

# Anode-less Lithium-ion cells

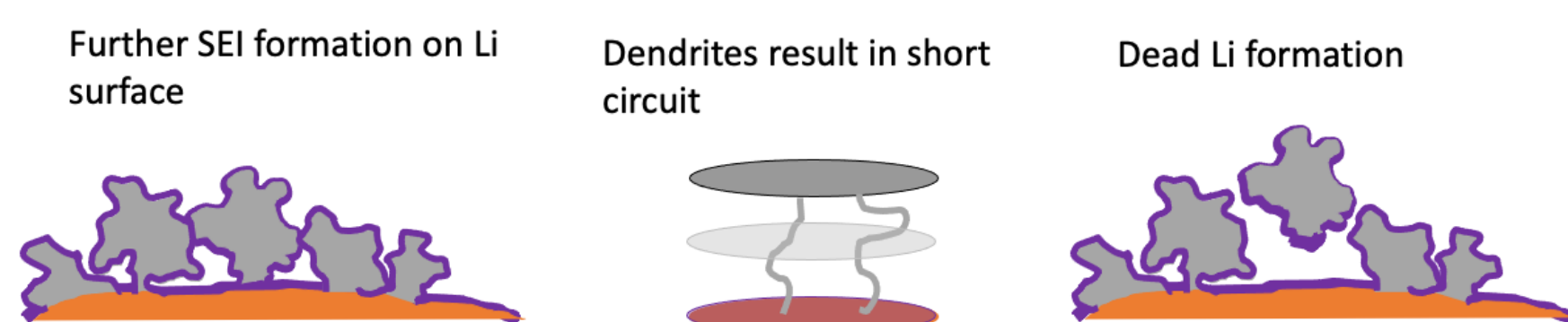
Investigating influence of current collector surface morphology on 'anode-less' batteries



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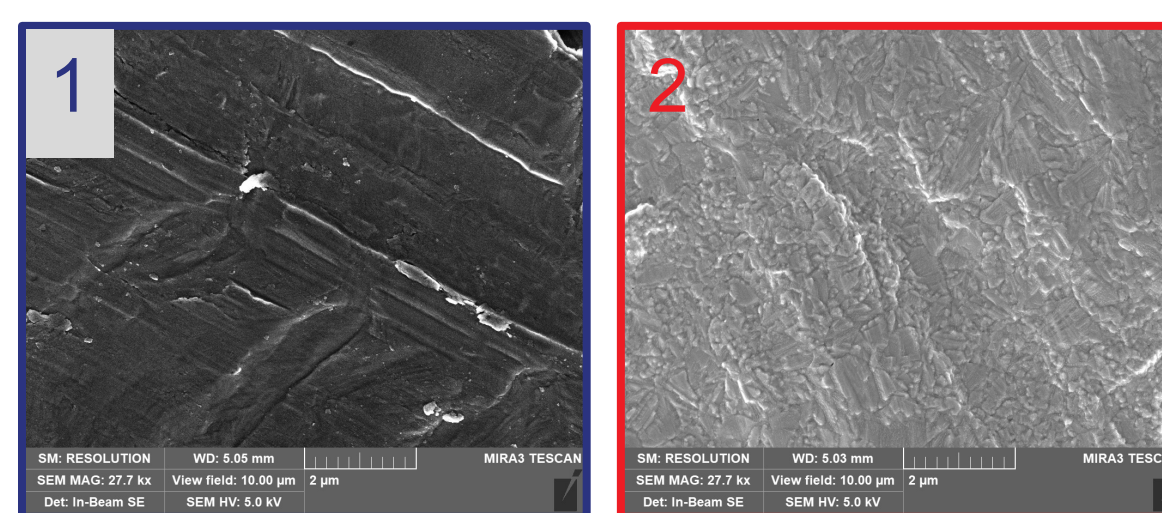
## Introduction

Anode-free batteries offer improved energy densities over graphite or lithium metal anodes, by having Li metal plate on to the current collector during charging. However due to the **lack of a Li reservoir**, Li losses directly decrease deliverable capacity and limits cyclability. Therefore Anode-free cells are held back by repeated **SEI formation, dead lithium (both Li loss processes) and dendrites**.



Schematic for phenomena limiting anode-less performance

Strategies for improving the reversibility of lithium plating include changing the **current collector, electrolyte and cycling conditions**. We will be focusing on the current collector.



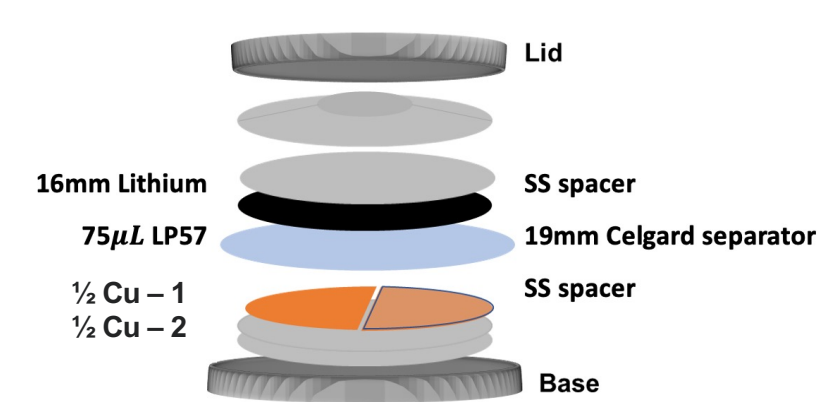
Coppers 1 and 2 surface morphologies, both untreated, un-plated.

We will be comparing the plating morphologies and cyclability of two different coppers current collectors, as well as developing methodology for **characterizing lithium plating**.

We hypothesize that **Copper 2** has a more **homogenous surface** and **lacks defined channels** leading to smoother plating and better cycling.

## Methodology

Produced 50/50-coin cells to create consistent plating conditions across the different coppers for SEM imaging.



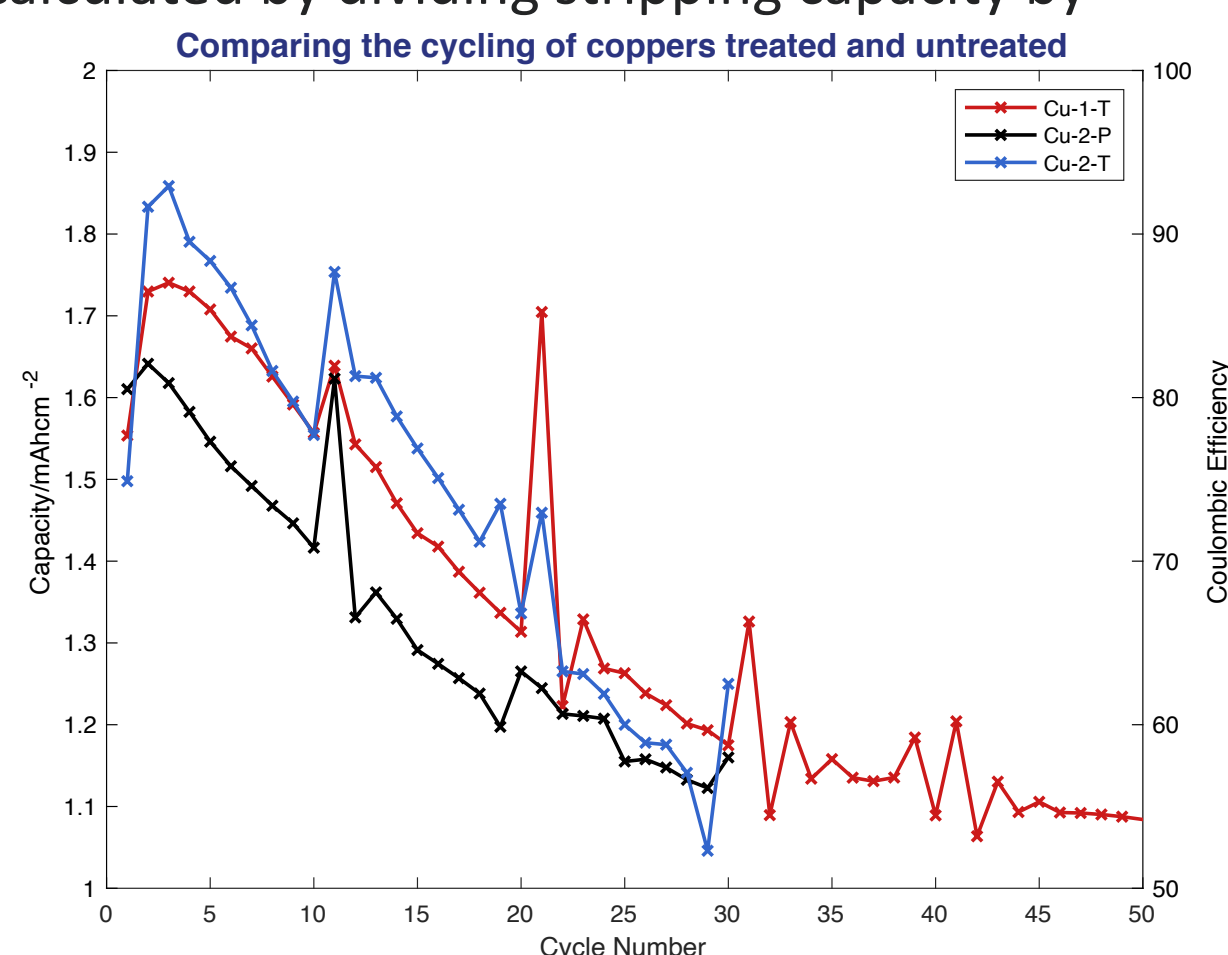
Cells were made in glovebox with <0.1ppm O<sub>2</sub> and <2ppm H<sub>2</sub>O

The cells were then deconstructed, and the Li plated copper samples were imaged under the SEM using the air transfer module.

## Electrochemical Data: comparing cycling performance

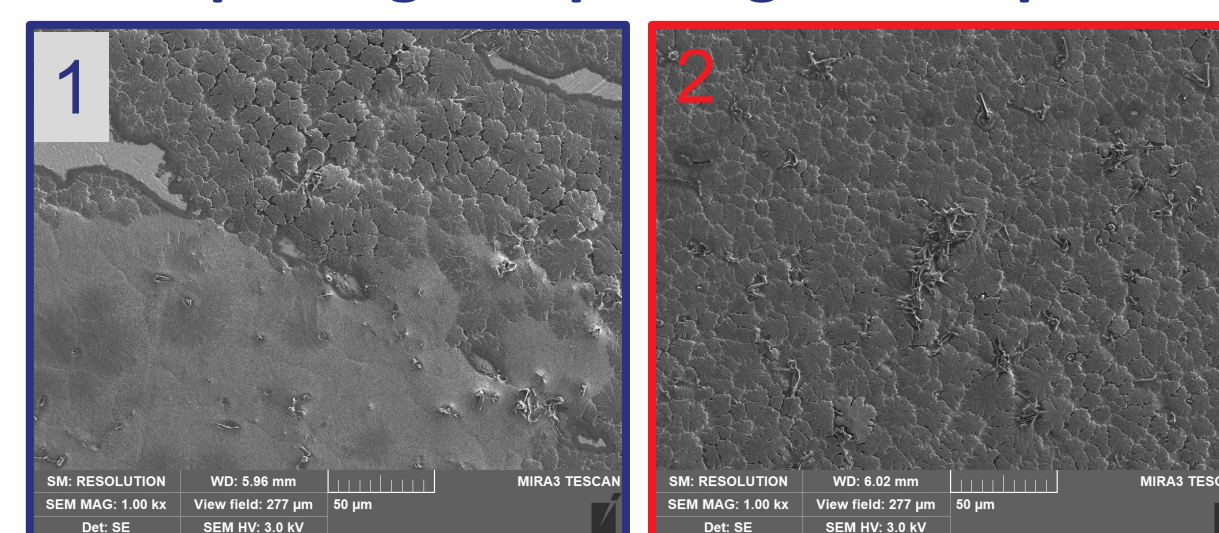
Coulombic Efficiencies were calculated by dividing stripping capacity by plating

- Acetic acid treated coppers outperform untreated
- Cells show increased CE when rested\*\* in discharged state, potentially due to lithium corrosion and SEI reformation
- Further cycling is ongoing to confirm trends



\*2mAh/cm<sup>2</sup> plated for each cycle at 0.4mA/cm<sup>2</sup> data is averaged from across 3-5 cells \*\*See peaks at cycle 11 and 21

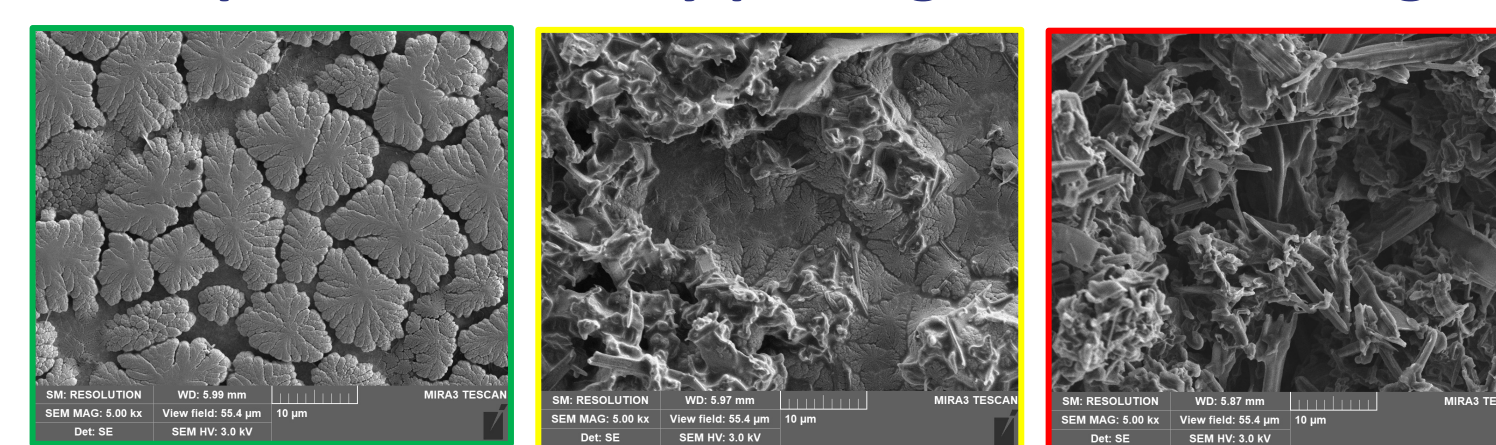
## Initial plating morphologies comparisons.



Copper 1 acid treated and Copper 2 pristine 0.1 mAh/cm<sup>2</sup> plated

- Plated a **small amount** of Li
- Observed **flat flowery plating** on both coppers
- potentially **denser flower-like plating** on Copper 2
- Regions of **un-plated copper** observed on both samples

## Development of mossy plating with increasing capacity.



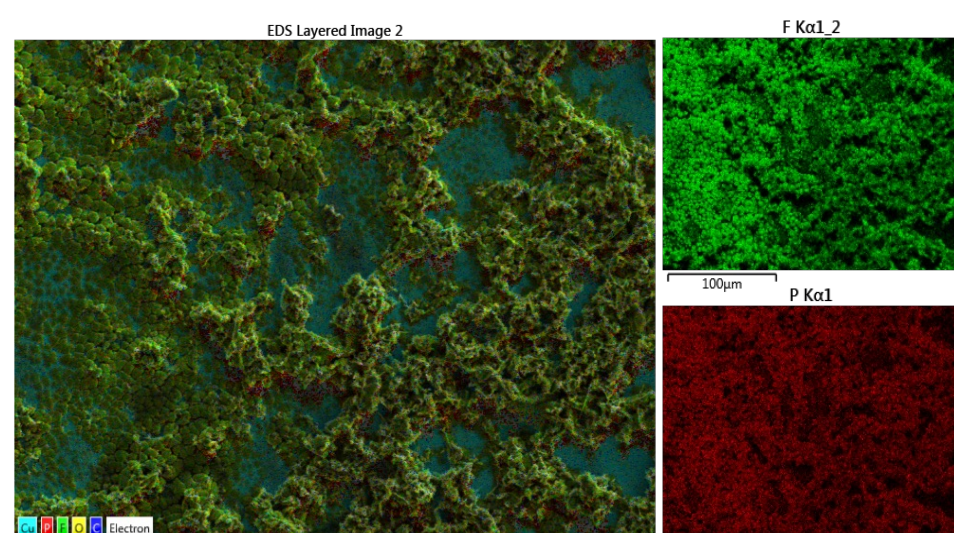
Increasing plating capacity

- Flowery morphology lithium plating first at **low capacity**.

- **Thinner dendrites form later** covering flowery lithium

Copper 2: 0.1, 0.5 and 2 mAh/cm<sup>2</sup> plated

## Investigating fluorine content of Cu Surfaces with EDX



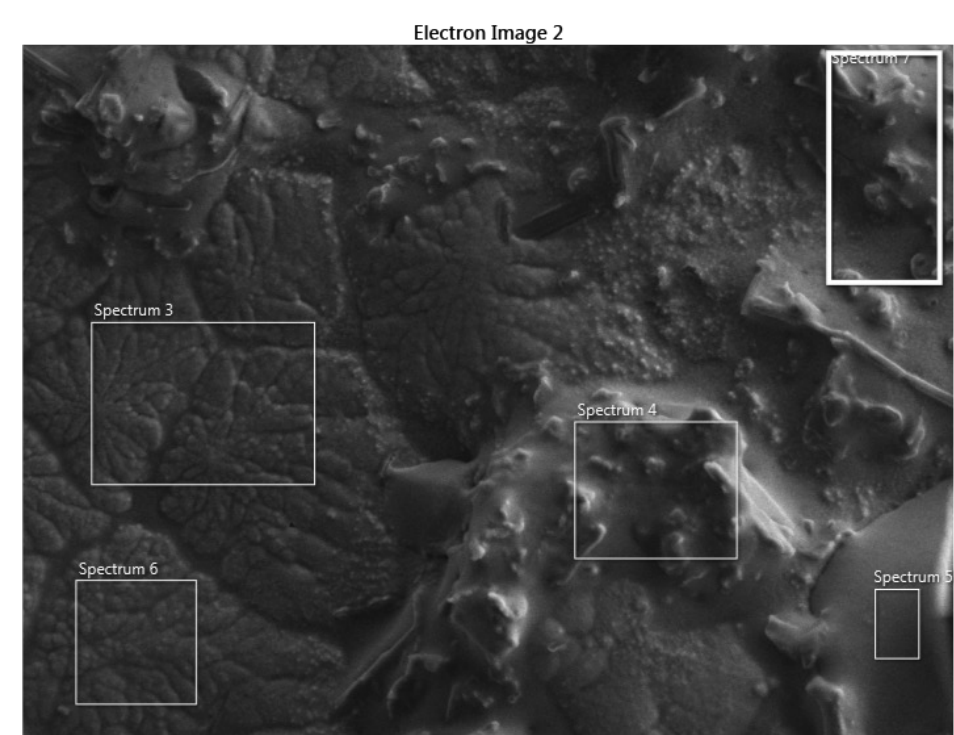
EDX map of 0.5 mAh/cm<sup>2</sup> on untreated Copper 2

Data suggest flowery plating has **potentially higher Fluorine to Phosphorus ratio** than mossy lithium indicating SEI and morphology are related.

Spectrum No.	F : P ratio (± 0.1)	F + P (wt.%) (± 0.5)
3 (flower)	3.68	81
4	2.79	49
5	2.75	61
6 (flower)	3.78	78
7	2.43	58

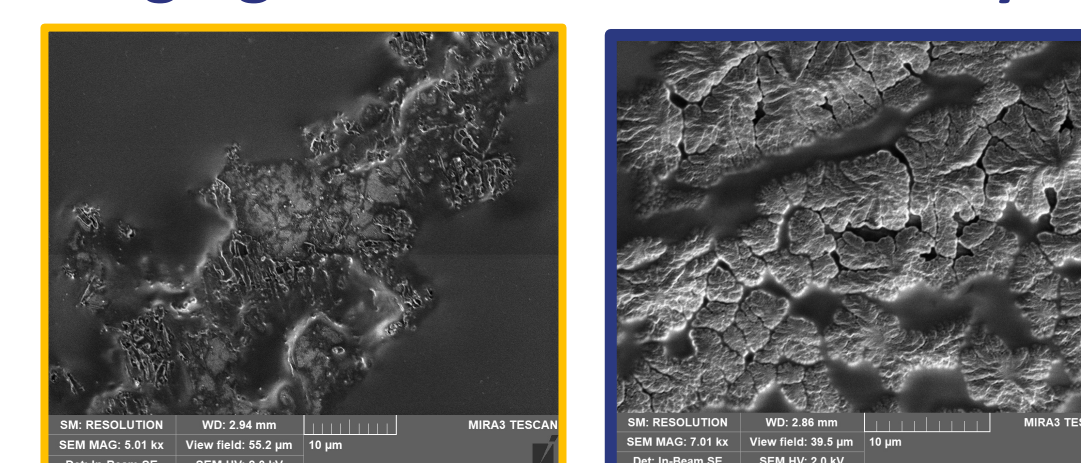
EDX spectra results from box spectra left

More extensive studies are ongoing to confirm this result.



EDX of 0.5mAh/cm<sup>2</sup> plated 0.2 stripped on Cu-2-T

## Imaging dead lithium after 1<sup>st</sup> cycle

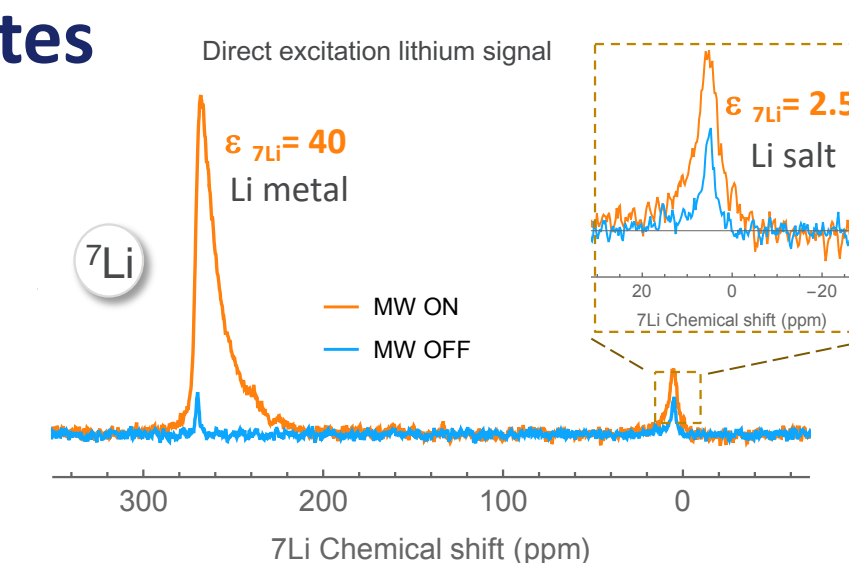


0.5mAh/cm<sup>2</sup> plated and stripped at 0.5mA/cm<sup>2</sup> on Cu-2-T and Cu-1-T

- Stripped as much lithium as we could after plating (1 cycle)
- Observed **dead lithium**, even in the **flowery morphology**

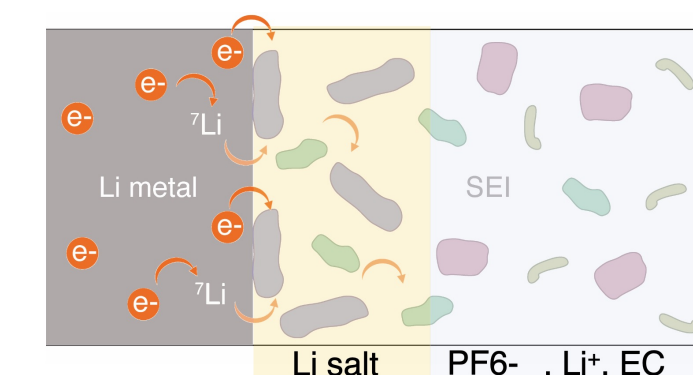
## DNP Method to study SEI on Li dendrites

NMR DNP offers increased **sensitivity and selectivity** that not only gives chemical composition measurements but also spatial arrangement.



**Large enhancement** implies close to Li metal and hence **Inner SEI**.

Spectra suggest Li salt in inner SEI and Fluorine species existing in outer. Results suggest SEI structure shown in figure.



## Conclusions

- Cu-2-T outperforms Cu-1-T in terms of CE and shows dense flowery plating
- Higher Fluorine concentration found on flowery plating relative to mossy lithium
- Dead lithium observed from 1<sup>st</sup> cycle
- Rests in discharged state result in spikes in CE

## Next steps

- Copper 2 will be used as current collector in Degradation project going forward
- Further investigation into why CE spikes after rests and more extensive work on the fluorine content in the SEI are needed.

## References

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