lightning

APPLICATION NOTE

Experimental Setup:

TEM & Objective lens

JEOL ARM200CF Probe corrected

In Situ System

Lightning D6+ (Heating or Biasing) system with Kethley 2601B Source Measure Unit

MEMS device

4 contact Lightning D6+ Nano-Chip

Sample

FIB lamella:
Au / $Li_{6.75}La_{2.84}Y_{0.16}Zr_{1.75}Ta_{0.25}O_{12}$ / $LiCoO_2$

Sample Preparation Technique

- All-solid-state battery was prepared with a FEI Helios 600i FIB-SEM
- Thinning and polishing procedure was performed on the MEMS chip

In Situ Environmental Parameters

Temperature: RT
Potentiostatic measurement: 0 - 2.4 V
Rate: 0.3V/sec

Analysis Techniques

ABF-STEM, HAADF-STEM

In Situ TEM study of Lithium-Ion Solid-State Battery

Keywords

In situ biasing, Li-ion Solid-State Battery, High Resolution Scanning Transmission Electron Microscopy, Focused Ion beam, MEMS Nano-Chips

Fields

Energy, Energy storage, Solid State Li-Ion Battery (SS LIB)

Abstract

Safety issues associated with the flammable organic liquid electrolytes in the Li-Ion Batteries (LIBs) force researchers to look for alternatives which contains safer solid state electrolytes instead.

In this work the authors reported the successful preparation of an all-solid-state LIB sample directly on the MEMS-based Nano-Chip. Atomic scale HAADF- and ABF-STEM imaging of the cathode during in situ electrochemical delithiation of the working battery cell has been achieved using DENSsolutions biasing system.

Purpose

- Driven force: Improve the power density and address the safety hazard of current LIB's by switching to solid state electrolytes
- Understand the behaviour of the promising $LiCoO_2$ cathode during in situ high voltage delithiation of all-solid-state-battery inside TEM

Challenges

- Prepare a solid state battery cell onto a MEMS-based sample carrier using FIB

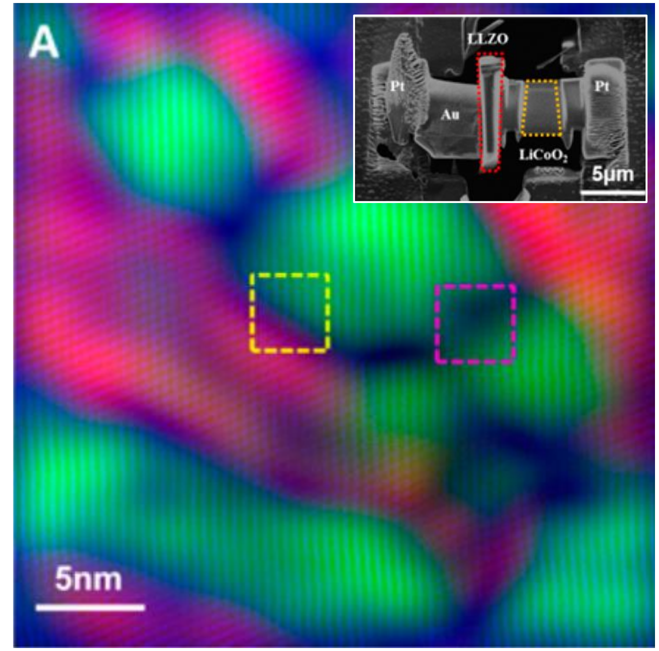

Figure 1. HAADF micrograph of the delithiated polycrystalline $LiCoO_2$ cathode colored using the Geometric Phase Analysis (GPA) method, showing two grains orientations colored with green and red. The inset shows the SEM image of the FIB fabrication.

- Final thinning directly on the MEMS-based sample carrier without damaging it
- Obtain working device (no electrical shortcuts)
- High lamella's quality, suitable for atomic resolution (thin with no FIB artefacts)
- Resolving Li-ions and atomic resolution imaging stability while biasing

Results

1. Sample preparation

In the current work, an all-solid-state LIB with a gold anode, a $LiCoO_2$ cathode, and Y and Ta-doped LLZO ($Li_{6.75}La_{2.84}Y_{0.16}Zr_{1.75}Ta_{0.25}O_{12}$) as solid-state electrolyte (SSE) has been constructed on the MEMS Nano-Chip using FIB milling. The battery cell was assembled step by step directly on the Nano-Chip, as shown schematically on Figure 2. The final thinning was performed using low energy ions (5 kV and 2 kV) and allowed to reduce the FIB generated damage and to reach the thickness below 50 nm.

The possible damage of the supporting membrane during final thinning onto the Nano-Chip doesn't affect the accuracy of the measurement.

The detailed description of the sample preparation is available in the supporting information and can be downloaded from here: http://pubs.acs.org/doi/suppl/10.1021/jacs.6b13344/suppl_file/ja6b13344_si_001.pdf

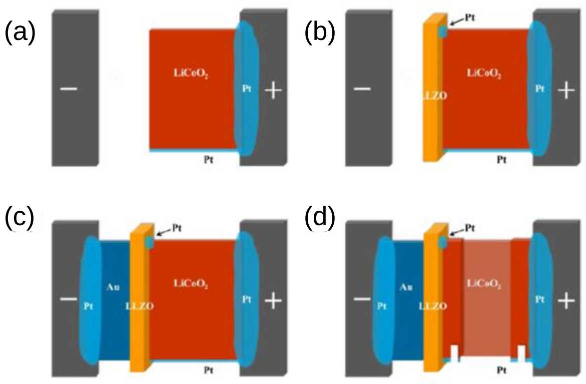

Figure 2. (a – d) Step by step schematics of the battery cell fabrication process in the FIB.

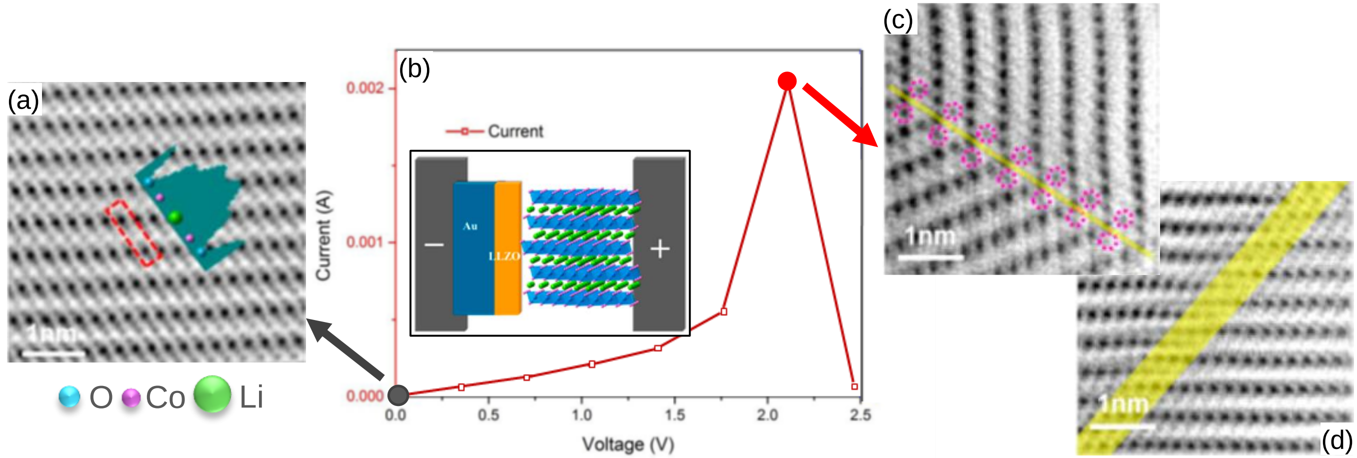

Figure 3. (a) ABF micrograph of the pristine $LiCoO_2$ sample. (b) Measured voltage-current-time plot of the delithiation process with an inset showing corresponding schematic of the battery cell. (c & d) ABF micrographs of the delithiated cathode, showing coherent twin and antiphase boundaries, respectively.

2. In situ biasing and STEM imaging of $LiCoO_2$ cathode

Using the Lightning D6+ system and 2601B Source Measure Unit from Ketihley an in situ charging cycle of the battery cell has been performed in the TEM (Figure 3 (b)). The authors has directly observed for the first time that when the voltage bias reaches 2.1 V, the pristine single crystal transforms into a polycrystalline structure having grains of 5-15 nm in size. The polycrystalline structure has two crystal orientations and consequently two types of grain boundaries, namely coherent twin and antiphase boundaries (Figure 3 (c & d)).

Collected atomically-resolved ABF images, Figure 3 (a, c & d) allowed to identify both light elements, lithium and oxygen, in the structure before and after the delithiation. The delithiation process could be confirmed by (i) a weakening of the lithium contrast and (ii) layer spacing expansion in the sample; additionally, Co ion migration into lithium-ion layers have been observed (Figure 3 (c)).

The collected atomic-scale in situ STEM results together with the theoretical calculations helped to explain why the polycrystallization phenomena occurs: the creation of the nanosized domains are connected to the preferred formation of the coherent domain boundaries with low lithium-ion diffusion interface energy-barrier under applied bias and with the physical contact between the electrode and the electrolyte.

3. Key Message

- These findings provide a better understanding of the all-solid-state battery operation and can be used for designing more energy efficient and safer energy storage devices
- In situ biasing &/or heating stimuli, together with the capability of functional devices preparation directly on the MEMS-based Nano-Chip with no effect on the measurement accuracy, opens exciting new avenues in Nanoscale research

Y. Gong et al . "In Situ Atomic-Scale Observation of Electrochemical Delithiation Induced Structure Evolution of $LiCoO_2$ Cathode in a Working All- Solid-State Battery." JACS, 2017, 139 (12) 4274 (2017). DOI: 10.1021/jacs.6b13344