Integrated Approach to Design, Testing and Characterization of Advanced Electrochemical Energy Storage Materials by Electron Microscopy Techniques

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Electrochemical systems for energy conversion and storage such as rechargeable batteries, fuel cells, and supercapacitors represent the preeminent technologies for sustainable energy generation and use in the 21st century [1]. Complex phase transformations and interfacial phenomena that govern the operation of electrochemical energy storage (EES) devices vitally need reliable nanoscale structural measurements that can be directly related to the capacity and electrical transport characteristics. Recent developments in nanostructured materials for EES (layered Li transition metal oxides, polyanionic compounds for cathodes, and Si, Si/CNT, transition metal oxide nanowires (NWs), Si-carbon composites, and graphenes for anodes, and Li-S (air) systems with mesoporous active carbons have demonstrated the potential to dramatically increase both energy capacity and power density. Further advances in EES technologies for emerging applications such as electrical vehicles (EVs) with large distance range of action or high-altitude long-endurance unmanned aerial vehicles (UAVs) are targeting the next generation of long-cycle life high-energy density systems with higher by an order of magnitude capacity than existing Li-ion/polymer batteries (>1000 mAh/g) and specific energy density over 400 Wh/kg [1, 2]. The utilization of active material and performance of the batteries at continuous high current discharge should be further improved via 3D design of cells and novel electrode materials. This requires detailed atomic level understanding of the fundamental mechanisms associated with charge transfer, structural and phase transitions in the electrodes.

Among all instrumental methods that can be used for these purposes, EM plays an increasingly important role even in spite of limitations caused by inevitable radiation damage. Stationary beam and scanning EM techniques enable high-spatial resolution imaging in various modes, single-crystal diffraction, and spectroscopy at sub-eV energy resolution, thus gaining indispensible 3D local morphological, crystallographic and chemical information to address key problems of EES systems [1,3]. In an attempt to realize this tremendous potential in full depth, we describe here an integrated approach to design, testing and multiscale structural and analytical characterization of perspective EES materials by the combination of (HR)TEM, STEM, AEM with EDS X-ray and EEL spectral imaging (SI), FESEM, and dual beam FIB/SEM. The EM techniques permit real-time studies of batteries along with galvanostatic (GS) testing of charge/ discharge reactions, compression effects and potentially the formation and spatial distribution of the solid-electrolyte-interphase (SEI) under varying processing conditions (T, P) *in situ* and e*x situ* [4-6]. Research can be conducted using environmentally protected multifunctional loading/transfer cell holders specifically designed for characterization and electrochemical processing of air-sensitive battery materials. Advanced statistical algorithms (automated feature sizing/chemical typing, multivariate statistical analysis) allow processing of high volumes of quantitative information from a series of acquisitions. This offers flexible means for various measurements (e.g., sizes/shapes of surface features, classification of the analyzed areas of electrodes vs. chemical contents of constituents, phase identification and enhancement of the SNR for SI signals limited by low acquisition rates) [3,4]. Furthermore, we designed original all-solid Li-ion nanobatteries (LiNBs), with essential parts transparent for (S)TEM, which comprise a $LiCoO_2$ cathode and electrolyte (LiPON) deposited onto a NW or thin film Si anode (FIG.1). The LiNBs and their components can be analyzed using various imaging, diffraction

and spectroscopic (S)(T)EM modes at up to the atomic level while GS cycling, impedance and cyclic voltammetry measurements are conducted. We illustrate how HRTEM, STEM coupled with valence and inner-shell EELS and EDX SI complemented by FESEM for surface analyses can be employed to clarify the morphology, chemical distributions (phases), electronic properties and bonding and their effects on the performance of the LiNBs (FIG.2). The single-crystal NW-based LiNBs are well suited for *in situ* electrical testing using a piezo actuated electrical nanoprobe and may serve as a diagnostic nanostructure since they allow the direct correlation of electrochemical and electrical transport properties tailored for specific performance with the structure on the same NW.

References

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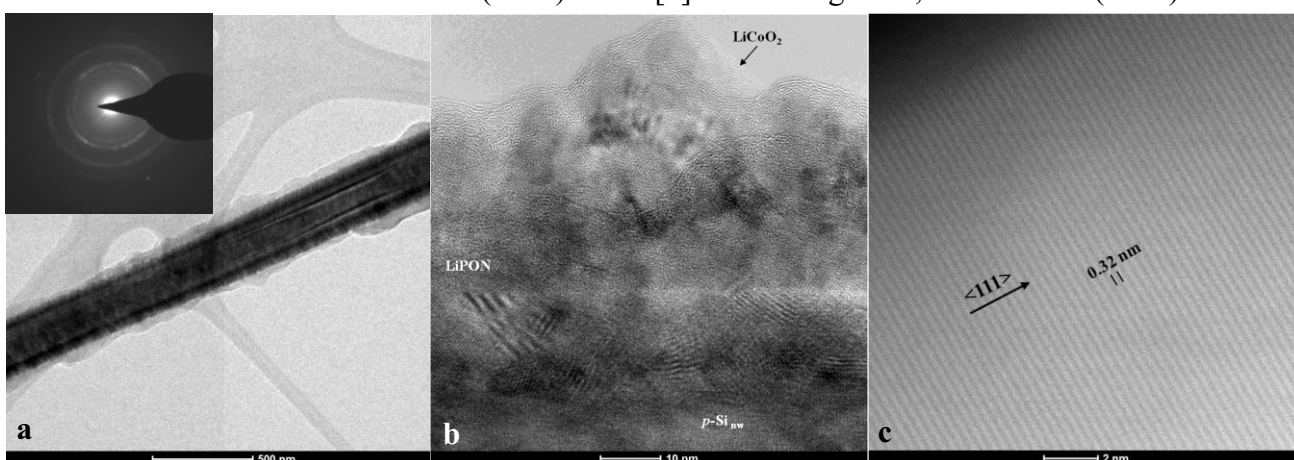
FIG. 1. LiNBs comprising 30-60 nm $LiCoO_2$ cathode and 50-60 nm LiPON electrolyte layers deposited onto a Si NW anode. (a) TEM, an internal arrangement of as fabricated battery. The SAED pattern (inset) shows discrete ring reflections assigned to HT hexagonal polymorph of $LiCoO_2$. (b) HRTEM, an interphase between the Si NW anode and solid electrolyte visualized through deposited layers of $LiCoO_2$ and LiPON. (c) STEM, Z-contrast image of a pristine single-crystal *p*-Si NW near its edge displays (111) lattice fringes with 0.32 nm interplanar spacing.
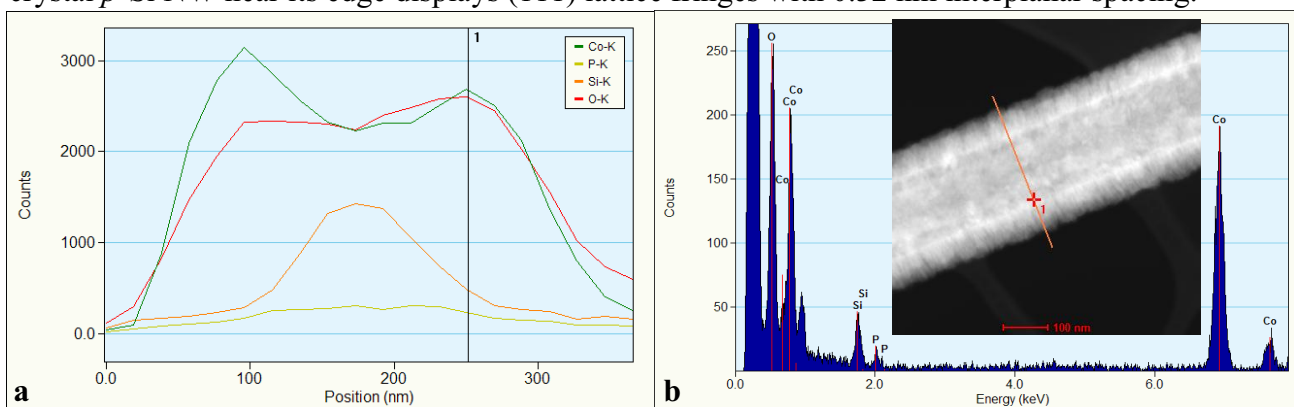

FIG. 2. STEM-EDS drift corrected line profile scan across a LiNB demonstrating local chemical distributions of the constituents. (a) Integral intensities of the CoK, PK, SiK and OK lines vs. probe position. (b) X-ray spectrum acquired in the point marked by red cross on the profile line in ADF-STEM image (inset). This point corresponds to the position of a vertical marker in graph (a).