

Structural Evolution During Electrochemical Cycling of Epitaxial LiCoO₂ Films Studied by S/TEM

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LiCoO₂ (LCO) has been the most important and most studied positive electrode material for lithium-ion batteries; thus for this work we have selected LCO as a model material for studying electrochemical property of single orientation, binder-free cathodes in a form of epitaxial thin films [1]. In order to capture the effect of crystallographic orientation of a cathode/electrolyte interface and diffusion anisotropy, the different orientation films were obtained by deposition on single-crystal substrates of different orientations. SrTiO₃ (STO) substrates with 111, 110, and 100 surfaces were used to induce 001, 110, and 104 out-of-plane orientation of LCO, respectively. In the course of this study it was realized that a layer of highly conductive SrRuO₃ (SRO) between LCO and STO is essential to (a) remove a rectifying Schottky barrier between LCO and STO, (b) act as high-conductivity current collector, and (c) preserve the intended orientation of LCO films. Both SRO and LCO films were deposited sequentially by pulsed laser deposition (PLD) at 600 °C temperature of a substrate, 200 mTorr oxygen pressure with a KrF laser (wavelength 248 nm) using repetition rate 0 Hz and the laser energy 100 mJ per pulse.

The analysis of the LCO/SRO/STO(111) cross-section sample prepared by FIB is shown in Fig. 1. The LCO surface is predominately flat, with crystallographic (001)_{r-LCO} plane (r-LCO – rhombohedral layered structure), but with occasional faceted grooves. According to the SEM image, Fig. 1b, the surface consists of triangular islands with faceted surfaces identified as {104}_{r-LCO} planes. From electron diffraction and HAADF/STEM imaging, Fig. 1c,d, the following orientation relationship is established: (111)_{STO}//(111)_{SRO}//(001)_{r-LCO}, [110]_{STO}//[110]_{SRO}//[100]_{r-LCO}. Similar analysis was performed for other two orientations, with conclusion that there is a single orientation relationship between LCO and STO, which can be understood though a common fcc oxygen sublattice for all three oxides. However a lower symmetry of the rhombohedral LCO phase introduces domains with different orientation of c-axis.

Cyclic voltammograms of the films with different orientations were obtained by using a specially constructed three-electrode cell, with lithium metal as counter and reference electrodes and 1 mol dm⁻³ LiClO₄/propylene carbonate as electrolyte. Example of a cyclic voltammogram for the LCO/SRO/STO(111) film is shown in Fig. 2a; the voltammogram shows the major redox charge/discharge peaks that are typical for the rhombohedral LCO and represent, according to literature [2], a series of phase transitions corresponding to the changes in Li content. In order to observe directly the phases and their spatial distribution, the electrochemical measurements were stopped at different stages of interest, e.g. at points C1-1 or D1-1 in Fig 2a, the film was cleaned from the electrolyte, and a TEM cross-section sample representing this stage was prepared by FIB (see schematic drawing in Fig.2b) and examined by TEM; example of the structure observed at C1-1 stage is shown in Fig. 2b. After extracting the TEM sample, the film was return to a glove box for continuing electrochemical testing until the next stage of interest. Structural changes, formation of defects and interfacial modification at different stages of lithiation/delithiation will be discussed in the paper in details.

References:

- [1] S. Takeuchi, H. Tan, K. Kamala Bharathi, G.R. Stafford, J. M. Shin, S. Yasui, I. Takeuchi, L.A. Bendersky, to appear in ACS Applied Materials and Interfaces (2015).
 [2] J.N. Reimers and J.R. Dan, J. Electrochem. Soc., **139**, (1992), 2091

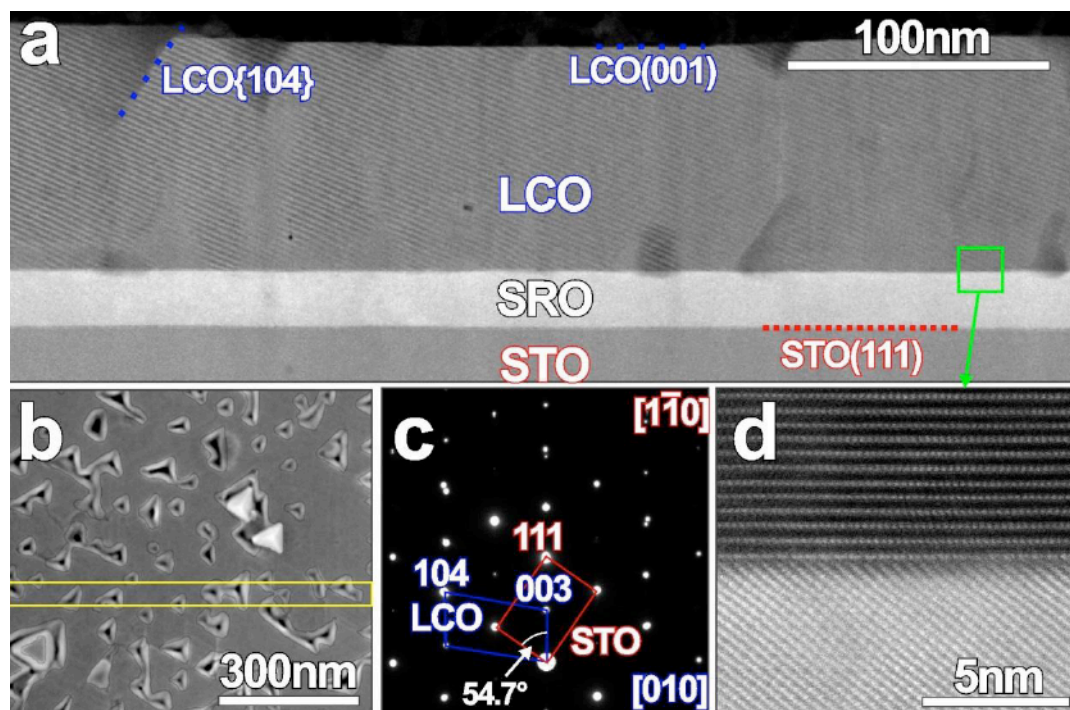


Figure 1. Characterization of the as-deposited LCO on STO(111) film by (a) STEM overview of cross-section, (b) SEM of a surface, (c) electron diffraction and (d) high resolution HAADF-STEM of LCO/SRO interface. The $\{104\}$ planes are 54.7° with respect to the horizontal STO(111) cut plane.

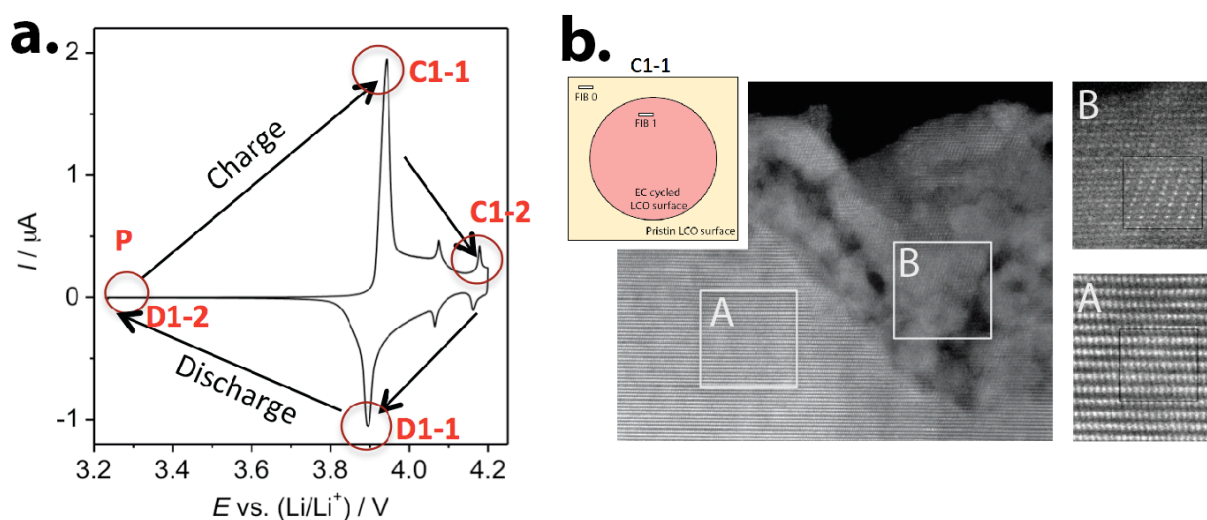


Figure 2. a. Cycling voltammogram of LCO/SRO/STO(111) film showing stages at which TEM samples were extracted; (b) Example of STEM imaging of a sample at C1-1 stage showing structural changes from layered (area A) to spinel-like (area B) structure in a near-surface region.