Surface evolution of lanthanum strontium cobalt ferrite thin films at low temperatures

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ABSTRACT

The ultra-high vacuum surface preparation of heteroepitaxial lanthanum strontium cobalt ferrite thin films has been studied using soft X-ray photoelectron spectroscopy. Specifically, the effect of annealing the films at low temperatures in low partial pressures of oxygen and argon has been investigated. We find that atmospheric surface carbon contamination of the films can be removed in select anneal temperature regimes in argon, but remains bound to the surface with oxygen annealing at any temperature.

Irrespective of the gas used, an insulating phase transition occurs near 300 °C due to strontium segregation at the surface. The surface develops more insulating character if annealed with oxygen. Different species are proposed to be responsible for the discrepancy in insulating character.

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1. Introduction

In the continued efforts to improve energy resource utilization for the twenty-first century, few technologies hold as much promise as solid oxide fuel cells (SOFCs) [1,2]. A diagram of fuel cell operation is shown in Fig. 1. On the left, fuel in the form of hydrocarbons is fed into the cell, where it thermally cracks into a number of products. Among those products is hydrogen, which reacts with oxygen ions at the anode. The oxygen ions are provided by the cathode, which reduces oxygen from air. The electrolyte is an ion-conducting material that provides a path for the oxygen radicals. Water is produced at the anode. Usable electric current is produced by the potential difference between the electrodes.

Perovskite-based fuel cell devices can reliably generate electrical power from a wide variety [3,4] of fossil fuels, using existing infrastructure and with high energy density in a small volume. Critical to the operation of a SOFC is the cathode material, which produces oxygen ions and transports them into the electrode. Indeed, cathode surface and interface modification is one of the primary contributors [5,6] to the operational degradation of an operating fuel cell. Understanding the processes at the cathode is critical to potential improvements and elucidating the factors limiting the life of these devices.

Many high-temperature fuel cells use lanthanum-doped strontium manganite (LSM) cathodes [7], the reaction kinetics of which are limited to the triple-phase boundary [8]. Overcoming the limitations imposed by the triple-phase boundary would allow for higher energy densities and efficiencies. Mixed ion-electron conductors can transport oxygen ions using more of their surface area, without relying on the electrode interfaces. One of the most promising mixed ion-electron conductors under popular investigation for use as a cathode is lanthanum strontium cobalt ferrite ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, abbreviated LSCF-6428). LSCF offers high electron and ion conductivity, as well as good compatibility with other standard SOFC construction materials [9]. This combination of features may be useful in engineering low-temperature fuel cells with the performance necessary for more widespread application.

Since the surface structure and composition of real cathodes determine many of the performance attributes of fuel cells, investigations into cathode surface evolution give valuable insight towards improvement. Soft X-ray spectroscopy can provide element-specific chemical environment information for shallow sampling depths — precisely the region at play during operation. Previous X-ray studies have observed strontium segregation at the surface of LSCF films during operational-temperature annealing in air [10]. Similar effects have been observed in other strontium-based perovskite cathode materials [11]. The segregation of strontium and its oxides/carbonates at the surface of perovskite films has been shown [5,12] to decrease the sites available for oxygen catalysis as well as retarding electron transport to the

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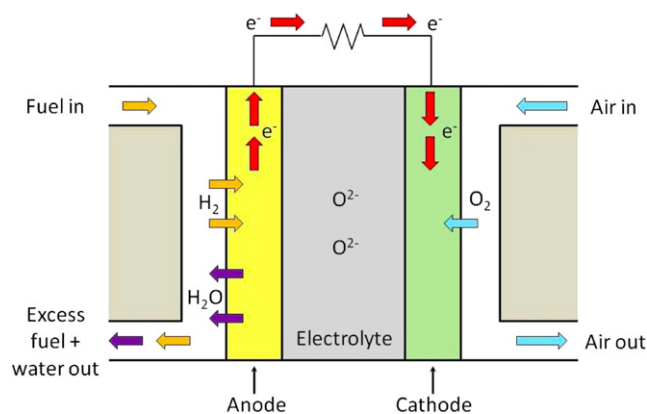E-mail address: dnewby@bu.edu (D. Newby).

Fig. 1. The operating principle of a solid oxide fuel cell.

surface, thereby negatively affecting the cell's long-term efficiency. It has also been shown that rapidly quenching the temperature of cathode films can preserve surface configuration changes, which allows for post-anneal or post-operation measurement [10].

Critically, exposure to atmospheric contaminants may interfere with surface-sensitive techniques, and surface treatment (e.g., degassing and cleaning) is necessary [13] for conventional soft X-ray measurements. In the case of perovskite thin films the effects of contamination are likely exacerbated due to the enhanced catalytic activity observed [14]. To that end, a study of the low-temperature surface evolution is of interest for future surface studies that may require pristine films. We report here the use of soft X-ray photoemission spectroscopy to determine the evolving chemical states on the surface of an LSCF film. Using very low (~10^{-8} Torr) partial pressures, we demonstrate that existing surface carbon can be removed from the surface via annealing in argon. This technique produces a clean, defect-free film. Using similar pressures of oxygen during anneal cycles has drastically different results, leaving surface carbon bound to the surface and bringing on a relatively strong insulating surface phase transition. These results serve as a template for clean surface preparation of LSCF thin films, useful for further investigation into the surface interactions of these interesting materials.

2. Materials and methods

Pulsed laser deposition was used to grow epitaxial films of LSCF-6428 on NdGaO$_3$ substrates, with the orientations (001) and (110), respectively. The films were deposited using an LSCF target, at an oxygen partial pressure of 10 mTorr with the substrate temperature at 550 °C. Films of approximately 250 nm thickness were produced. Characterization via atomic force microscopy, X-ray diffraction, and transmission electron microscopy confirmed the film quality and orientation. The mean surface roughness was measured at 0.68 nm. All film deposition and characterization were conducted at the Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory.

Soft X-ray spectroscopy measurements were performed at the soft X-ray undulator beamline X1B at the National Synchrotron Light Source, Brookhaven National Laboratory. Ultra-high vacuum (UHV, <10^{-10} Torr) was maintained in the experimental chamber during data acquisition. X-ray photoemission spectroscopy (XPS) was performed using a hemispherical analyzer and monochromated incident X-rays at 250 and 900 eV. The total resolution of these spectra is approximately 0.4 eV full-width at half-maximum (FWHM) at the Sr 3d edge, and 0.7 eV FWHM at the oxygen and carbon K-edges. Binding energies were calibrated with reference to the 4f core levels of clean gold foil in electrical contact with the sample. In order to probe the surface chemistry of these materials, the soft X-rays employed are primarily surface-sensitive, and by varying the relative angle between

the film surface and the photoelectron spectrometer, it is possible to tune the depth sensitivity for photoelectron spectroscopy. This has been used here to differentiate between surface and bulk chemical species.

After sonication in acetone, samples were mounted on tantalum foil, with the film grounded by tantalum strips. Samples were radiatively heated through the substrate using a bare tungsten filament. The power supplied to the filament was monitored using a constant voltage/current power supply. Temperatures reached on the sample surface were calibrated with a K-type thermocouple in contact with the surface.

Precautions were taken to ensure that chromium contamination, originating from the K-type thermocouple alloy, did not affect the films. The calibration was completed after XPS data were taken for all anneals, in order to avoid the thermocouple (TC) affecting the surface. While chromium poisoning is a well-known vulnerability of LSCF [8, 15,16], it is worth noting that no chromium features were observed in XPS survey scans taken after the TC-contact calibrations. This suggests that chromium poisoning is not a concern at the temperatures used here, which is in reasonable agreement with thermodynamic calculations performed [15] for other perovskites. Contact thermocouple temperature measurement may be utilized in this regime without negative consequence.

High-purity oxygen and argon were selectively dosed through a constant pressure valve (10^{-8} Torr) with continuous pumping in the chamber, creating a steady supply of fresh gas across the sample surface. Oxygen was chosen for its role in the operational environment of SOFCs, and argon in order to provide contrast as an inert gas at the same partial pressures. For each anneal cycle, dosing and heating were combined for a period of time resulting in 50 L of total exposure. The samples were then quenched via abrupt power cutoff to the filament, and allowed to cool to room temperature in their respective annealing gases. The preparation chamber was then evacuated, and the film moved into a measurement chamber maintained at 10^{-10} Torr.

3. Results and discussion

3.1. Carbon 1s

Once a film has been exposed to air, it is subject to a number of contaminating adsorbents. For the present system the most notable contaminant is carbon in the form of atmospheric carbon dioxide; carbonates will tend to form [17] on surface strontium and its oxides. Since the measurement chamber is maintained under UHV, surface carbon carried in by the film can become a prime source of carbonate formation in addition to unavoidable carbon species already present in the chamber. An excess of surface carbon and its derivatives could potentially modify the surface chemistry in ways unrepresentative of the operating conditions we seek to mimic; it is therefore worthwhile to monitor the evolution of signal from carbon as the experiment proceeds.

The extent of carbon contamination on the surface can be directly studied through measurement of the carbon 1s core level. The relative height of the C 1s XPS peak near 285 eV compared to the strontium 3p peaks near 268 eV and 278 eV gives a good indication of how much carbon is adsorbed on the surface, since no carbon should be included in the bulk LSCF film. Fig. 1 shows the core-level scans in the region of C 1s, for successive anneals in argon at 10^{-8} Torr.

3.1.1. Argon atmosphere annealing

Fig. 2 shows the photoemission spectra taken after each annealing temperature for anneals in an argon partial pressure. The spectra show the C 1s peak at binding energy of 284.6 eV (with dotted line as a guide to the eye), as well as the strontium 3p doublet at 268.4 eV and 278.7 eV. It is clear that as the annealing temperature increases, the intensity of the C 1s peak reduces in intensity. This suggests that