

STEM of a Single Crystal Lithium Ion Battery Anode during Electrochemical Cycling

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The lithium ion battery (LIB) is currently the preferred power source for most portable applications. Despite the LIB's importance, *in situ* observation of the cycling process at small length scales still remains an open problem in the research community. As a LIB is charging, lithium ions are electrochemically inserted, or intercalated, between the graphene layers of the graphite anode, creating a lithium-carbide structure [1]. Little is known, even in the ideal case, about this process at the macromolecular level. Liquid cell based *in situ* transmission electron microscopy is a promising route to reveal lithium kinetics, electrode/electrolyte interactions, and rate limiting physics [2, 3]. Here, we use *in situ* scanning transmission electron microscopy (STEM) to image the electrochemical intercalation of lithium in single crystal graphite and observe a key failure mode in LIBs.

The *in situ* fluid cells consist of two Si/SiO₂ chips, each with an electron-transparent, Si₃N₄ window, sandwiched together back-to-back. Natural graphite (NGS Naturagraphit GmbH) is mechanically exfoliated and wet-transferred to an electron-transparent window in a silicon chip. The window is equipped with a Ti/Pt (5/25 nm) electrode patterned via optical lithography. A thin conformal capping layer (10 – 20 nm) of Al₂O₃ deposited via atomic layer deposition encapsulates most of the exposed Pt electrode. This capping layer reduces unwanted chemistry on the Pt and minimizes its influence on the electronic transport data. A small droplet of electrolyte (1M lithium perchlorate, LiClO₄, in ethyl carbonate and dimethyl carbonate, EC:DMC, mixed at a 1 to 1 volume ratio) is placed on the chip with the electrode and the graphite. (We find this electrolyte to be more beam-stable than alternatives studied by other authors [4].) The second, smaller chip is then placed on top of the droplet and manipulated to align the two windows, sandwiching the graphite and a thin layer of electrolyte between them. Finally, the two chips are sealed together with epoxy, creating a vacuum-compatible fluid cell.

A Gamry Reference 600 potentiostat is used to electrochemically intercalate a graphite flake via cyclic voltammetry (CV). The cell potential is cycled at 10 mV/s from its open circuit potential (OCP), -0.9 V, to -4 V (Fig. 1a). Both the pseudo-reference and counter electrodes are platinum. We use a Hummingbird Scientific biasing holder to electrically contact the fluid cell, and we image the sample in an FEI Titan 80-300 S/TEM using an accelerating voltage of 300 kV. Graphite in the electrolyte chosen is an excellent system for STEM study, as it is nearly immune to degradation in the electron beam: imaging for hours with 50 pA beam currents shows little beam-induced sample damage.

Before any electrochemical bias, bright field (BF) STEM of the graphite flake shows it to be pristine, with uniform contrast (Fig. 1b). The Pt electrode is visible in the top left of the frame. As the flake reaches an intercalating potential (Fig. 1a), it changes contrast and shows a variety of bright and dark bands (Fig. 1c – the flake is outlined in yellow) that are associated with intercalation [3]. In the subsequent frame (Fig. 1d), before the graphite can fully intercalate, circular dendrite structures, 100 –

200 nm in diameter, form on the graphite's surface. These dendrites grow rapidly and use lithium that would otherwise be available for intercalation. After the potential ramp is reversed, the dendrites continue to grow, reaching their maximum size (Fig. 1e) 200 mV later. Even after the graphite is returned to the OCP, the dendrites still coat the flake (Fig. 1f). In an actual LIB such a coating would compete with the graphite for lithium ions, and thus would lead to decreased capacity, lifetime, and safety [5].

References:

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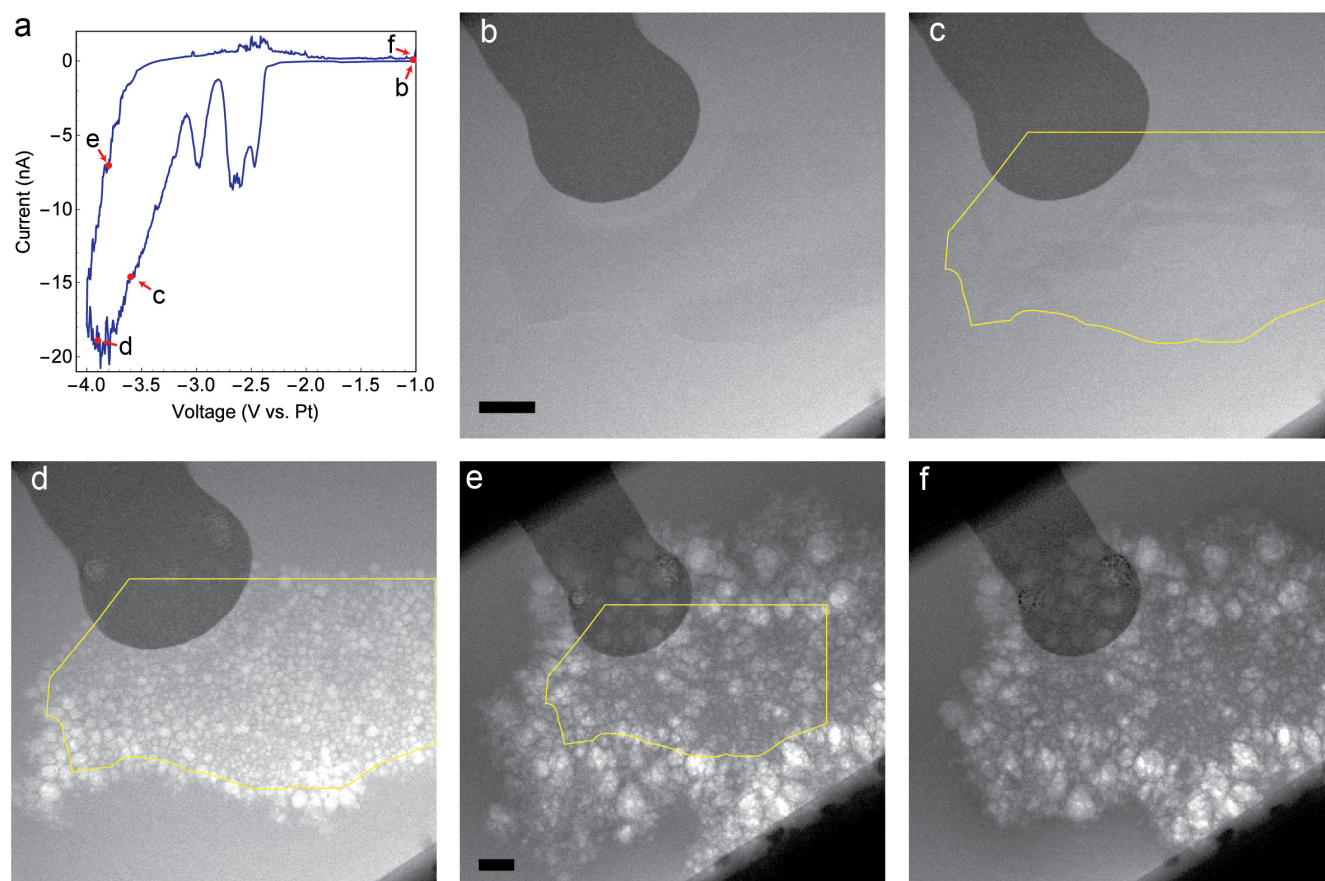


Figure 1. (a) Cyclic voltammogram acquired *in situ*. (b-f) Bright field STEM images of a graphite flake in a fluid cell during electrochemical cycling. The flake is electrically connected to a Ti/Pt (5/25 nm) electrode seen in the top left. The voltage and measured current for each frame (b-f) is highlighted in (a) by a red dot and arrow. A yellow line delineates the graphite flake's edge in (c-e). Each 512×512 pixel frame was acquired in 30 s. The scale bars in (b) and (e) are 1 μm .