Development of Nano-scale Lithium Batteries for In Situ Observations in Analytical Electron Microscopy

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Introduction

When coupled with spectroscopy (energy dispersive and energy loss), transmission electron microscopy (TEM) and diffraction is one of the most powerful tools for obtaining information regarding the morphology, structure and compositions at the nano scale. TEM studies of lithium battery materials have revealed valuable information on structural changes, phase transitions, and interface modifications that occur during the lithium (de)intercalation processes. Nonetheless, observations of these phenomena on real in situ cells during cycling remain very challenging.

Recently, several in situ TEM studies have been reported. To avoid contamination in the high vacuum TEM column from evaporation of the organic liquid electrolyte, the in situ battery operations in these studies are realized by using either all-solid-state cells or vacuum compatible ionic liquid electrolytes (ILs). By using the all-solid-state battery strategy, the electric potential distribution around the positive electrode (LiCoO2) and electrolyte interface has been successfully quantified by using electron holography (EH). The in situ observations of morphology and structural changes of SnO2 nanowires during electrochemical lithiation are realized in two different setups using ILs. However, the large plasmon loss peak from the ionic liquids limit the quantitative analysis of Li concentration.

In this work, we focus on the development of a procedure to prepare nano-batteries from all-solid-state micro batteries. To ensure its transparency to the electron beam and minimize artifacts, the nano-battery must be very thin (<100 nm). The barriers need to be overcome include (i) ensure the electrochemical functionality of nano-battery, (ii) robust electric contacts to current supply, and (iii) accurately controlled low current supply (pA to nA).


Experimental setup design

Schematic (left) and SEM image (right) of the experiment setup showing a multi-layer nano-battery stack mounted on a special designed Triton TEM grid. The sample consists of: protective layer +/− current collectors, +/− electrodes and electrolyte layers, and connections to cycle is realized through the Au contact pads on the Triton grid.

Problems encountered

• Shorting occurs during the milling depth of 2 to 1.5 um (3rd step), when partial of LiCoO2 layer starts to expose. A thicker electrolyte layer (>1.5um) should help avoid shorting.

• Porous feature of LiCoO2 layer smearing, & discontinuity of Au current collector (+)

• Porous films (SO method) cause difficulties in FIB fabrication (e.g. delamination etc.).

• Layer smearing between LIPON & LiCoO2 is observed in some region.

• Discontinuity of current collector (over non-conductive substrate) causes disconnection of nano battery to current supply.

All-solid-state micro battery

µ battery features

• Prepared by sputtering deposition (SD) method, 2 mm in diameter,
• Au and Cu as current collectors (thickness ~1um)
• Non-conductive alumina substrate.

Cross section layer assignment

1. Cu (current collector), 2. Sn (anode),
3. LIPON (electrolyte), 4. LiCoO2 (cathode),
5/6. Au/Ni (current collector/adhesive layer),
7. Alumina (substrate).

Electrochemical tests

• An isolated Si area of sub-micron size was successfully created & tested.
• Stable current supply @ 1nA was achieved.
• Charge behavior (e.g., process @ 3.3V) resemble normal LiCoO2 vs. a Si battery.
• Discharge has a large over potential (~1.6V).

Conclusions & Future Plans

• Experimental setup of nano batteries designed for in situ TEM observations has been developed.
• All solid-state micro-batteries prepared by sputtering deposition method are characterized.
• Problems encountered during nano-battery fabrications are (partially) identified.
• Steady current control of 1nA is realized and the charge/discharge behavior of an isolated Si trench of sub-micron size is obtained.
• New micro batteries with improved design/features will be prepared (PLD).
• Further electrochemical tests and a pseudo in situ type experiment will be conducted.

General procedure for nano-battery fabrication

Step 1: Create a cross-section trench from the µ battery using focused ion beam (FIB) in a dual beam FIB/SEM instrument, trench thickness ~ 5um;
Step 2: Use micro-manipulator to lift the created cross-section trench out from the µ battery;
Step 3: Mount the lift-out cross-section trench to a window on a Triton TEM grid & clean both sides, trench thickness reduce to ~ 1um;
Step 4: Create two end cuts to realize the nano-battery configuration & further thin down the nano-battery thickness to ~ 100 nm (or thinner).

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