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Supplementary Information

Visualization of Inhomogeneous Current Distribution on ZrO_2-Coated $LiCoO_2$ Thin-Film Electrodes using Scanning Electrochemical Cell Microscopy

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SECCM setup

SECCM uses a moveable nanopipette probe (radius of 50 nm) usually containing 3 M LiCl electrolyte solution and an Ag/AgCl quasi-reference counter electrode (QRCE).[1] The nanopipette was brought into close contact with a sample electrode surface via a liquid meniscus at the nanopipette end. When the meniscus just made contact with the surface, a small anodic current flowed and a set point of 2 pA triggered the nanopipette to stop approaching. During imaging, the tip height position at this point was recorded, enabling the topography of the surface to be tracked.

Sample preparation and Characterization

$LiCoO_2$ thin-films were deposited on platinum coated Silicon substrates by the PLD. The laser ablation was performed using an Nd:YAG laser of 266 nm with a power of 200 mW. $LiCoO_2$ was deposited for 60 min under an oxygen pressure of 0.01 Pa at a temperature of 873 K.[2] After preparing the $LiCoO_2$ thin-films, ZrO_2 was deposited on the $LiCoO_2$ films by the PLD for different preparation periods (30 s and 180 s) at room temperature (RT).

The thickness of the deposited ZrO_2 on the $LiCoO_2$ films were confirmed by scanning transmission electron microscopy (STEM) combined with energy dispersive X-ray spectrometry (EDX). The samples for STEM-EDX analysis were prepared by focused ion beam milling.

Cyclic voltammograms

In order to characterize the ZrO_2 coating effect on the electrochemical properties of the $LiCoO_2$ thin-film electrode, cyclic voltammetry is carried out using SECCM for the uncoated $LiCoO_2$ electrode and the ZrO_2-coated $LiCoO_2$ electrodes. Figures S1a and 1b show the cyclic voltammograms (CVs) of the uncoated and 180 s ZrO_2-coated $LiCoO_2$ electrodes. CV measurements are performed from 0.2 to 1.0 V vs. Ag/AgCl at a scan rate of 10 mV/s and 2 μm radius micropipette is used to create a large electrochemical cell for obtaining a stable electrochemical response. The uncoated $LiCoO_2$ electrode shows sharp anodic and cathodic current peaks at around 0.93 V corresponding to Li^+ deintercalation/intercalation associated with a first-order phase transition between two different hexagonal phases of $LiCoO_2$. On the other hand, the 180 s ZrO_2-coated $LiCoO_2$ electrode shows broader peaks with a large peak separation. The thick ZrO_2 layer increases the diffusion resistance of the lithium ions in the ZrO_2 layer.

Figures S1c shows the cyclic voltammograms (CVs) of the 30 s ZrO_2-coated $LiCoO_2$ electrodes. CV measurements are performed from 0.2 to 1.0 V vs. Ag/AgCl at a scan rate of 10 mV/s and used 50 nm radius nanopipette. Two different types of typical current responses are observed. One shows relatively sharp peaks, similar to those of the uncoated $LiCoO_2$ electrode, and the other shows a mixture of sharp and broader peaks. The appearance of the relatively sharp peaks is the result of Li^+

deintercalation/intercalation at the relatively thinner regions of the ZrO_2-coated layer. The broad reduction peak appearing at less positive potential in the reverse scan originates from intercalation at the relatively thicker regions of the ZrO_2-coated layer.

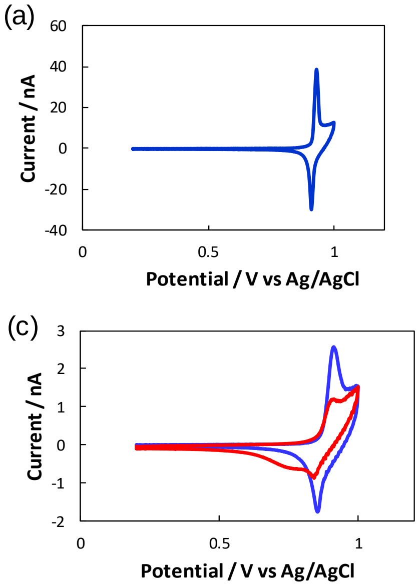

Figure S1. Local cyclic voltamogram using SECCM of (a) $LiCoO_2$ thin film electrode, (b) 180 sec ZrO_2-coated $LiCoO_2$ thin film electrode. (c) 30 s ZrO_2-coated (red) and ZrO_2 non-coated (blue) $LiCoO_2$ thin film electrode. Scan rate was 10 mV/s. The pipette radius of (a,b) and (c) were 2 μm and 50 nm, respectively.

1. Y. Takahashi, A. Kumatani, H. Munakata, H. Inomata, K. Ito, K. Ino, H. Shiku, P. R. Unwin, Y. E. Korchev, K. Kanamura and T. Matsue, *Nat Commun*, 2014, **5**, 5450.
2. D. Takamatsu, S. Mori, Y. Orikasa, T. Nakatsutsumi, Y. Koyama, H. Tanida, H. Arai, Y. Uchimoto and Z. Ogumi, *J. Electrochem. Soc.*, 2013, **160**, A3054-A3060.