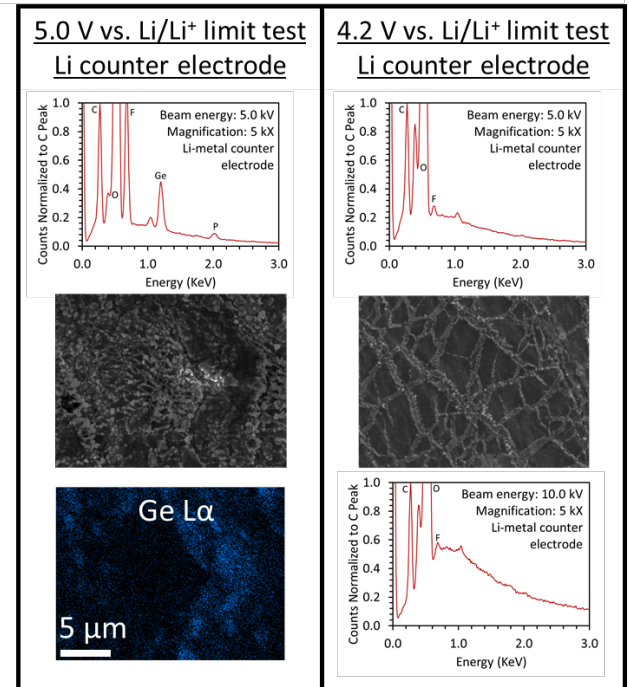
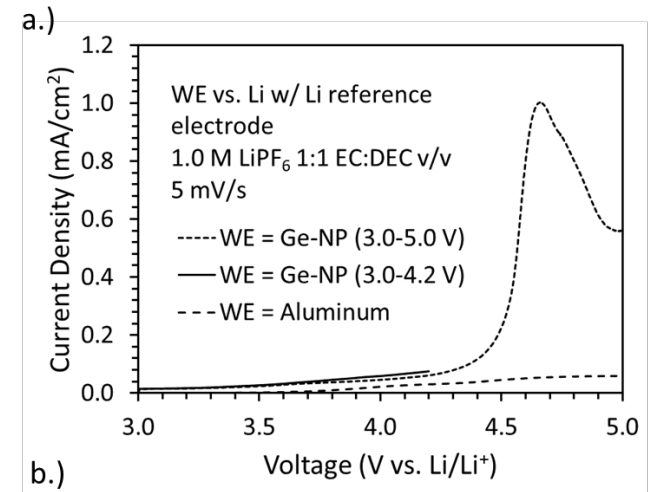


- Model predictions, while difficult to account for all factors, still help understand what can be achievable at cell level with new materials
- Model based on material densities, capacity and composite porosities
- Model built for an 18650 format Li-ion cell

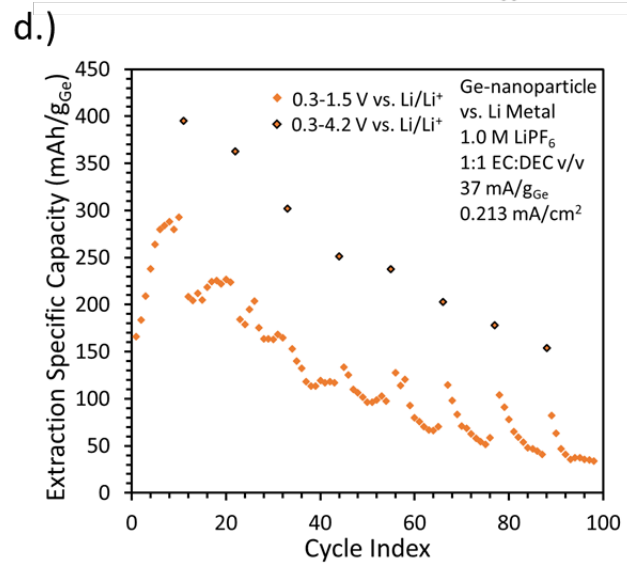
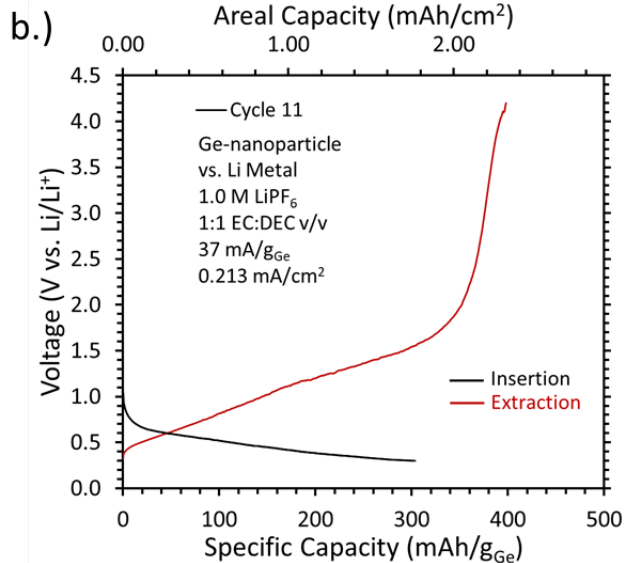
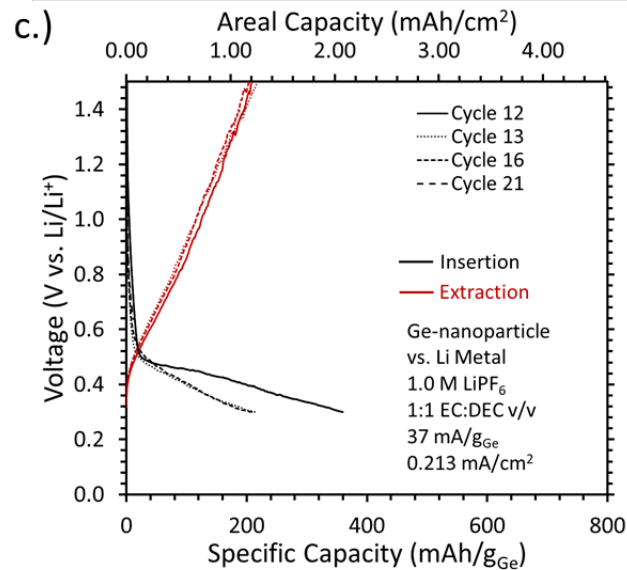
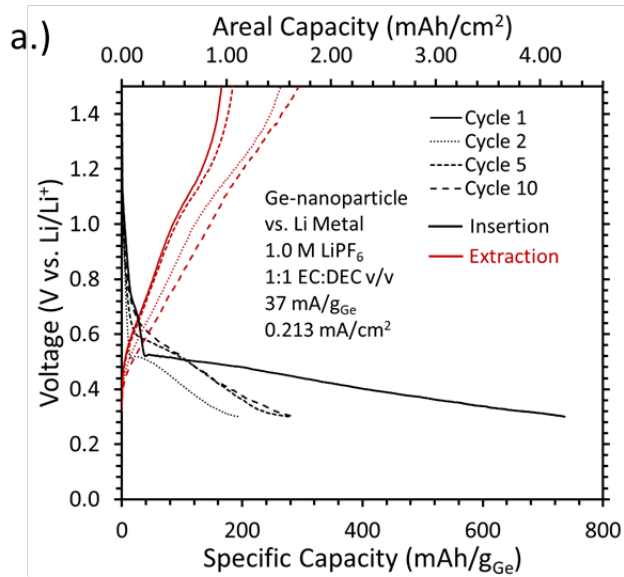
- Results show that achievable cell-level specific energy and energy density is very similar to the conventional, state-of-the-art materials
- Promising that Ge-Al electrodes could be used without significant performance trade-offs



- Two major aspects to the high potential stability of an anode materials
  - The material stability
  - The stability of the passivation layer (SEI) that forms during cycling
- Linear sweep voltammetry of an un-cycled Ge-Al electrode probes the material stability
- Inflection in the oxidative current begins at 4.2 V vs. Li/Li<sup>+</sup>
- After testing, disassembly and rinsing SEM/EDS shows that a linear sweep up to 5.0 V vs. Li/Li<sup>+</sup> results in germanium on the counter electrode, indicating germanium dissolution
- A linear sweep up to only 4.2 V vs. Li/Li<sup>+</sup> produces no germanium on the lithium counter electrode
  - *An upper material stability limit of 4.2 V vs. Li/Li<sup>+</sup> assigned based on this result, where germanium dissolution is the instability mechanism*



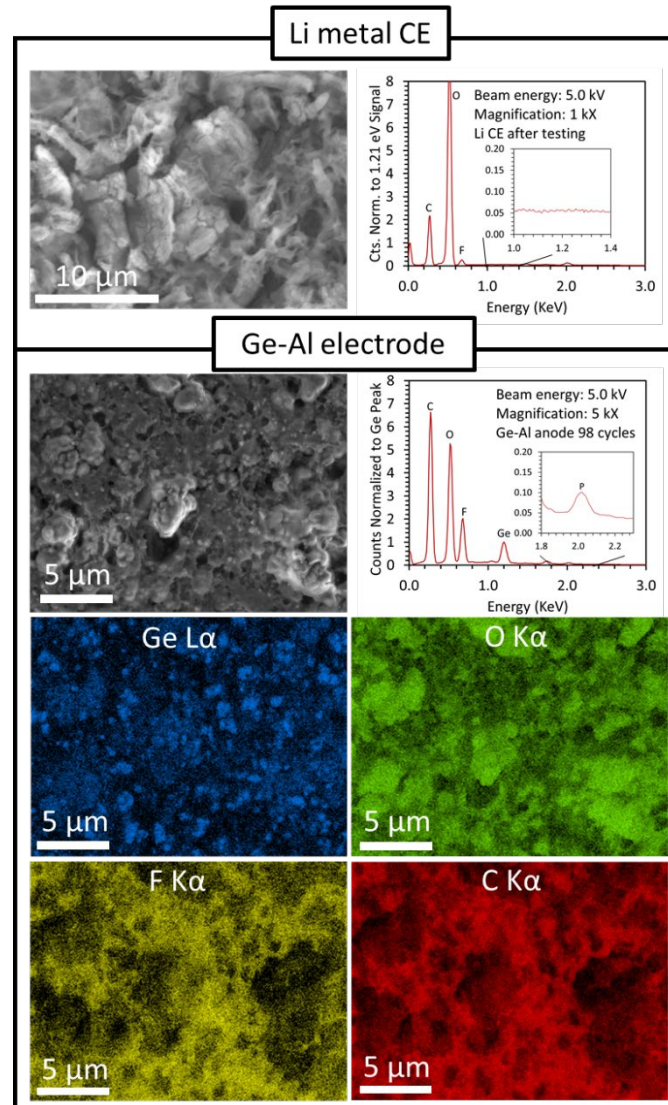
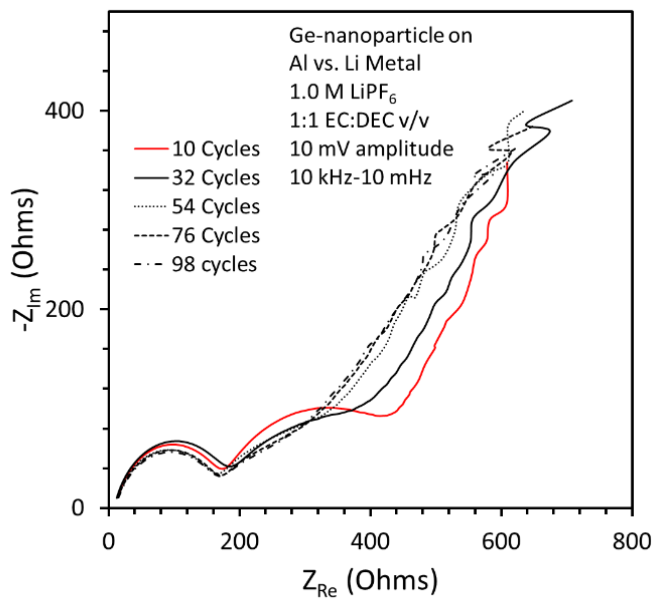




- The stability of the SEI to high potential is studied by cycling the Ge-Al electrode and every 10<sup>th</sup> cycle raising the high potential cutoff to 4.2 V vs. Li/Li<sup>+</sup>
  - Based on assigned material high potential stability limit
- Results show the high potential extraction limit cycles are significantly accelerating capacity fade
- Likely indication that the passivation layer is not stable to the high potential



# High potential cycling post mortem



- SEM/EDS of the lithium counter electrode shows no deposited germanium, consistent with the material stability limit found by LSV
- SEM/EDS shows increases oxygen, fluorine and phosphorous content in the anode, consistent with additional SEI formation as a result of high potential cycles
- XPS and FTIR (not shown) show some more Li<sub>2</sub>O formation and more phosphate formation

- EIS indicates disruption of the mid-frequency semicircle, consistent with SEI disruption by the high potential extraction cycles
  - Particularly the interface between the germanium and SEI



- Germanium nanoparticle electrode composites with an aluminum current collector is an anode design for Li-ion cells that can potentially enable overdischarge tolerance
- This study has shown that:
  - Ge cycled with a 0.3 V vs. Li/Li<sup>+</sup> lower potential cutoff has better cycling stability than with a more conventional 0.005 V vs. Li/Li<sup>+</sup> lower potential cutoff
  - Less Oxygen buildup, germanium carbide formation, lower degree of pulverization, less mid-frequency impedance growth and less Li<sub>2</sub>O formation
  - Ge material is stable to potentials up to 4.2 V vs. Li/Li<sup>+</sup>, where Ge dissolution is evidenced to begin
  - Passivation layers don't seem to be stable up to 4.2 V vs. Li/Li<sup>+</sup>, and future work would need to improve this to achieve an overdischarge tolerant lithium-ion anode





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**Michael Hladky, *engineer*** – Lab work and data analysis

## *Questions*

