

In situ hard x-ray nano-imaging study of morphology evolution for battery materials

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Battery materials in lithium-ion batteries (LIBs) undergo lithiation and delithiation process, yielding strains in host materials and possible structure change. Particularly, the induced large strain at anode materials (such as widely studied silicon and tin based anodes) can lead to large volume change, fracture, and pulverization, which is considered as a major challenge for anode materials of LIBs. To address these challenges, it is crucial to understand the fundamental reactions occurring inside the electrode materials by observing the morphological/structural evolution during the operation of a battery. In-situ measurements have yielded valuable information about the function of electrochemical cells. However; most of conventional in situ methods still face many technical challenges including limited sample size and thickness, surface or spatially averaged information etc.. Particularly, most of in situ electrochemical cells cannot provide true electrochemical reactions of battery materials due to its special design and complicate operation, which may result in inaccurate information and misunderstanding.

Synchrotron hard x-ray transmission microscopy is non-destructive, element sensitive, environmental friendly, and highly penetrating. It holds larger potentials to image micron sized battery materials with a large sample thickness. The experiment set-up is located at beamline X8C (National Synchrotron Light Source). This newly developed transmission x-ray microscope (TXM) has several unique capabilities to overcome the difficulties in the existing TXM systems.^[1-3] Here, we report in-situ LIB study using the TXM x-ray nano-imaging with a special home-designed electrochemical cell consisting of anode particles, a commercial carbonate electrolyte, lithium metal as a counter/reference electrode. Different from widely used open nano-battery in in situ TEM study, our designed battery excellently simulates the true working circumstance and reflects truly the electrochemical reaction in a working LIB. In addition, our robust battery is very stable for long time electrochemical cycling and x-ray characterization.

Fig. 1 shows direct observation of in situ 2D morphology change of CuO particles at different potentials during electrochemical lithiation-delithiation process.^[4] CuO particles continuously develop into a core-shell structures with a grey shell, a dark core, and an interface phase in between. This core-shell structure is a typical character of electrochemical interfacial conversion reaction within lithium-ion batteries. In contrast to these larger sized CuO particles, small CuO particles undergo faster volume change, as marked by the red arrow, which demonstrates the classic core-shell kinetic theory that the time required for a system to be lithiated is proportional to the square of the diffusion distance, i.e., particle diameter in this case.^[5] Particularly, during delithiation process, some cracks appear within the shell and extend along the radial direction toward the dark core, and the formation of these cracks results from the existence of tension stress due to the volume change and lithium extraction during the delithiation. The above lithiation-delithiation process

were also confirmed by synchrotron x-ray diffraction (XRD) and transmission electron microscopy (TEM).

In addition to in situ 2D study, we also performed in situ 3D tomography study of anode particles during electrochemical cycling. It was observed that all the anode particles exhibit volume expansion with minor morphology deformation when lithiated and volume shrinkage accompanying with further and severe pulverization when delithiated.. The 3D statistics information including true volume change, specific area and particle size will be discussed. A simulation about the stress distribution and the relation to material's pulverization will also be presented.

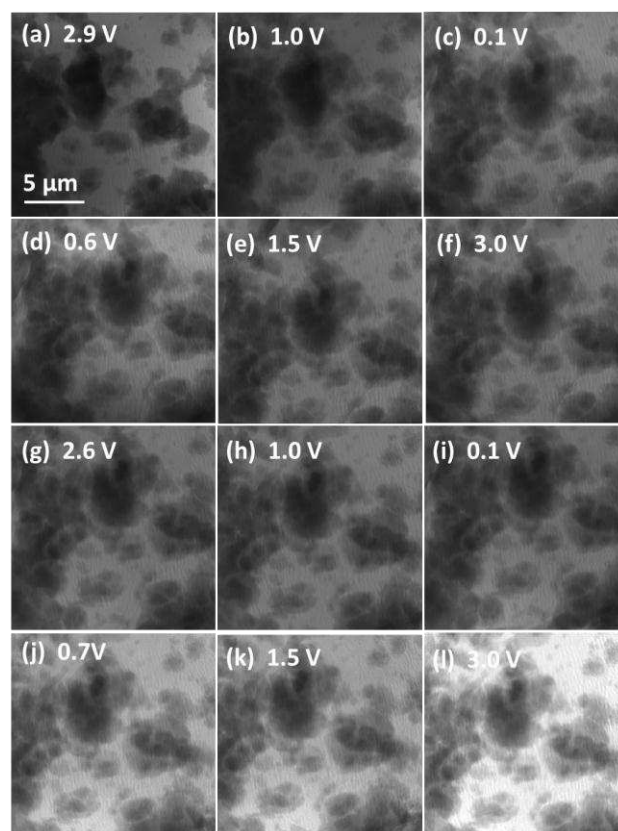


Fig. 1. The in situ 2D morphology evolution of CuO electrode during the first (a-f) and second cycle (h-l) with hard x-ray microscopy.

Reference

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