

Liquid-Cell TEM Observations of Sn Lithiation reactions: A Temperature Case Study

Subrahmanyam Goriparti¹, Zoey Warecki², Katharine L. Harrison¹, Andrew Leenheer¹, John Cumings² and Katherine L. Jungjohann¹

¹. Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, NM 87185

². Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742

In recent years, the increasing use of portable electronics and the rise of eco-friendly electric vehicles put tremendous pressure on high-energy rechargeable lithium-ion batteries [1,2]. As a result, significant research has been focused on more advanced, high-capacity electrode materials such as Si, Sn, Ge and Li as anode and S and O₂ as cathode materials [2-4]. These electrode materials are attractive due to their higher specific capacities than present commercial electrode materials such as graphite (anode) and lithium metal oxides (cathode). However, issues like volume expansion, capacity fading and unwanted electrolyte reactions upon cycling prevent the commercialization of these electrode materials. Over the last decade, in order to address the degradation of high-capacity electrode materials, significant investigations have been carried out with in-situ/ operando S/TEM, X-ray diffraction, NMR, Raman and Mass spectrometers [5]. In fact, to diagnose the effect of size and morphology of electrode materials at or near working electrochemical conditions, S/TEM can be used to visualize the lithium insertion and de-insertion of electrode materials at atomic resolution in some commercial volatile electrolytes such as organic carbonates. In addition, the electrode/electrolyte interface reactions can also be visualized while cycling. We are using a highly customized TEM liquid cell that successfully performs quantitative electrochemical control on ultramicroelectrodes for testing nanomaterials in volatile electrolytes during nanoscale imaging [6,7]. This design allows up to 10 electrodes incorporated into an even liquid gap of ~ 150-200 nm, where controlled assembly of nanomaterials onto the custom patterned electrodes allows for an ideally designed working cell inside the TEM.

Here, we present an in-situ S/TEM analysis of lithium insertion and de-insertion of nanostructured Sn and its electrochemical behavior with the effect of temperature in a volatile liquid electrolyte. The TEM liquid cell is optimized for quantitative control of pA-level electrical currents[8]. The chip was designed for Sn as working and Ti as counter and reference electrodes with a 50-nm thick silicon nitride (SiN_x) window. Similarly, the lid chip contains a SiN_x window along with fluid fill ports. The chip and lids were sealed with epoxy and filled with an electrolyte in a glove box and then connected to the holder for in-situ S/TEM studies. The in-situ electrochemical experiments were carried out with an FEI Tecnai F30 TEM operated at 300 kV. The temperature controlled measurements were carried out by a custom designed heating setup [8]. Among the ten electrodes, some of the electrodes were designed with two resistors near the center of SiN_x window, one is serpentine resistor act as a heater, while the straight line resistor acts as a sensor. The temperature was calibrated using a four-point resistance measurement. The remaining electrodes were used for Sn-lithium alloying electrochemical studies.

References

- [1] L Lu *et al*, Journal of power sources, **226** (2013), p. 272
 [2] A Fotouhi *et al*, Journal of power sources, **56** (2016), p. 1008
 [3] L Croguennec *et al*, Journal of the American Chemical Society, **137** (2015), p. 3140
 [4] S Goriparti *et al*, Journal of power sources, **257** (2014), p. 421
 [5] P.P.R.M.L. Harks *et al*, Journal of power sources, **288** (2015), p. 92
 [6] K L Jungjohann *et al*, Microscopy and Microanalysis, **18** (2012), p.621
 [7] A J Leenheer *et al*, ACS Nano, **9** (2015), p.4379
 [8] A. J. Leenheer *et al*, J. Microelectromech. **24** (2015) 1061
 [9] A J Leenheer *et al*, Microscopy and Microanalysis, **21** (2015), p.1293
 [10] This work was performed at the Center for Integrated Nanotechnologies (CINT), a U.S. DOE Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly-owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC0494AL85000. This work was funded by the Nanostructures for Electrical Energy Storage, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science.

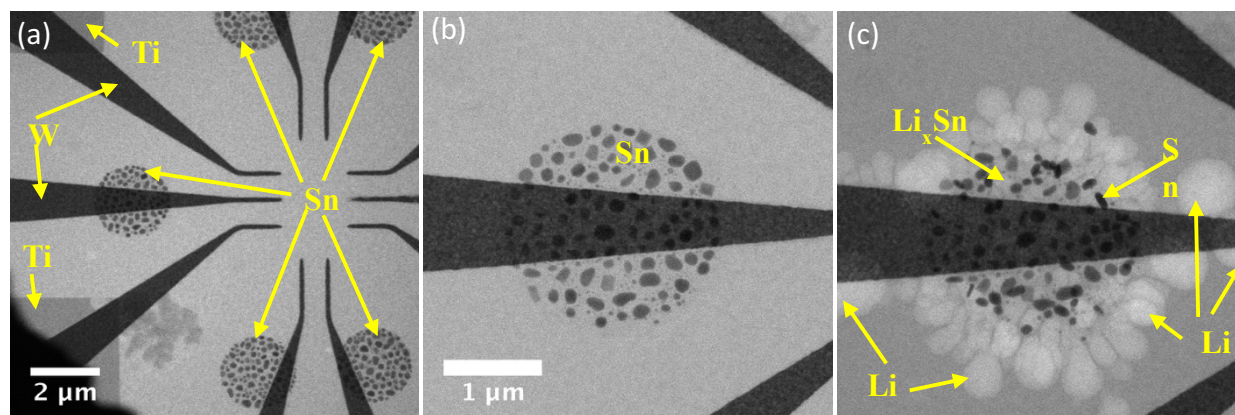


Figure 1. Bright-field STEM images of (a) Sn working electrode along with Ti counter and reference electrodes, cell is filled with 1M LiPF₆ in 1:1 EC/DMC; and Sn working electrode (b) prior to electrochemical lithiation, (c) after electrochemical lithiation at a current density of 1mA cm⁻² with no exposure to electron beam during lithiation and total electron dose of <math>< 10 e \text{ \AA}^{-2}</math>, imaging at the end of each cycle step. Note: lithiation continued beyond alloying with the Sn, which formed Li deposits seen on the electrode surface.