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In Situ and Post Mortem Observation of Bias Cycling Effects in Thin Film $La_{0.8}Sr_{0.2}CoO_3$ Solid Oxide Fuel Cell Cathodes

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Oxygen vacancies have been proposed to control the rate of the oxygen reduction reaction and ionic transport in complex oxides used as solid oxide fuel cell (SOFC) cathodes [1,2]. In this study oxygen vacancies were tracked, both dynamically and statically, with the combined use of scanned probe microscopy (SPM) and scanning transmission electron microscopy (STEM). Two types of epitaxial ≈50 nm thick films of $La_{0.8}Sr_{0.2}CoO_3$ (LSC_{113}) were grown by pulsed laser deposition: (1) ≈50 nm thin film of LSC_{113} deposited on a GDC/YSZ(001) electrolyte [3] and (2) ≈50 nm thick LSC_{113} with a ≈15 nm $LaSrCoO_4$ (LSC_{214}) capping layer deposited on the same electrolyte substrate.

The resulting heterostructure of LSC_{113} and layered perovskite LSC_{214} showed increased electrocatalytic activity at moderate temperature (~520 °C) [4]. Pico-scale chemical expansivity [1] during bias cycling of the LSC_{113} and LSC_{214} surfaces were recorded as strain loops by the electrochemical strain microscopy (ESM) [5]. To observe the effects of local electrochemistry and ionic diffusion on the thin film and determine if vacancy ordering [2,6] was present below the surface, 100 kV STEM imaging and electron energy loss spectroscopy (EELS) were employed. Focused ion beam (FIB) milling was used to fabricate a cross-section, post mortem, of the 15 V and 20 V bias cycled cathode regions. In-situ observations of the effects of biasing the LSC cathodes were performed at +/-10 V using a double-tilt Nanofactory STM/STEM holder.

At a bias of 8 V LSC_{214} capped cathode showed significantly larger cycling response than LSC_{113} type. Bias cycling at 8 V, 15 V and 20 V on the LSC_{113} cathode surface caused an irreversible expansion as shown in the topographic image of Fig. 1. Multiple effects of ESM biasing were observed by STEM high angle annular dark field (HAADF) imaging: an amorphous layer was present on the LSC_{113} surface, voids formed at the amorphous/crystalline interface, and cracking was present in the crystalline region (Fig. 2.). Lattice parameter maps from the HAADF STEM micrographs revealed vacancy ordering (Fig. 3.) in LSC_{113} as evidenced by lattice parameter modulation of the La/Sr columns.

TEM in situ biasing of an atypical partially amorphous LSC_{113} film with voids close to the surface resulted in Co segregation, additional void formation, cracking and re-crystallization (Fig. 4.). The evolution of oxygen vacancy concentration and ordering with applied bias and the effects of bias cycling on the SOFC cathode performance will be discussed [7].

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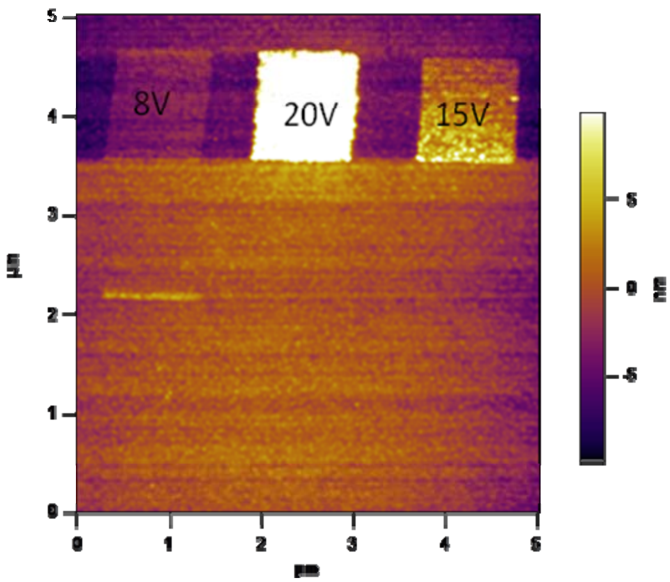

FIG. 1. ESM cycling resulted in permanent changes which evolved on the cathode surface.

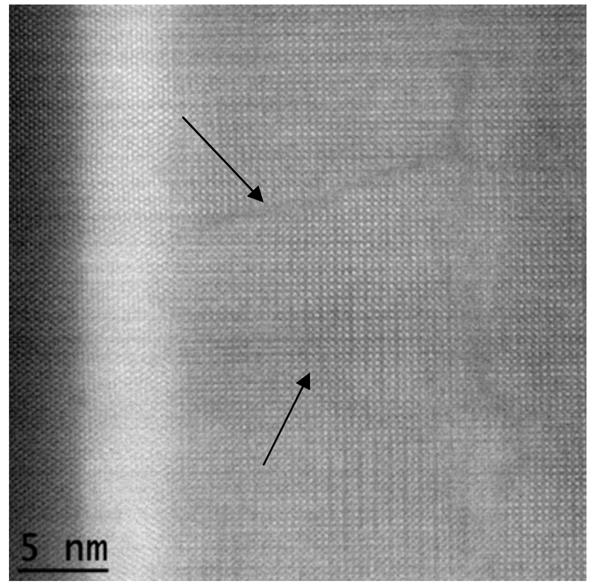

FIG. 2. HAADF micrograph of 20 V biased topographical region. Cracking and vacancy ordering were observed below the surface.

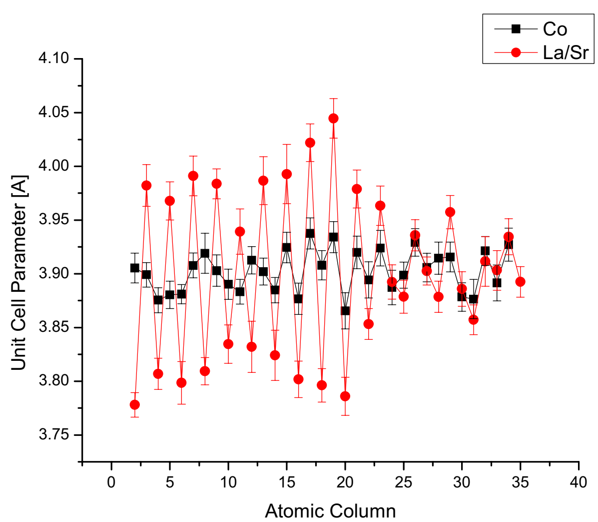

FIG. 3. Lattice parameter modulation LSC_{113} film on thick of the La/Sr columns indicated vacancy ordering was present in the 20 V biased region (FIG. 2.).

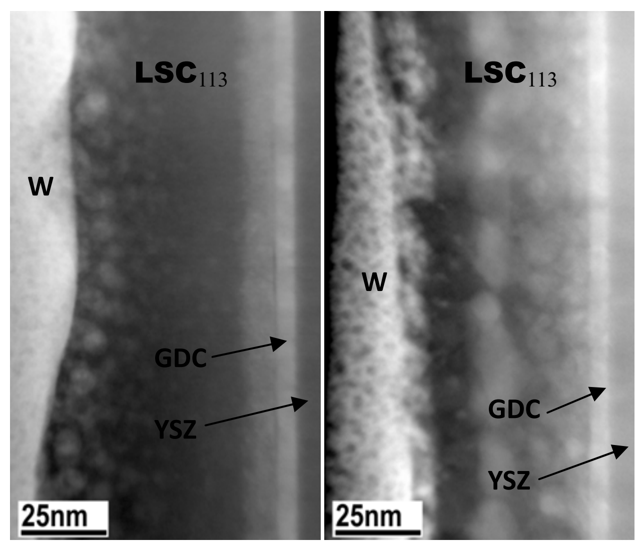

FIG. 4. (left) As deposited atypical, partially amorphous GDC buffer layer / YSZ substrate (arrow). (right) After 10 V bias cycling Co segregation, voids and cracking developed.