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*Changing the World's Energy Future*

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# The Effect of Artificial SEIs on Lithium Metal Anode Morphology and Conductivity

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## Abstract

Lithium metal has often been termed the “Holy Grail” of battery technology, due to its high capacity (2,061 mAh/cm<sup>3</sup>) and low electrochemical potential (-3.04 V vs. SHE). However, lithium's low potential also drives it to be highly reactive in the presence of organic solvents, making it difficult to harness its high energy capabilities for rechargeable batteries. Common failure of lithium metal batteries occurs by rapid dendrite growth leading to a hazardous short-circuit. Various methods have been brought forth to better understand the fundamental mechanisms of lithium metal batteries, as well as modifications made to better stabilize lithium metal. A common route of modification is done through interface engineering, with attempts to artificially produce a stable solid-electrolyte interphase (SEI). The stability of the SEI has direct effects on the reaction rate distribution, which initiates a waterfall effect of progressive issues such as dendrite growth, dead lithium accumulation, and electrolyte consumption. This work aims to produce a mixed LiI-LiF artificial SEI to improve ionic conductivity while retaining a high elastic modulus.

## Experimental Methods

Lithium foil (170 μm) is punched into 9/16” diameter samples, after which they are rolled onto stainless steel spacers. The samples are then mechanically polished via toothbrush to remove the native film. A mixed SEI film of iodine and fluorine is produced from reaction of lithium and I<sub>2</sub>-PVDF-DMF reactant solution. The artificial SEI is deposited by placing a 5/8” diameter Celgard® 2320 wet with reactant onto the lithium foil for 3-5 seconds.<sup>1</sup> Iodine has been shown to improve ionic conductivity through surface coatings and electrolyte additives. Fluorine is a common reactant for artificial SEIs, due to its ability to provide a chemically stable and high modulus layer that can fluctuate with the large volume changes of lithium metal during plating and stripping.



Symmetric cells were used to test the cyclability and failure mechanism of both control samples and the artificial SEI samples. Controls were polished Li (Li||Li) and LiF artificial SEI via the same mechanism with PVDF-DMF (LiF||LiF).<sup>1</sup> The amount of iodine included in the reaction was also examined, with varying molar ratios of 1:3, 1:5, and 1:9 I:F (LiI-LiF||LiI-LiF). Symmetric coin cells with 32 μL of 1M LiTFSI in 1:1 DOL:DME + 2 wt.% LiNO<sub>3</sub> electrolyte were tested at varying current densities of 1 mA/cm<sup>2</sup> and 3 mA/cm<sup>2</sup> to 1 mAh/cm<sup>2</sup> capacity (1C and 3C rates, respectively).

Characterization of the samples was done both after treatment and after cycling. A PHI-5600 XPS (Physical Electronics) with an Al-source was used to provide surface analysis, while an Ar<sup>+</sup> ion gun (2kV, 1.2 μA) was used for sputter depth profiling. A Hitachi S-3400N SEM and a FEI Teneo FESEM were used to observe morphology and elemental make-up (via EDS) of both surface and cross-sections of samples.

## Results

Deposition of the artificial SEIs were confirmed via XPS (Figure 1).

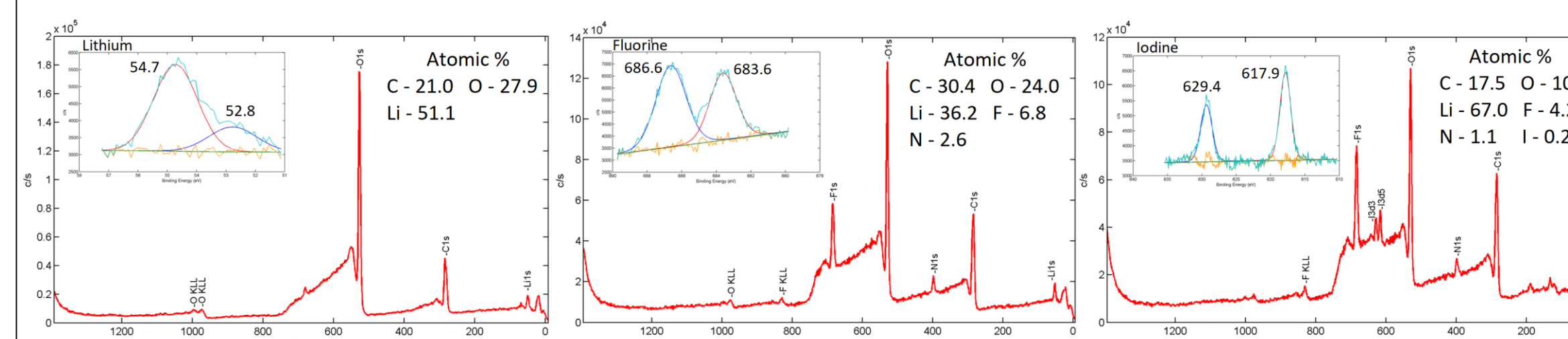


Fig 1. XPS survey spectra and atomic percentages of (a) polished Li, (b) LiF artificial SEI, and (c) LiI-LiF artificial SEI (1:5 I:F) with high-resolution elemental insets.

Figure 2 shows the electrochemical cycling results of varied symmetric cells. The Li||Li cells appear to fail via soft short circuit, observed by the sudden decrease in cell potential. As for the artificial SEI cells (LiF & LiI-LiF), the failure mechanism is observed at later cycling via increasing impedance. This could be caused by electrolyte consumption and dead Li accumulation.

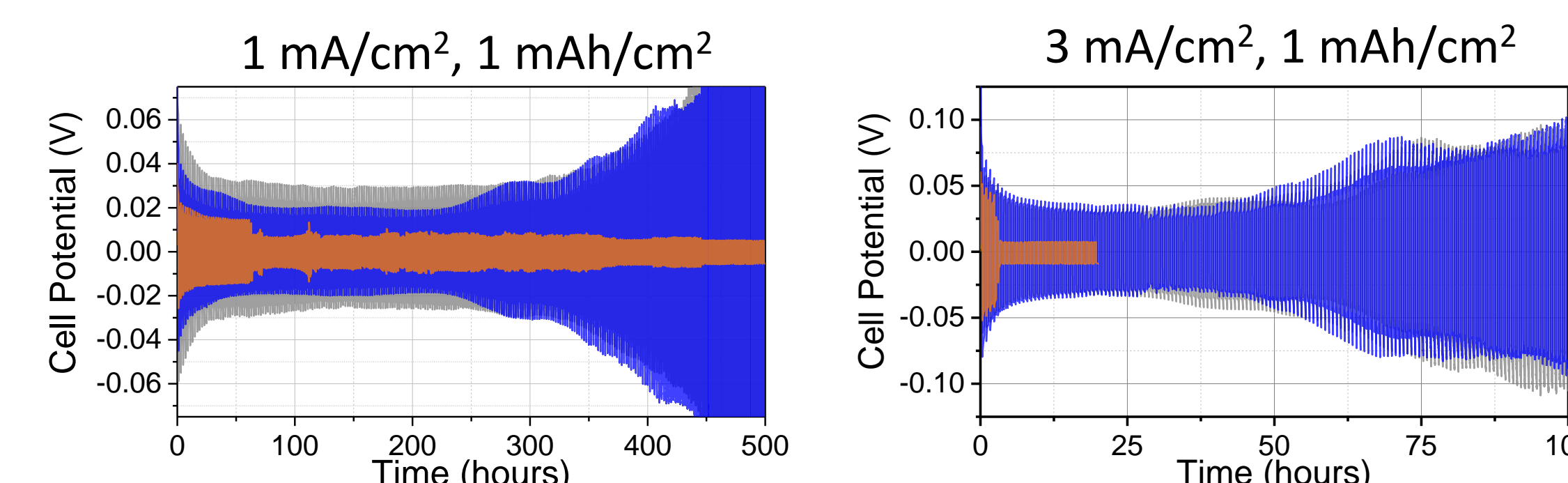


Fig 2. Electrochemical cyclic behavior of symmetric cells. (Left) 1C rate cycling for 250 cycles. (Right) 3C rate cycling for 150 cycles.

Post-mortem analysis of spent surfaces and cross-sections are shown in Figure 3.

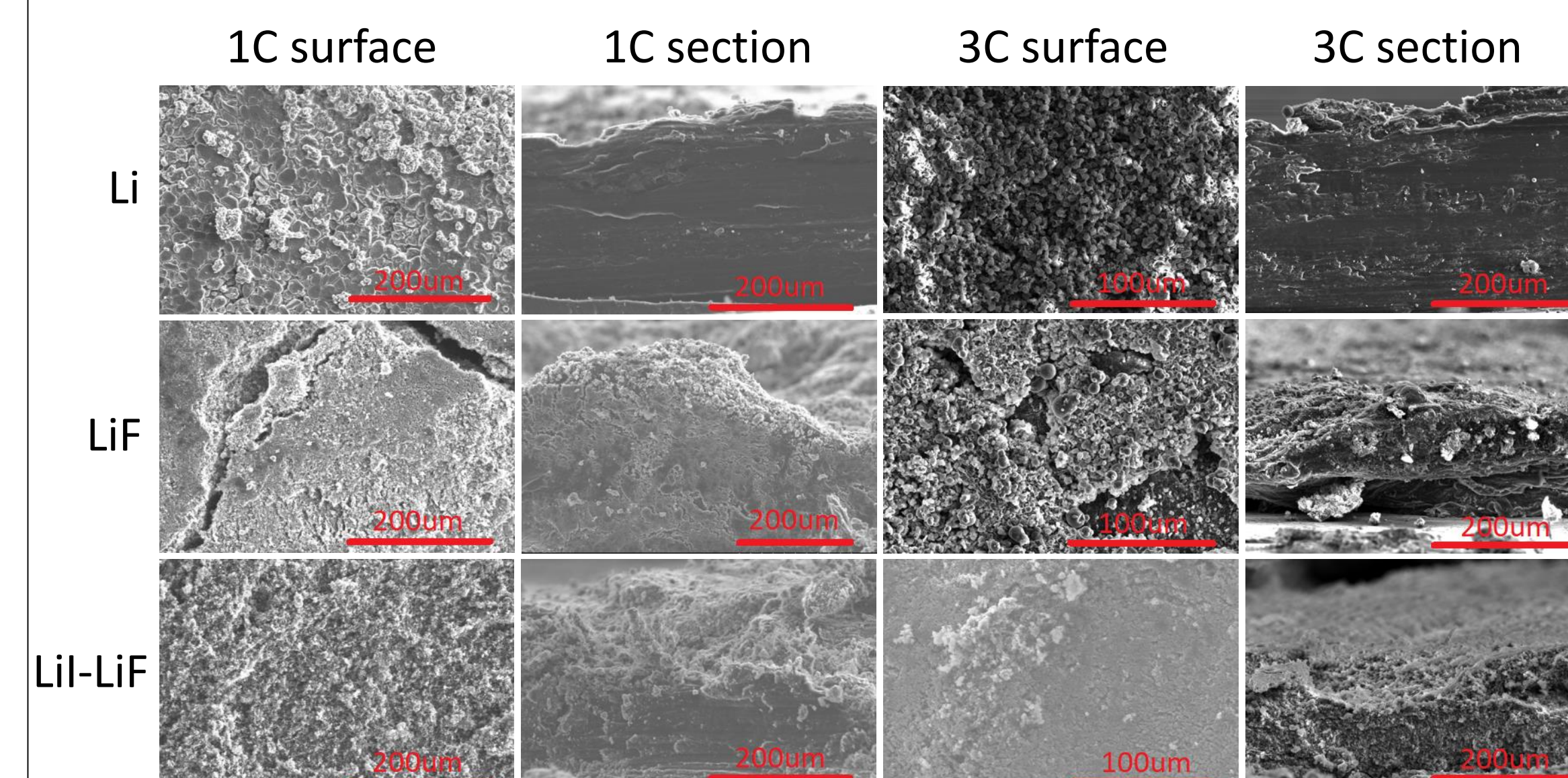


Fig 3. Post-mortem SEM of (Top) Li, (Middle) LiF, and (Bottom) LiI-LiF. From left to right the surface after 1C, cross-section after 1C, surface after 3C, and cross-section after 3C.

## Results Cont.

Cells were cycled to intermittent periods to provide “snap-shots” of the samples after 1 cycle at 3C rate (Figure 4) and 50 cycles at 1C rate (Figure 5).

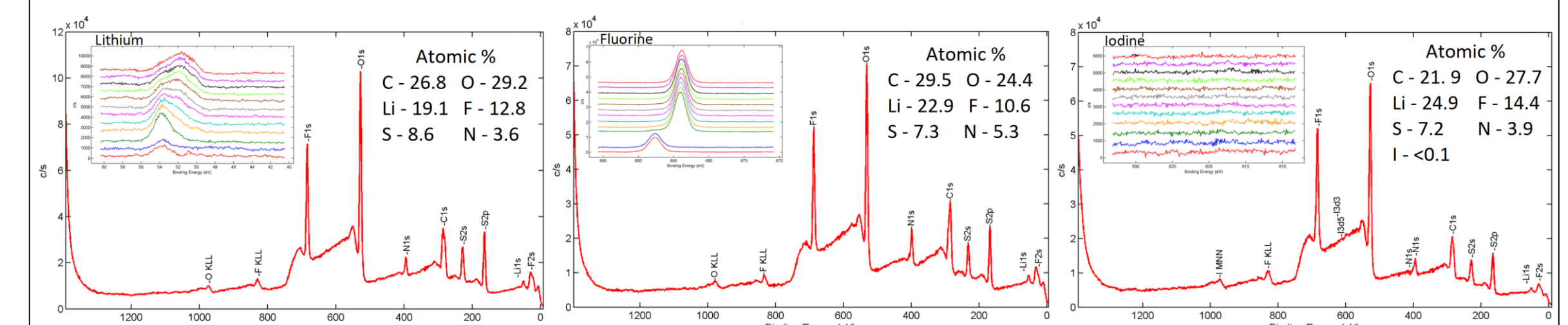


Fig 4. (Top) Post-mortem XPS and (Bottom) SEM of (Left) Li, (Middle) LiF artificial SEI, and (Right) LiI-LiF artificial SEI after 1 cycle at 3C.

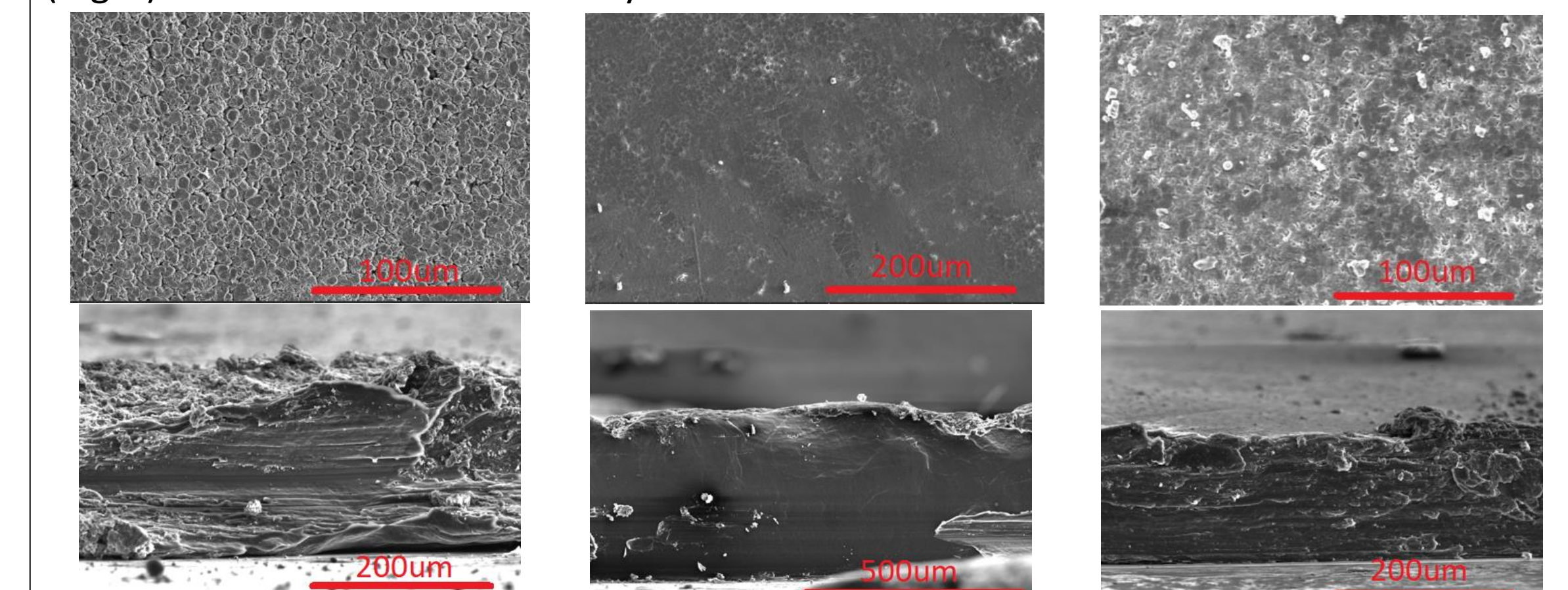


Fig 5. Post-mortem SEM of (Left) Li, (Middle) LiF, and (Right) LiI-LiF after 50 cycles at 1C.

## Future Work

- Determine the role of iodine in forming the artificial SEI
- EIS testing – confirm Li||Li soft short circuit, SEI growth mechanisms, etc.
- Develop a more controlled mechanism of artificial SEI deposition
- Expand to full-cell electrochemical testing (Sulfur-based cathode)
- AFM testing – EC-AFM, QNM & SKPFM for better understanding of plating/stripping, nanomechanical properties & conductivity, respectively

## References

1. J. Lang, Y. Long, J. Qu, X. Luo, H. Wei, K. Huang, H. Zhang, L. Qi, Q. Zhang, Z. Li, and H. Wu, *Energy Storage Mater* **14**, 85 (2018).

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