## *In Situ* and *Ex Situ* Diagnosis of Nanoscale Electrochemical Processes Using Miniature All-Solid-State Li-Ion Batteries

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Rechargeable Li-ion batteries are considered among the most preeminent electrochemical energy storage (EES) technologies in the 21<sup>st</sup> century [1]. Further advances in the EES require deeper understanding of the fundamental mechanisms associated with charge and discharge processes, including bulk diffusion of charge carriers, transport of charge across interfaces, and overlapping structural and phase transitions in the electrode and at interfaces [1-4]. Higher capacity over 1000 mAh/g and specific energy density over 400 Wh/kg demanded for emerging EES applications such as long-endurance unmanned aerial systems, electric vehicles with large distance range of action (up to 300 miles), portable electronics, etc. continuously push EES to the edge of stability; yet these devices must be safe, environmentally friendly and reliable through hundreds or thousands of rapid charge-discharge cycles [2]. The need to mitigate the volume and structural changes to the active sites accompanying the charge - discharge cycle at the atomic level encourages exploration of nanoscale controlled structures and recent developments have demonstrated both dramatically increased the energy capacity and power densities [3]. The multitude of morphologies, complex interfacial phenomena and transformations that govern the operation of Li-ion batteries (LiBs) require reliable high spatial resolution 3D structural measurements which can be directly related to the capacity and electrical transport characteristics providing insights into evolution of the components during the battery processes [4, 5].

To realize tremendous potentialities of electron microscopy for solving this problem, we develop a flexible MEMS-based inter-instrumentation platform for nanometrology of LiBs employing Echips compatible with FIB, FESEM and S/TEM. Furthermore, we have designed miniature all solid-state LiBs suitable for *in situ* S/TEM or FESEM electrical testing in a sub-pA range, which comprise: a) a LiCoO<sub>2</sub> cathode, a LiPON electrolyte and Si anode deposited onto metallized Si nanowires and wired with electron-beam-deposited Pt contacts (FIGs. 1 and 2); b) LiCoO<sub>2</sub>/ LiPON/Si thin film stacks (FIG. 3). Such individual batteries allow the correlation of electrochemical properties tailored for specific performance with their structure being analyzed in desirable imaging, diffraction and spectroscopic modes up to the atomic resolution. Using *in situ* cycling of the LiBs in a TEM and FESEM followed by *ex situ* S/TEM observations coupled with EDX/EEL spectral imaging, we have found that a substantial reduction in the electrolyte thickness to 110 nm could lead to rapid self-discharge via space-charge limited electronic conduction, effectively shorting the battery [5]. This demonstrates the usefulness of the proposed approach for clarifying effects of scaling on the LiB's performance.

References: [1] M. Roco et al., (eds.) *Nanotechnology Research Directions for Societal Needs in 2020*, Springer, 2010. [2] V.P. Oleshko, et al., Microsc Microanal 15 (2009) 718, 1398. [3] M.-K. Song, et al. Materials Sci Eng R 72 (2011) 203. [4] V.P. Oleshko et al., Microsc Microanal 17 (2011) 1658. [5] D. Ruzmetov et al. Nano Letters 12 (2012) 505.



FIG. 1. A Si nanowire core – LiCoO<sub>2</sub>/LiPON/Si multishell diagnostic LiB assembled for electrochemical testing. (a) BF-TEM, red circle marks the position of the nanowire LiB wired with electron-beam deposited Pt contacts on a chip. (b) *In situ* TEM, the pristine battery and (c) the processed battery after 7 charge-discharge cycles (c). Red box includes a LiCoO<sub>2</sub>/LiPON interface where significant structural changes are observed.



FIG. 2. *Ex situ* STEM of the same cycled nanowire LiB demonstrating 50-100 nm voids and 10-40 nm particles at or near the LiCoO<sub>2</sub>/LiPON interface. (a) BF-STEM, (b) HAADF-STEM. FIG. 3. HAADF-STEM, cross-section of a cycled thin film LiB showing two distinct cathode layers (upper LiCoO<sub>2</sub> transformed under processing (1) and largely pristine LiCoO<sub>2</sub> (2). HRTEM of an irregular interphase between layers of the LiCoO<sub>2</sub> cathode and solid electrolyte (enlarged top right inset) displays (101) lattice fringes of a HT hexagonal LiCoO<sub>2</sub> polymorph with 0.24 nm interplanar spacing.