# Spectrum Imaging of a Lithium Ion Battery Anode Using Thin Fluid Cells

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#### Meeting-report

## **Spectrum Imaging of a Lithium Ion Battery Anode Using** Thin Fluid Cells

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Lithium ion batteries (LIBs) are becoming ever more ubiquitous in today's society. One major safety concern with LIBs is that, due to high usage or over-charging, conductive filaments (i.e. dendrites) that short the cell can form and cause chemical fires. Microscopy of a live lithium-ion cell as it charges and discharges is difficult because the chemicals involved are air sensitive. Here we present a TEM fluid-cell sample fabrication technique that avoids air exposure during assembly and mimics standard LIB manufacturing practices. Our LIB fluid cell samples show chemistry that matches their bulk counterparts and allow us to observe an operando LIB with excellent spatial resolution in a TEM.

The optical images in Figure 1a and b show an example of an exfoliated graphite flake transferred to a platinum electrode on a 25-nm-thick  $Si_3N_4$  electron-transparent window [1]. The current collectors for the working electrode (WE), the pseudo-reference (RE), and the counter (CE) electrodes are platinum. A small droplet (~0.2 pL) of 1M lithium perchlorate (LiClO<sub>4</sub>) in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 by volume) is the electrolyte and lithium source. A second chip with a similar electron transparent  $Si_3N_4$  window acts as the top of the fluid cell. Robust inward bowing of the  $Si_3N_4$  windows (Figure 1c) is arranged by sealing the fluid cell under vacuum using a magnetically controlled epoxy manipulator. This bowing minimizes the cell thickness in the middle of the chip, as is desired for good imaging access to the electrode's active area [2].

STEM images during the first charging show defects dynamically moving within the graphite flake as lithium ions are inserted between the graphene layers (Figure 2a-e) [3]. A Gamry 600 potentiostat controls the cell voltage and measures the current (Figure 2f). A second, electrically isolated graphite flake (top left corner in Figure 2a-e) serves as a control. This flake did not change during the entire experiment, ruling out the possibility that the observed contrast changes during cycling are induced by the electron beam or perhaps by strain from the fluid cell itself.

Figure 3 shows a different LIB fluid cell after multiple cycles and intensive spectrum imaging. This cell has been over-charged, causing a thick solid electrolyte interphase (SEI) to form around the graphite's edge. Using electron energy loss spectroscopy (EELS), we observe from a dendrite within the SEI in the lithium core loss signal the signature of lithium hydride [4]. The SEI also has a distinct signature in the lithium core loss energy window due to a chemical shift in the spectrum. Acquiring reference spectra from representative regions allows us to map the lithium hydride and the SEI across the whole electrode-electrolyte interface with multiple linear least square (MLLS) fitting. When combined with the TEM's capability of chemical identification at high spatial resolution, these realistically fabricated samples show great promise for improving the understanding of LIB charge-discharge dynamics at a fundamental level [5].



Fig. 1. a Electrode architecture. b Transferred graphite before fluid cell assembly. c Cross section of cell labeled with relevant dimensions.



Fig. 2. a-e Changing of graphite structure during charging (i.e. intercalation). f Voltage vs. current during charging.



Fig. 3. a Spectrum image. b Spectrum shown from red ROI in a. c,d core loss MLLS mapping using the characteristic chemical shifts of the LiH and SEI. e False color map of the LiH and SEI together.

### References

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