Lithiation of Sn Microspheres: Li FIB vs Electrochemistry

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With the development of Li focused ion beams (Li-FIB) from cold-atom ion sources,[1,2] the possibility has arisen of inserting Li ions into electrochemically active battery materials with nanoscale resolution to study ion transport on the smallest scales. As a step toward establishing the relevance of focused ion beam lithiation to the study of battery materials, we have conducted a comparison of lithiation via focused ion beam implantation with lithiation through conventional electrochemical means.

Using a Li-FIB with probe size of a few tens of nanometers, we selectively injected Li cations into isolated β-Sn microspheres with diameters ranging from 1 µm to 10 µm. The microspheres were mounted on a carbon substrate, as provided in the form of a commercial scanning electron microscope resolution target. Individual microspheres were exposed to a 1 pA, 3.9 keV Li^+ beam for up to 6 hours. Identical microsphere samples were lithiated via electrochemical reactions using a liquid electrolyte and a Li metal counter electrode. Cyclic voltammetry was carried out to determine an optimum lithiation voltage of 0.35 V relative to Li/Li^+, where the sample was held for one hour to perform the lithiation.

The microspheres lithiated by both methods were characterized via field emission scanning electron microscopy (FESEM) and Ga^+ focused ion beam cross-sectioning. The observed similarities of the Sn upon lithiation in both the ion-beam and electrochemically lithiated materials suggest that the Li-FIB can be a powerful tool for exploring dynamical Li ion-material interactions at the nanoscale in a range of battery materials.

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[1] B. Knuffman, A.V. Steele, J. Orloff, and J.J. McClelland, New J. Phys. **13**, 103035 (2011).
[2] K.A. Twedt, L. Chen, and J.J. McClelland, Ultramicroscopy **142**, 24 (2014).

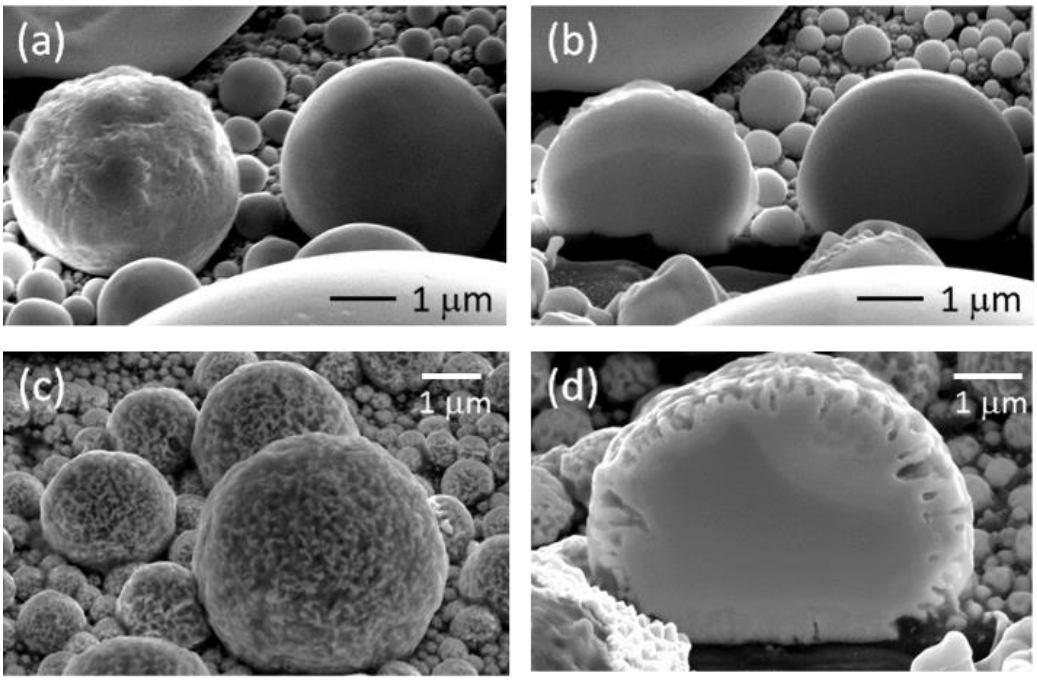

Figure 1: FESEM images of lithiated Sn microspheres. (a) Li-FIB lithiated (left) and unlithiated (right) 3-μm-diameter spheres. (b) Ga^+-FIB cross sections of spheres shown in (a). (c) Electrochemically lithiated spheres of similar size. (d) Ga^+-FIB cross section of an electrochemically lithiated sphere.