Crystallographic Anisotropy of Oxygen Surface Exchange in (La,Sr)MnO_3 Thin Films

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The oxygen reduction reaction (ORR) takes place in the solid oxide fuel cell (SOFC) cathode and the overall reaction is rather complex; it involves a variety of sub-reactions, such as surface adsorption, dissociation, election transfer, incorporation, and bulk diffusion. Although a considerable amount of effort has been expended in correlating processing / microstructural features to cathode performance, there is unfortunately relatively little known about the fundamental surface properties of oxide surfaces and their relation to cathode activity. In this study, to avoid the complex structural perturbation on the oxygen uptake pathways, we adopted the thin film approach to isolate the surface response from the bulk properties. The aim of this research is to understand the fundamental surface activity of cathode materials, including $La_{0.7}Sr_{0.3}MnO_3$, and to shed light onto the utility and stability of potential infiltrate materials as surface modifications to improve cathode performance.

Perovskite type $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films were deposited on $SrTiO_3$ (100), (110) and (111) single crystal substrates using Pulsed Laser Deposition with a KrF excimer laser (λ = 248nm). The LSMO films are of high crystalline quality with smooth surface morphologies that are similar to each other. In this study, it is found that: firstly, LSMO (600nm-thick) thin films are good proxy for bulk/single crystals. Secondly, LSMO (100nm to 600nm thick) films have surface dominated response to oxygen exchange. Thirdly, there is crystallographic anisotropy in LSMO to surface response. Furthermore, the crystallographic anisotropy to oxygen surface exchange is temperature dependent: at higher temperatures (110) is the most active orientation, while at lower temperatures (111) has the highest activity. The relvance to SOFC cathodes will be discussed.