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Probing Structural and Chemical Evolution of Electrode Materials in Lithium Ion Batteries Using In-Situ TEM Imaging and Spectroscopy

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Li-ion batteries, similar to many other electrochemical energy storage devices, are complex multi-component systems that incorporate widely dissimilar phases in physical and electrical contact [1]. Repeated charging and discharging of the Li-ion batteries induces microstructural changes both at the interface between the electrolyte and the electrode and within the electrode. Although it has been established that this microstructural evolution is responsible for the failure of the battery, the mechanisms of microstructural change as a function of charging/discharging are not well understood. In this work, we review and discuss the fundamental designing concepts that enable in-situ TEM studies of lithium ion battery aging. To deal with high vacuum of a TEM, the design approaches include: use of a low vapor pressure ionic liquid based electrolyte, design of a closed liquid containing cell, and preparation of thin battery section including a solid electrolyte. The fundamental challenges with each method will be reviewed. Important insights into battery aging have been explored using a model system with a SnO_2 single nanowire anode, a $LiCoO_2$ cathode and an ionic liquid based electrolyte.

The miniature prototype battery with a $LiCoO_2$, SnO_2 nanowire as anode and an ionic liquid electrolyte was assemble as follows. The cathode was a mixture of $LiCoO_2$ particles, conductive carbon and PVDF binder, and coated as a thin film on an aluminum foil. The use of the SnO_2 nanowire anode provides electron transparency and therefore allows in-situ observation of both chemical and structural change under TEM during the operation of the battery. The air stable electrolyte was made by dissolving salt lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in a hydrophobic ionic liquid 1-butyl-1-methylpyrrolidium (P_{14}) bis(trifluoromethane sulfonyl)imide (P_{14}TFSI). The overall composition of the electrolyte was 10% LiTFSI in P_{14}TFSI. It has been tested that this ionic-liquid-based electrolyte is stable in the column of the TEM with a typical vacuum of 10^{-5} Pa and showed no significant evaporation following one week in the TEM column, therefore allowing a systematic cyclic charging and discharging of the battery in the TEM [2]. The overall designing of the battery is shown in Figure 1.

It has been observed that following the initial charging the nanowire retained a wire shape, although highly distorted. The originally straight wire is characterized by a zig-zag structure following the phase transformation, indicating that during the phase transformation of $SnO_2 + Li \leftrightarrow Li_xSn + Li_yO$, the nanowire was subjected to severe deformation, as similarly observed for the case when the SnO_2 was charged sequentially from one end to the other. High magnification TEM imaging revealed that the Li_xSn phase possesses a spherical morphology and is embedded into the amorphous Li_yO

matrix, indicating a simultaneous partitioning and coarsening of Li_xSn through Sn and Li diffusion in the amorphous matrix accompanied the phase transformation. The observed composite configuration gives detailed information on the structural change and how this change takes place on nanometer scale.

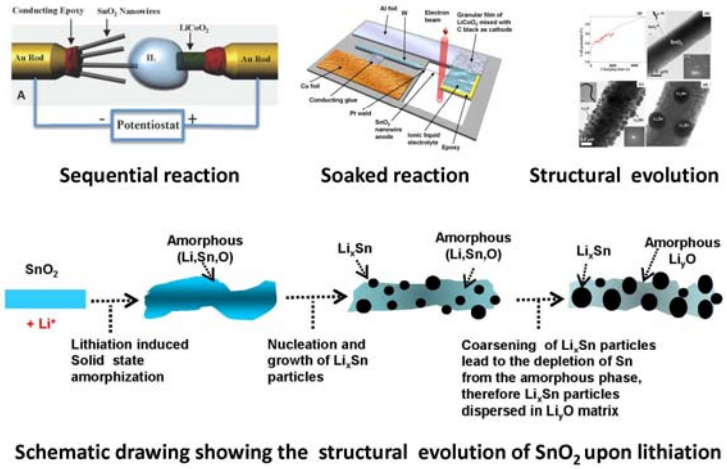

Fig. 1 Fundamental concept on the design of prototype lithium ion battery cell using a single nanowire and ionic liquid based electrolyte. Note the different configuration of the cell may lead to either a sequential reaction or a fully soaked configuration that mimic the situation in a real battery. The overall observed structural feature is illustrated at the up-right corner and the bottom is a schematic drawing showing the proposed model of overall structural evolution of SnO_2 upon initial lithiation.

Although the work was carried out using SnO_2 nanowires, it has been demonstrated that in combination with nanomanipulations in a TEM [3,4], the present model work can be applied in parallel to explore the dynamic microstructural and phase evolution of other materials system. In perspective, controlled lithiation and delithiation in combination with direct quantitative microstructural analysis and multiscale computational simulation will enable correlation of microstructural evolution features with mass and charge transport kinetics and mechanisms in a battery system.

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