Coupling In-situ TEM and Ex-situ Analysis to Understand Heterogeneous Sodiation of Antimony

We employed an in-situ electrochemical cell in the transmission electron microscope (TEM) together with ex-situ time-of-flight, secondary-ion mass spectrometry (TOF-SIMS) depth profiling, and FIB - helium ion scanning microscope (HIM) imaging to detail the structural and compositional changes associated with Na/Na⁺ charging/discharging of 50 and 100 nm thin films of Sb. TOF-SIMS on a partially sodiated 100 nm Sb film gives a Na signal that progressively decreases towards the current collector, indicating that sodiation does not proceed uniformly. This heterogeneity will lead to local volumetric expansion gradients that would in turn serve as a major source of intrinsic stress in the microstructure. In-situ TEM shows time-dependent buckling and localized separation of the sodiated films from their TiN-Ge nanowire support, which is a mechanism of stress-relaxation. Localized horizontal fracture does not occur directly at the interface, but rather at a short distance away within the bulk of the Sb. HIM images of FIB cross-sections taken from sodiated half-cells, electrically disconnected and aged at room temperature, demonstrate non-uniform film swelling and the onset of analogous through-bulk separation. TOF-SIMS highlights time-dependent segregation of Na within the structure, both to the film-current collector interface and to the film surface where a solid electrolyte interphase (SEI) exists, agreeing with the electrochemical impedance results that show time-dependent increase of the films’ charge transfer resistance. We propose that Na segregation serves as a secondary source of stress relief, which occurs over somewhat longer time scales.

Biography:
David Mitlin is a Professor and General Electric Chair at Clarkson University, jointly in the Departments of Chemical & Biomolecular Engineering and Mechanical Engineering. His expertise is in synthesis and structure-properties relations of carbons, applied electrochemistry, materials for batteries, fuel cells and supercapacitors, corrosion, and microstructural characterization. Dr. Mitlin has published 130 peer-reviewed journal articles, holds 6 granted or pending patents 3 of which are licensed, and has presented 80 invited or keynote talks. In addition to his Clarkson activities, Dr. Mitlin an Editor for Journal of Materials Science and serves on the Board of Review for Metallurgical and Materials Transactions. He has supervised and graduated 13 Ph.D. students, 7 M.S. students and 8 post docs. Dave received a Doctorate in Materials Science from U.C. Berkeley in 2000.

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