

Microstructural effects on the oxygen exchange kinetics of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films

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To improve the total performance of solid oxide fuel cells (SOFCs), it is desirable to reduce the losses on the cathode side of the cell. The oxygen reduction reaction (ORR) takes place in the SOFC cathode and it is rather complex; it involves a variety of sub-reactions, such as surface adsorption, dissociation, electron transfer, incorporation, and bulk diffusion. Although a considerable amount of effort has been expended in correlating processing / microstructural features to cathode performance, there is relatively little known about the fundamental properties of oxide surfaces, how they are affected by surface chemistry, and how they are related to overall cathode activity. We use thin film approaches to isolate the surface response from the bulk properties and to control structural perturbations / surface chemistry. The aim is to understand the fundamental surface activity of the most commonly used cathode material $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM). Here we investigated the relative contribution of the native surface and of the grain boundaries intersecting the surface to the chemical surface exchange of LSM thin films. This research shed light on the activity of nanoscale infiltrates used as surface modifications to improve cathode performance.

600 nm thick, (110) $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films were deposited on (111) YSZ (8% Y_2O_3 stabilized ZrO_2) single crystal substrates using Pulsed Laser Deposition with a KrF excimer laser ($\lambda = 248\text{nm}$). Films were found to be singly oriented out-of-plane and to have several degenerate in-plane orientations. These highly textured LSM films had smooth surface morphologies. The chemical surface exchange coefficients, k_{chem} , a basic parameter indicative of the electrocatalytic activity of SOFC cathodes, were determined experimentally using electrical conductivity relaxation (ECR). The transient relaxation experiments were carried out from 600 °C to 900 °C. Two k_{chem} values were extracted from the data, indicating two parallel surface exchange processes occurred. These two k_{chem} s had different activation energies (E_A), which were interpreted as belonging to (1) the native surface response of individual grains/variants and (2) the variants boundaries / grain boundaries of the textured films. The first (native surface) process has an activation energy of $E_{A,1} \approx 1.5$ eV, while the second (extended defect) process $E_{A,2} \approx 0.75$ eV. The interpretation of these observations and their relevance to SOFC cathodes will be discussed.