

Multi-Length Scale Characterization of Graphite Anodes from Fast-Charge Lithium-Ion Cells

Saran Pidaparthy¹, Daniel Abraham², Marco-Tulio Rodrigues² and Jian-Min Zuo³

¹Argonne National Laboratory, Urbana, Illinois, United States, ²Argonne National Laboratory, Lemont, Illinois, United States, ³University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Safe and reliable fast-charging (i.e., >2C or < 30 minutes to full charge) lithium-ion batteries (LIBs) are critical to enable widespread consumer migration toward the growing electric vehicle sector. However, the application of such high charge rates restricts the long-term utility of LIBs in part due to damage sustained by the graphite anode under these conditions. At these rates, a key issue is that lithium ions do not intercalate into the anode homogeneously resulting in steep concentration gradients throughout the anode as well as resulting in lithium metal plating on the anode surface [1]–[3]. These underlying issues manifest as morphological, chemical, and structural changes to the graphite host material that persist across the atomic-scale to the bulk-scale. In this work, we probe the nature and extent of the damage exhibited by fast-charged graphite at different length scales using a suite of advanced analytical electron microscopy strategies and X-ray diffraction (XRD). This presentation will emphasize both the characterization methods employed and the resulting findings.

We examine the anode changes after cycling LIB cells using charging rates up to 6C. The graphite samples for *post-mortem* characterization are from *as-prepared* electrodes as well as *cycled* electrodes harvested from the cells. The samples are fabricated as cross-sections via ion milling to understand the morphological, structural, and chemical heterogeneity as a function of depth into the electrode. At the bulk-scale, we employ scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and XRD to uncover changes in electrode thickness and graphite morphology. At the nano- to atomic-scale, we rely on scanning transmission electron microscopy (STEM) to unveil local structural disorder and chemical variation within individual graphite particle cross-sections through a combination of atomic-resolution images, scanning electron nanodiffraction (SEND) and EDS acquired via a ThermoFisher Scientific Themis Z aberration-corrected STEM. We also use the Hitachi 9500 TEM equipped with the K2 direct electron detector in counting mode to acquire low-dose, high-resolution images.

SEM imaging reveals large-scale inter- and intra-particle morphological changes, including formation of cracks, roughening of particles, and an irreversible anode thickness increase with increasing cycling rate (see Figure 1). SEM-EDS further shows chemical changes to the graphite surface with solid electrolyte interphase (SEI) compounds becoming embedded in the graphite pores and gaps. Moreover, within individual particles, the extent and localization of the lattice disorder is quantified through both SEND and power spectra analysis of high-resolution imaging data. STEM-EDS data also reveal intra-particle spatial heterogeneity of the SEI compounds (see Figure 2). The results of these diagnostic techniques are being used to design fast-charging protocols that minimize electrode degradation and enhance the lifespan of LIB cells [4].

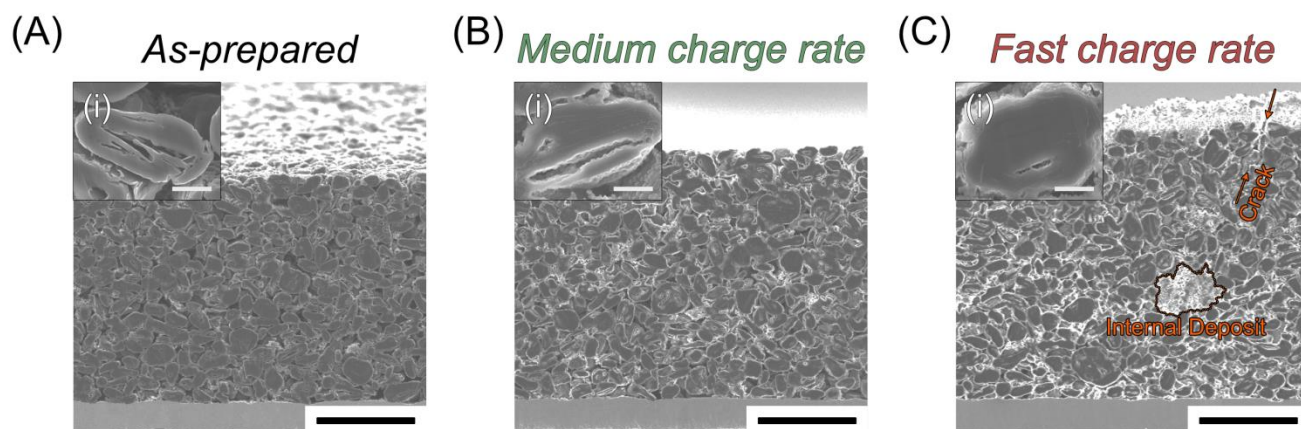


Figure 1. SEM images of graphite anode cross-sections: (A) as-prepared, (B) after cycling at an intermediate rate, (C) after cycling at a fast-charge rate. For (A) – (C), The inset figure (i) shows the individual particle cross-section. Scale bars: (A) – (C) are 25 μm , (A) (i) – (C) (i) are 2 μm .

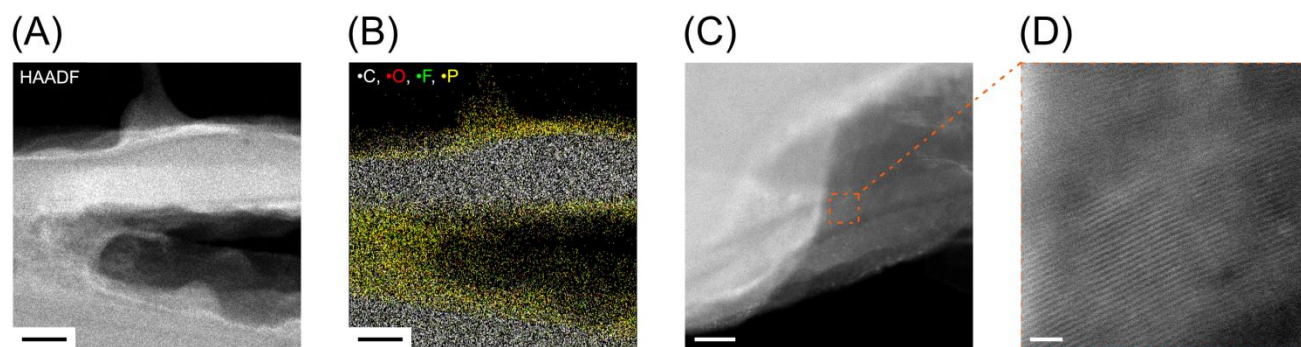


Figure 2. STEM images of locally disordered graphite from a fast-charge cell. (A) The image with (B) its corresponding EDS map showing spatial distribution of oxy-fluoro-phosphate SEI compounds. (C) The edge of a graphite band with (D) a corresponding higher magnification image showing disordered graphite lattice. Scale bars: (A), (B) are 50 nm, (C) is 20 nm, and (D) is 2 nm.

References

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