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High Resolution Transmission Electron Microscopy Study on the Degradation of $IrO_x/SrIrO_3$ as an Oxygen Evolution Catalyst

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Oxygen evolution reaction (OER) electrocatalysis is an essential process for converting electrical energy into valuable chemicals and fuels, including hydrogen production from water splitting ($H_2O \rightarrow O_2 + 4H^+ + 4e^-$) [1]. Recently a perovskite $SrIrO_3$-based catalyst grown using pulsed laser deposition (PLD) on STO substrates showed a high OER activity and good stability in acid [2]. It has been identified by X-ray Photoelectron Spectroscopy (XPS) that during electrochemistry, the initial $SrIrO_3$ thin film evolves into an IrO_x coated $SrIrO_3$ structure, providing exemplary water oxidation activity and stability [2]. Theory has predicted that the high activity could arise from anatase IrO_2 or IrO_3 overlayer structures. However, these predictions on the degradation pathway are very difficult to validate by conventional materials characterization techniques.

In this paper we present our work on using High-resolution Transmission Electron Microscopy (HR-TEM) to analyze the mechanism of degradation. Pre-test and post-test PLD $SrIrO_3$ thin films were prepared for cross-section TEM characterization using a conventional method [3]. The HR-TEM images were taken at NCSI conditions in a FEI Titan aberration corrected TEM operating at 300kV. As shown in Figure 1 (a) and (b), the loss of strontium iridate following electrochemical testing in a sulfuric acid environment for six hours can be demonstrated by comparing the thickness of pre- and post-test thin film. While the thickness of the film decreased from 40 nm to 18 nm, losing more than 50% of its materials, the surface of the pre-test thin film can be seen to change from smooth to rough by comparing Figure 1 (c) and (d). An epitaxial growth and isostructural relationship between the thin film and substrate was confirmed for both pre- and post-test as shown in Figure 1(e) and (f) although bulk $SrIrO_3$ has a monoclinic crystal structure. The lattice spacings along in-plane ([010]) and out-of-plane ([001]) directions of both thin films were measured using the reference of STO (001) d-spacing (0.391 nm). As a result, both thin films have the same in- and out-of-plane d-spacings which are 0.391 nm and 0.398 nm respectively. This indicates that the film has a 1.8% lattice expansion along the out-of-plane direction and that the in-plane spacing is constrained to that of the substrate. It also shows that the structure of the thin film remains the same while a large amount of material loss happens during the test in acidic and strongly oxidizing conditions. Analysis of the surface structure is being carried out, the results showing that the structure is consistent with a more disordered perovskite $SrIrO_3$, viewed from other zone axis directions.

This work shows the usefulness of advanced TEM characterization to illuminate changes in catalytic thin film structures after electrochemical testing in a harsh environment, which is rarely carried out. [4]

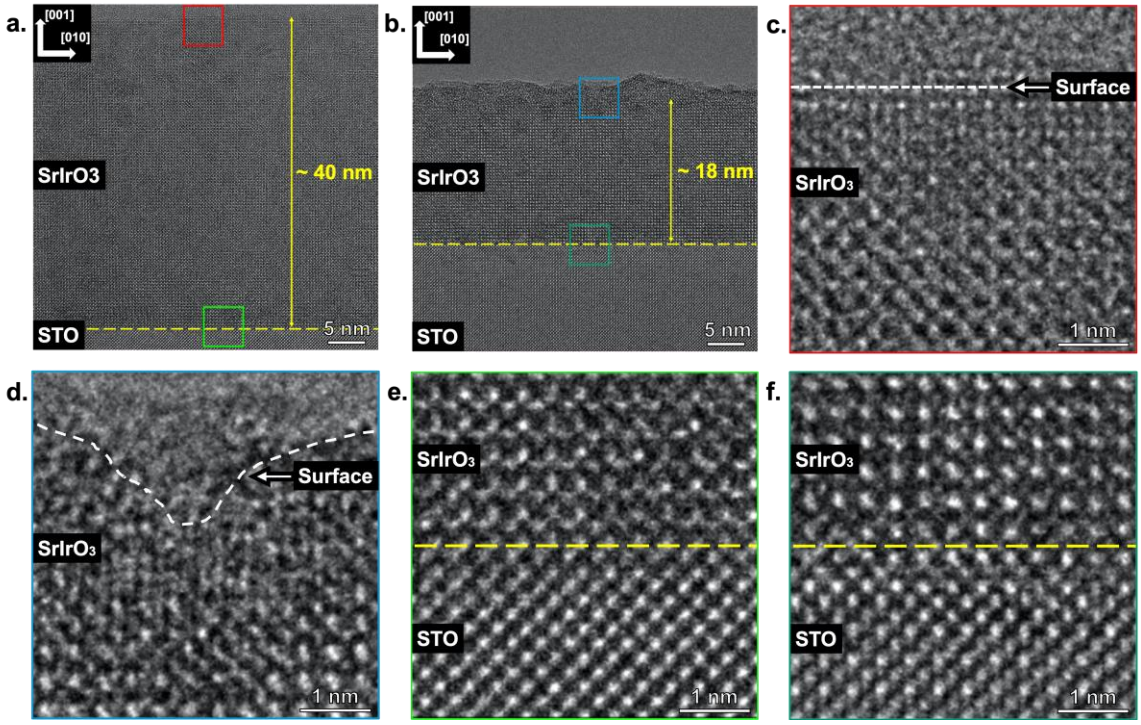

Figure 1. HR-TEM images of pre-test and post-test thin films. (a) HR-TEM image of the pre-test strontium iridate thin film and STO substrate showing the thickness of the thin film is around 40 nm whereas (b) is showing the thin film decreased to around 18 nm post-test, (c) magnified image of the red boxed region in (a), showing a smooth surface on top of the thin film, whereas (d) magnified image of the blue boxed region in (b) showing a rough and less oredered surface after cycling, (e) and (f) corresponding magnified images of green and aquamarine boxed regions at the thin film interface in (a) and (b), both showing the epitaxial growth relationship between the thin film and substrate, indicating that the structure of the thin film has not changed during the electrochemical test.

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