Direct Atomic-Scale Imaging of Multistep Phase Transition during the Lithiation of Nanowires by In-Situ (S)TEM

Anmin Nie,1,3 Robert F. Klie,3 Sreeram Vaddiraju,2 Reza Shahbazian-Yassar1,3,4

1Department of Mechanical Engineering-Engineering Mechanics, Michigan Technological University, 1400 Townsend Dive, Houghton, Michigan 49931, USA
2Artie McFerrin Department of Chemical Engineering, Texas A&M University, 3122 TAMU, College Station, TX 77843, USA
3Department of Physics, University of Illinois at Chicago, Chicago, Illinois 60607, USA
4Mechanical and Industrial Engineering Department, University of Illinois at Chicago, Chicago, Illinois 60607, USA

Sb-based alloy, such as Zn-Sb1-3, are promising anode materials because of their high theoretical capacities and suitable operating voltages. However, there have been very few studies on the detailed dynamical process of the phase transition during lithiation in the Sb-based intermetallic compounds, especially at atomic scale. By employing in-situ (scanning) transmission electron microscopy4, we studied the lithium-ion diffusion and multistep phase transition during the electrochemical lithiation of individual single-crystal Zn4Sb3 nanowires with atomic-resolution. Continuous phase transition from crystalline rhombohedral Zn4Sb3 to hexagonal LiZnSb and then to cubic Li2ZnSb phases has been directly monitored upon successive lithium-ion intercalation, which is mediated by the formation of amorphous LixZn4Sb3 at the early stage of lithiation. The kinetics of lithiation has been found to be highly anisotropic and relevant to the dynamics of the interfacial structures of the reaction front at different stages of lithiation.

References:
Figure 1 (a) TEM images recording the reaction front migration of the individual Zn$_4$Sb$_3$ nanowire during charging -3.0 V against lithium metal coating with Li$_2$O layer. (b) Electron diffraction pattern of the un-lithiated part of the nanowire indicated by the box, which is determined to be single crystal Zn$_4$Sb$_3$. (c) Electron diffraction pattern of the lithiated part of the nanowire, which shows that Zn, LiZnSb, Li$_2$ZnSb, and Li$_3$Sb are formed after lithiation. (d) Low-mag HAADF image of a partial lithiated nanowire, which clear show a wedge interface between the lithiated and un-lithiated part in the nanowire. (e) High-mag HAADF image of the interface area. (f) Atomic scale resolution HAADF image of the interface, which indicates a lithiation-induced amorphous-crystalline interface at the early stage during charging. (g) EELS spectra taken from crystal and amorphous parts (Site 1 and Site 2 in panel f) of the nanowire indicating the existence of the lithium element in the lithiated part.