Mechanisms of Performance Degradation of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ Solid Oxide Fuel Cell Cathodes

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In recent years, mixed ionic-electronic conducting (MIEC) materials such as (La,Sr)(Fe,Co)O$_{3-\delta}$(LSCF) have been studied and developed as solid oxide fuel cell (SOFC) cathodes, due to their activity for the oxygen reduction reaction at intermediate temperatures ($<800^\circ$C) [1-4]. On the other hand, a number of such MIEC materials including LSCF exhibit Sr surface segregation, which has been proposed to hinder the oxygen exchange reaction at the surface [5-8].

In this work, we present the study of long-term degradation mechanisms of porous La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF6428) cathodes under thermal annealing. LSCF6428 symmetric electrode cells with Gd$_{0.1}$Ce$_{0.9}$O$_{1.95}$ (GDC) electrolytes were maintained at an elevated SOFC operating temperature of 800°C for ~800 hours in ambient air, without current/polarization. As illustrated in Fig. 1, electrochemical impedance spectroscopy (EIS) measurements taken periodically at 700°C showed a polarization resistance increase of ~120%, from 0.15 to 0.33 Ω·cm$^2$. The electrode morphological changes and Sr surface segregation were examined using a combination of three-dimensional (3D) tomography via focused ion beam-scanning electron microscopy (FIB-SEM) and surface composition measurements using XPS and a chemical etching procedure with inductively coupled plasma-optical emission spectrometry (ICP-OES) detection [9]. The 3D imaging showed that there was no coarsening or sintering of the LSCF6428 electrode microstructure that could affect electrochemical performance during annealing. However, the ICP-OES analysis found an increased amount of water-soluble Sr on the surface of annealed samples, from 1.3 nmol Sr/cm$^2$ to 3.9 nmol Sr/cm$^2$, when normalized to the LSCF6428 particle surface measured from 3D image data. Assuming that the measured Sr phase is SrO, the water-soluble Sr amount on freshly prepared cells would correspond to 1.04±0.22 atomic layers and agree well with reports on Sr-doped perovskite-type model thin films suggesting a SrO termination [9]. The Adler-Lane-Steel (ALS) model was then applied, again making use of 3D image data, to examine the effect of Sr surface segregation on the oxygen surface exchange process.

Fig. 1. EIS results showing polarization resistance measured for a single LSCF6428 cathode during 800°C anneal. Temperature was temporarily reduced to 700°C during EIS measurements and back to 800°C afterwards.

References


