In-Situ Analytical Transmission Electron Microscopy Study of Electrochemical Lithiation of a Sulfur – Carbon Nanotube Composite Cathode

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Rechargeable Li-S batteries have the potential to meet the high power demands of next generation lightweight, low-cost, and environmentally friendly batteries useful in both small-scale portable devices and large-scale applications such as electric vehicles. Lithium-sulfur (Li-S) batteries offer a high theoretical capacity of 1,672mAh/g and a theoretical energy density of 2567Wh/kg, roughly five times larger than that of currently utilized carbon-based Li-ion batteries. [1] In addition, sulfur is light weight, earthly abundant, and nontoxic. Despite its promise, Li-S batteries still suffer from poor cycling performance caused by the polysulfide shuttle process which occurs during the multistep reduction of sulfur to Li_2S. Due to the insulating nature of sulfur, this reaction relies on the incorporation of sulfur into a conductive carbon host structure. Various carbons serve as both an electrically conductive pathway, as well as a structural network to accommodate the volumetric expansions associated with cycling. Carbon nanotubes (CNTs), possessing a high electrical conductivity and mechanical strength, are considered a prospective material to serve this role. In spite of extensive efforts, significant gaps still remain in the understanding of the behavior of lithium and reduced sulfur species at the carbon-sulfur interface during working conditions. Therefore a deeper understanding of the fundamental electrochemical reaction mechanisms and kinetics of this system is required to develop the next generation of ultrafast, long-life, high-energy density Li-S batteries. [2]

We employ *in-situ* transmission electron microscopy (TEM) which offers the opportunity to investigate complex reactions in real time while obtaining valuable information on the structural, chemical, and electrical properties during these processes. Using energy-filtering TEM (EFTEM) and scanning TEM (STEM) imaging modes, as well as various analytical methods, such as electron energy loss spectroscopy (EELS), energy-dispersive X-ray spectroscopy (EDXS), and electron diffraction, we have monitored the evolution of these complex structures starting from pristine composites (FIG. 1). Our *in-situ* work utilizes a customized TEM sample holder. The holder has a small piece of metallic lithium attached to a movable piezo-driven STM tip, which served as the anode and reference electrode. A thin layer of Li_2O formed during loading, was used as a solid electrolyte. The Li/Li_2O tip is then contacted with the S-CNT cathode and cycled through the application of an external bias. *In-situ* observations indicate complex morphological and compositional changes of both the Li anode and S-CNT cathode during cycling. (FIG. 2)

References:

[1] P.G. Bruce, *et al,* Nature Materials **11** (2012), p. 19.
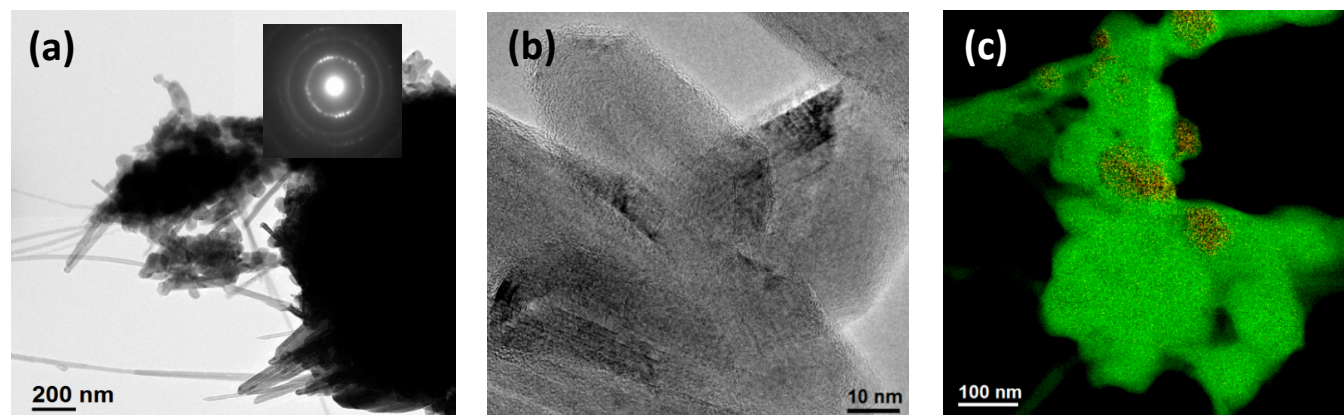[2] V.P. Oleshko, *et al*, Microsc Microanal **15** (2009), p. 1398.

Figure 1. (a) Zero-loss energy filtered TEM image of a thick pristine S-MWCNT composite and corresponding SAED pattern of the composite (right inset). (b) HRTEM image showing nanoscale morphologies of the S-MWCNT composites. (c) Overlaid electron spectroscopic S $L_{2,3}$- map (orange) and C K- map (green) of the S-MWCNT composites
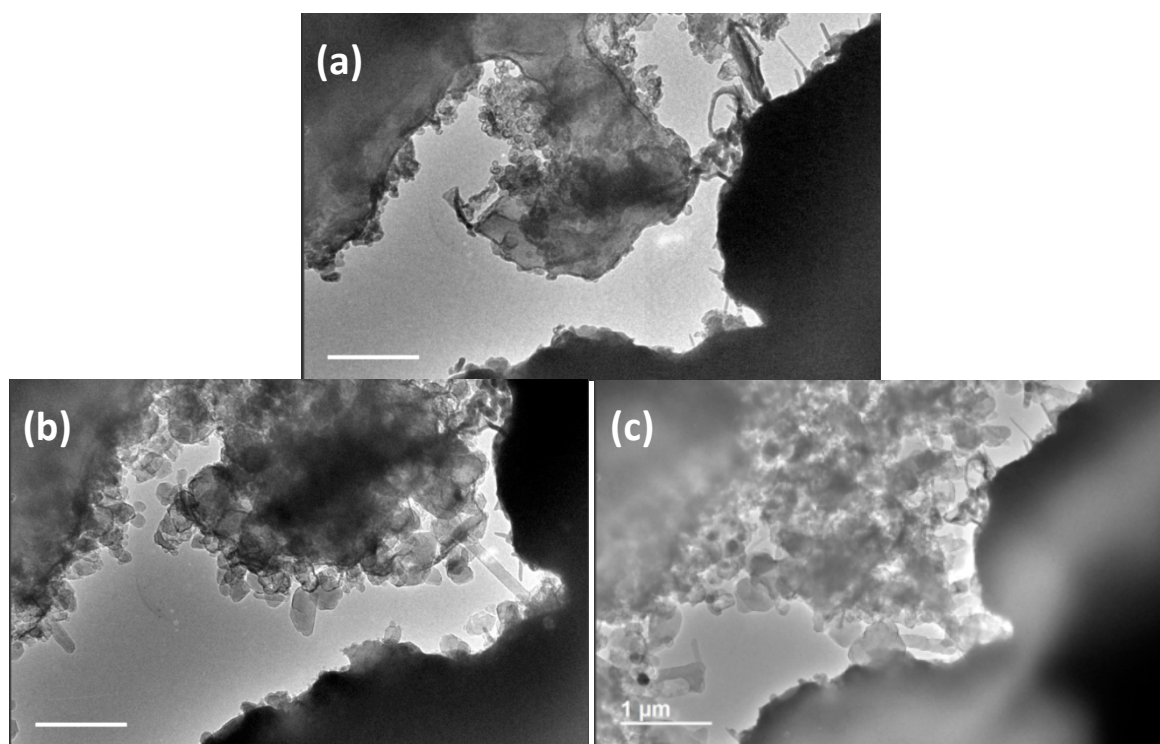

Figure 2. In situ TEM frames acquired during lithiation of S-MWCNT composites at negative 3 V relative to the Li electrode. (a) after initial contact of Li/Li_2O (left) and S-MWCNT composite (right); (b) after 50 minutes of discharge; (c) after 100 minutes of discharge. All scale bars are 1μm in length.