LaFe$_x$Co$_{(1-x)}$O$_3$ Thin-Film Oxygen Reduction Catalysts Prepared Using Spray Pyrolysis without Conductive Additives

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Supporting Information

ABSTRACT: LaFe$_x$Co$_{(1-x)}$O$_3$ thin films were prepared on fluorine-doped tin oxide conducting glass substrates by spray pyrolysis without any conductive additives and evaluated for their ability to catalyze the oxygen reduction reaction. Onset potential and current density were found to be comparable to platinum, and the resulting crystallite size was on the order of 20 nm. Coordination of the precursor metal ions by citrate was found not to be advantageous. Results from multiple scan linear sweep voltammetry suggest lattice oxide saturation during reduction of oxygen and lattice oxide depletion upon water oxidation. The color of the best-performing composition changes dramatically between 1.2 and −1.15 V versus saturated calomel electrode, so X-ray photoelectron spectra of the fully oxidized and reduced films were compared, demonstrating that cobalt in the film changes oxidation state. Performance of the films as a function of iron-to-cobalt ratio is consistent with what others have reported in the literature, indicating that spray pyrolysis is an efficient method to prepare and evaluate new catalytic materials.

INTRODUCTION

The oxygen reduction reaction (ORR) determines the overall performance of several renewable energy technologies, involving energy production, conversion, and storage, such as photoelectrochemistry, fuel cells, and metal–air batteries. This is because the ORR is a kinetically slow process compared to the hydrogen oxidation reaction. Precious metal-based cathodes are thus far the best electrocatalysts for the ORR; however, the utilization of catalysts such as Pt and Ir in the cathode greatly hinders the large-scale commercial applications because of their limited supply and high cost. Pt-based air electrodes have a similar performance when compared to Pt. More importantly, spray pyrolysis provides a more efficient method to screen potential catalysts without the added complexity of a conductive additive and binder such as Nafion.

We report the preparation of LaFe$_x$Co$_{(1-x)}$O$_3$ thin films using the spray pyrolysis deposition technique. Thin-film, well-crystallized, single-phase perovskite materials have been previously prepared by spray pyrolysis. This technique has been widely used to deposit metal oxide thin films due to its cost-effectiveness and suitability for mass production; however, this is the first time LaFe$_x$Co$_{(1-x)}$O$_3$ materials have been prepared by spray pyrolysis and electrochemically evaluated on conductive fluorine-doped tin oxide (FTO) substrates. The catalytic properties of LaFeO$_3$, LaCoO$_3$, and LaFe$_x$Co$_{(1-x)}$O$_3$ mixed perovskite oxides have been previously reported in the literature. Sunarso et al. synthesized several La-based binary perovskite oxide powders through an ethylenediaminetetraacetic acid (EDTA)–citrate complexing process and annealed them on glassy carbon disk electrodes. Wang et al. used a co-nanocasting technique to synthesize a LaFe$_x$Co$_{(1-x)}$O$_3$ carbon composite starting with a metal nitrate/citric acid mixture followed by calcination over a silica template. We have found that simple spray pyrolysis of nitrate precursors without the addition of inorganic carbon is a practical technique to prepare electrocatalytic materials for the ORR, and the resulting electrodes have a similar performance when compared to Pt. More importantly, spray pyrolysis provides a more efficient method to screen potential catalysts without the added complexity of a conductive additive and binder such as Nafion.

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RESULTS AND DISCUSSIONS

We first prepared thin-film catalysts on FTO substrates by spraying both simple nitrate salt solutions of the metal ions and the metal ions complexed with citric acid/ethylene glycol, finding that citrate complexation is not required for the preparation of these materials; in fact, we found that the films prepared from citrate precursors do not adhere well to the FTO substrate. Figure 1 shows the linear sweep voltammograms (LSVs) for the ORR of LaFeO₃ prepared from a nitrate precursor, LaFeO₃ (citrate precursor), and LaCoO₃ (nitrate precursor). The Co citrate precursor solutions did not adhere well to the FTO; hence, no LaCoO₃ (citrate precursor) films could be produced.

The ORR onset potential improved in the order of LaFeO₃ (nitrate precursor), LaFeO₃ (citrate precursor), which was only slightly better, and LaCoO₃ (nitrate precursor), which was significantly better (200 mV more positive onset potential). The expected positive shift in onset potential was observed when switching Co for Fe. The LaFeO₃ (citrate precursor) performed slightly better than the film prepared from LaFeO₃ (nitrate precursor); however, because the citrate films did not adhere well to the FTO substrate and could be easily wiped off, all further films were prepared from simple nitrate, 10% ethanol solutions. The slightly better performance of the citrate precursor material may be due to its greater surface area (flakes barely attached to the surface vs a fully attached film), as shown by the scanning electron microscopy (SEM) image in Figure S1. In comparison, the LaFeO₃ film prepared from nitrate solutions produced a smooth film with large cracks (∼1 μm wide). No noticeable cathodic current between −0.75 and +0.1 V was observed for our films in a nitrogen (N₂)-saturated solution, as expected for an oxygen-free solution. The slightly basic Na₂SO₄ electrolyte was chosen to test potential catalytic materials to avoid any dissolution of the materials in either too acidic or basic solution. Many metal oxides dissolve in acidic solution and some can also dissolve in highly basic solution. These amphoteric metal oxides form soluble hydroxo complexes at high pH, which can lead to the deterioration of the material and may lead to misinterpreting poor catalysis due to the low stability of the material at high pH. After purging the 0.1 M Na₂SO₄ electrolyte with oxygen, the pH was typically 8.2.

Figure 2 shows LSVs representing the ORR in oxygen-saturated 0.1 M Na₂SO₄ using thin films of LaFeₓCo_(1-x)O₃ (x = 0, 0.20, 0.25, 0.30, 0.40, 0.50, and 0.75). The ORR current is improved in the order of LaFe₀.₇₅Co₀.₂₅O₃, LaFe₀.₃₀Co₀.₇₀O₃, LaFe₀.₂₀Co₀.₈₀O₃, and LaFe₀.₄₀Co₀.₆₀O₃; and finally the best material, LaFe₀.₄₀Co₀.₆₀O₃ (four layers) (all films were produced from a nitrate precursor solution, which were eight layers thick except where noted). Increasing the amount of Co in the material clearly enhances the catalytic activity and shifts the onset potential to more positive values up to the optimum LaFe₀.₄₀Co₀.₆₀O₃ composition. In 2012, Sunarso et al. also pointed out the beneficial catalytic effect from having two transition metals sharing the B-site and Wang et al. found that this specific composition was the best of the mesoporous LaFe₀.₄₀Co₀.₆₀O₃ series produced from co-nanocasting citric acid complexed metal nitrate precursors onto a silica template. Interestingly, they did not observe LaCoO₃ to display any catalytic effect in contrast to our results and others. We note also in Figure 2 that the thickness of LaFe₀.₄₀Co₀.₆₀O₃ film is an important parameter: the most active film was obtained when four layers of material were deposited.

Figure 3A compares the LSVs for the ORR in oxygen-saturated 0.1 M Na₂SO₄ of the LaFe₀.₄₀Co₀.₆₀O₃ film (four layers), a Pt metal flag electrode, and the plain FTO substrate. To directly compare the performance of the LaFe₀.₄₀Co₀.₆₀O₃ film and Pt flag electrodes, a bipotentiostat was used to scan both electrodes at the same time under the exact same conditions. Current densities were determined by dividing the measured current by the geometric surface areas of the electrodes. We can see that LaFe₀.₄₀Co₀.₆₀O₃ shows comparable ORR activity to Pt, and they both surpass the performance of the FTO substrate. The Pt flag electrode was first heated to red hot in a glassblowing torch and then conditioned (cycled between +0.2 and −0.8 V vs SCE) for 30 min until a reproducible LSV was observed. This conditioning was found to be very reproducible and stable: the Pt electrode could be left out on the counter and placed back in solution after days to yield the same voltammogram, which made it a good reference for comparison. Figure S2 shows the LSV of the Pt electrode after polishing with 0.3 μm alumina, flame treatment, and flame treatment followed by conditioning. The flamed/conditioned Pt was the most reproducible and stable, but the polished Pt...
We measured the ORR of our optimized comparison of our material to others reported in the literature, saturated 0.100 M NaOH (Figure 4) correcting for both drop, as determined by alternating current (AC) impedance, Sr2+ for some of the La3+ or the preparing material de

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evolution reaction (OER)) and then the ORR LSVs were done after sweeping out to the potential, where the OER occurs. All scans were done at a scan rate of 6 mV/s in oxygen-saturated 0.1 M Na2SO4 solutions vs SCE.

Successive LSVs of the ORR for the four-pass LaFe0.4Co0.6O3 thin film and Pt foil were run simultaneously in a four-electrode cell. (B) Successive LSVs of the ORR from a four-pass LaFe0.4Co0.6O3 thin film. The legend gives the time order of the scans. Note scans 6 and 7 were done after sweeping out to the potential, where the OER occurs. All scans were done at a scan rate of 6 mV/s in oxygen-saturated 0.1 M Na2SO4 solutions vs SCE.

Figure 4. LSV of LaFe0.4Co0.6O3 film in oxygen-saturated 0.100 M NaOH measured at 6 mV/s in a quiescent solution on a stationary FTO substrate. The voltammogram was corrected for ohmic electrolyte and substrate resistance (iR) and normalized to the geometric area of the electrode. A Tafel plot of the LSV is shown in the inset (see Experimental Methods and Supporting Information).

surface gave the best onset potential; however, it varied with each polishing and changed over time. Figure 3B shows successive LSVs for the LaFe0.4Co0.6O3 film. We note that the first scan is quite different and positive of the following two scans. Next, the film was cycled twice between 0.2 and 1.5 V versus SCE (1.5 V is slightly above the onset of the oxygen evolution reaction (OER)) and then the ORR LSVs were measured again. The first scan after OER is even better (more positive onset) than the first scan of the fresh film, and the subsequent scan matches well with the second and third scans of the fresh film. It is possible that the material becomes saturated with oxide during ORR, reducing its catalytic effectiveness after the first scan, and during OER, oxygen vacancies are generated in the lattice, improving catalysis. The formation of oxygen vacancies due to substitution of Ba2+ or Sr2+ for some of the La3+ or the preparing material deficient in La3+ has been attributed to improved catalysis.20,21−23 Interestingly, the presence of iron also has been shown to improve adsorption/desorption of oxygen.24 Because of the significant difference between the first scan and subsequent scans, in this study, we report/compare second and third scans of the different materials (Figures 1, 2, and 3A). For the direct comparison of our material to others reported in the literature, we measured the ORR of our optimized film in oxygen-saturated 0.100 M NaOH (Figure 4) correcting for both iR drop, as determined by alternating current (AC) impedance, and calibrating the potential to the real hydrogen electrode (RHE) by defining the point of zero current as 0 V from the hydrogen oxidation/evolution reaction at our Pt flag electrode in the same cell and electrolyte (Figure S3). The solution resistance measured by AC impedance between the Pt flag electrode and Pt mesh counter electrode in our cell was on the order of 10 Ω. The resistance measured between a bare FTO electrode and the Pt mesh electrode was 110 Ω, and the resistance between LaFe0.4Co0.6O3 film on FTO and the Pt mesh electrode was 130 Ω obtained from the Bode plot shown in Figure S3.

The onset potential is typical for similar perovskites reported in the literature.19,23,25−27 The current density is however lower than what is typically seen because all our voltammograms are measured on stationary electrodes in quiescent solutions, while much of the work in this field has been performed on rotating disk electrodes, which provide forced convection of the oxygen to the electrode. Our currents are limited by oxygen diffusion to the electrode and, as shown in Figure 3a, similar to the Pt foil electrode under the same conditions. Suntivich et al. demonstrated the significant increase in current density with rotation rate at a rotating disk electrode for a LaCu0.3Mn0.7O3 electrode.19 Therefore, care should be taken comparing our current densities and Tafel plot (Figure 4 inset) with those derived from hydrodynamic voltammetric experiments at rotating disk electrodes.

The catalytic activity of perovskites is strongly influenced by the transition-metal cation in the B-site.7,9,11 In addition, the ORR activity of La-based perovskites is believed to be strongly associated with the ability of the transition-metal cation in the B-site to be able to vary its valence state. Wang et al. attributed the active site for ORR activity to the Fe3+/Fe2+ redox couple and claimed that the semiconducting band structure of LaFeO3 offers much lower electrical conductivity than that of LaCoO3, which results in suppressed catalytic activity for ORR at overly high Fe-doping levels.18 They reported that LaFe0.4Co0.6O3 represents the best balance between the ability of the B-site transition metal to change oxidation state and the overall electrical conductivity of the film.

Spectroelectrochemistry has been used to follow changes in the oxidation state of transition metals in thin films on FTO.28
Because FTO is an optically transparent electrode, we were able to observe a reversible color change of the LaFe\(_{0.4}\)Co\(_{0.6}\)O\(_3\) film during the voltammetry, and so did a spectroelectrochemical characterization of the film between the applied potentials of −1.15 to +1.2 V versus SCE. Figure 5A shows the absorbance spectrum of a LaFe\(_{0.4}\)Co\(_{0.6}\)O\(_3\) thin film at different applied potentials. The ability to oxidize and reduce the film several times and see no decrease in the absorbance of the film is a testament to its stability.

The absorption measurements were taken after allowing enough time under applied potential for the complete stabilization of the absorption by repeatedly measuring the spectra at each potential until the spectra were consistent. The color of the oxide layer appears brown/black after annealing as well as under positive applied potentials, but lightens to tan when reduced (inset of Figure 5A). This change in absorbance suggests that one or more of the metal ions is changing its oxidation state and that the change is reversible. This is an unusual color change for a spectroelectrochemical study of a transition metal, as it is more typical to see a shift in color rather than a change in color intensity. CoO solid is olive green in color and can be oxidized to Co\(_3\)O\(_4\) which is a black mixed valent oxide. Considering these oxides, one might expect to see an absorption band growing in the red region upon reduction; however, the perovskite structure clearly alters the cobalt ion’s absorption in our materials.

X-ray photoelectron spectroscopy (XPS) has been used to determine oxidation state\(^{26}\) and subtle changes in structure\(^{29}\) in perovskite materials. To determine which transition-metal ion is undergoing a change in oxidation state, we took two electrodes cut from the same substrate, fully oxidized one and fully reduced the other, and did an XPS analysis (Figure 5B–D) of the resulting films to determine which redox couple, Fe\(^{3+}/Fe^{2+}\) or Co\(^{3+}/Co^{2+}\), changed its oxidation state and thus contributes to the ORR activity using the Thermo Scientific elemental XPS website as a reference.\(^{30}\) The XPS results for iron show the expected 2p\(_{1/2}\) and 2p\(_{3/2}\) spin–orbit peaks. The binding energy of the 2p\(_{3/2}\) at 710 eV with no lower-energy shoulder is consistent with the Fe\(^{3+}\) oxidation state, and there appears little spectral difference between the two electrodes.\(^{31,32}\) The cobalt region, however, shows a significant difference between the oxidized and reduced films. Cobalt also displays 2p\(_{1/2}\) and 2p\(_{3/2}\) spin–orbit peaks; however, Co\(^{2+}\) is shifted to higher binding energy than Co\(^{3+}\) and has satellite peaks at 786 and 802 eV. This is an exception to the general rule that binding energy increases with oxidation state.\(^{27,33,34}\) The oxidized film best matches Co\(^{3+}\) and the reduced film clearly contains Co\(^{2+}\) with the shift of the two spin–orbit peaks to higher energy and the significant growth of the two satellite peaks. This clearly indicates that the cobalt and not the iron is changing oxidation state. The XPS of the La 3d region shows the four expected spin–orbit peaks.\(^{35,36}\) The binding energy of these peaks is consistent with the +3 oxidation state; however, the split between the peaks and the overall binding energy shift between the two films suggest that the chemical environment around the lanthanum changes between the two potentials. This change in structure might be contributing to the unusual color change observed with reduction of the material.

The films were characterized using X-ray diffraction (XRD) to confirm the crystal structure and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) to identify the elemental composition, distribution, and

Figure 5. (A) Visible absorption spectra of the four-layer LaFe\(_{0.4}\)Co\(_{0.6}\)O\(_3\) thin film in 0.1 M Na\(_2\)SO\(_4\) solution vs SCE as a function of applied potential. Applied potentials corresponding to the absorption spectra are provided in the legend. The inset is a photo of the oxidized and reduced film. (B–D) X-ray photoelectron spectroscopy (XPS) spectra of the fully oxidized film (blue) and reduced film (red) in the 2p binding energy region of iron (B), cobalt (C), and 3d binding energy region of lanthanum (D).
thickness of the catalyst layer. XRD data were collected using Bragg–Brentano geometry (Figure 6) and showed the expected cubic perovskite pattern along with the SnO2 (cassiterite) phase (PDF#00-046-1088) of the underlying FTO conductive layer (blue overlaid lines). The remaining peak at 54.5° is unknown but comes from the substrate (Figure S4).

The lines of the indexed LaFe0.6Co0.4O3 crystalline phase (red lines, PDF#00-040-0224) are also overlaid on the XRD pattern (red). We note that the ratio of iron to cobalt in our material and the indexed perovskite are opposite. This results in the lines of our LaFe0.4Co0.6O3 phase being shifted to higher 2θ values due to the difference in the size of Fe3+ versus Co3+ ions relative to indexed LaFe0.6Co0.4O3 phase. Our material having less iron (the larger ion) causes a lattice contraction and thus the peaks shifting to higher 2θ.18 The broad scattering intensity or "halo" seen in the lower 2θ region of the XRD pattern is due to the amorphous glass substrate. Low-angle, fixed-incidence scans did not yield strong scattering halos. As the incident angle was reduced, the penetration of the X-rays into the substrate is reduced, which resulted in the halo decreasing (Figure S4). This suggests that there is little amorphous material in our film because as the X-rays interact more with the film and less with the glass substrate the halo due to the presence of amorphous material decreases significantly. It is interesting to note that the widths of our peaks are wider than expected, suggesting our material is nanocrystalline. The peak at 2θ = 47.1° has an full width at half-maximum of 0.534 compared to the expected instrument line width of 0.125, indicating that the crystallite size in our material is on the order of 20 nm, as calculated using the Scherrer equation. This is consistent with the crystallite size observed with the spray pyrolysis deposition of La1−xCaxMnO3 (40–70 nm)16 and LaFeO3 (25–35 nm),17 with the crystallite size depending on the spray pyrolysis conditions. Traditional methods of perovskite catalyst preparation require high-temperature calcination steps, resulting in the sintering of the material, producing particles typically ranging in size from 200 nm to 1 μm. The increase in crystallite size reduces the surface area and thus the catalytic efficiency of the material.8,9,25 This highlights another advantage of our relatively low-temperature (500 °C) spray pyrolysis preparation method.

Figure 7A shows the backscattered SEM image of LaFe0.4Co0.6O3. The composition of the film is uniform with very small cracks, which can only be seen at a high magnification. Elemental maps shown in Figure S5 demonstrate an even distribution of La, Fe, and Co in the sample and confirm the atomic ratio of La/Fe/Co to be 11.1:4.1:6.1. The oxygen in the film cannot be determined because of the contribution of oxygen signal from the underlying FTO and glass substrate. Figure 7B shows the backscattered SEM image of the edge of a freshly broken LaFe0.4Co0.6O3 sample showing the thickness of the film to be approximately 430 nm.

### CONCLUSIONS

Spray pyrolysis of simple, uncomplexed metal nitrate salt solutions onto FTO can be used to produce LaFe1−xCoxO3 electrocatalysts, showing comparable oxygen reduction reaction activity to Pt without conductive additives. The spray pyrolysis procedure requires fewer steps and lower temperatures than the more common methods of preparation and produces smaller crystallites, on the order of 20 nm. High-temperature preparation has been found to be detrimental due to the tendency of perovskites to sinter, thus reducing their surface area and catalytic performance. In addition, because the LaFe0.4Co0.6O3 was grown on an optically transparent electrode, we could observe the color change of the films and
perform spectrophotometry coupled with XPS analysis to
demonstrate that the cobalt ion sharing the B-site with iron is
undergoing reversible oxidation/reduction during voltammetry
and thus is most likely responsible for the electrocatalysis.
Finally, we have found that the catalysts produced behave in
a similar way to other literature preparations: specifically, in the
LaFeCo$_{1-x}$O$_3$ series, the LaFe$_2$Co$_3$O$_7$ is the best-perform-
ing composition, and the onset potential of that composition is
comparable to other perovskite materials reported in the
literature. This suggests that spray pyrolysis may be an ideal
method to screen and compare potential catalysts and possibly
to manufacture these materials.

## EXPERIMENTAL METHODS

### Oxide Electrode Preparation.

Lanthanum(III) nitrate hexahydrate (99.0% purity), iron(III) nitrate nonahydrate (99.95% purity), cobalt(III) nitrate hexahydrate (99.999%, this level of purity is not necessary), citric acid (99.5% purity), and ethylene glycol (99.8% purity) were purchased from Sigma-
Aldrich and used without further purification. Spray solutions of lanthanum/iron/cobalt nitrate were prepared by dissolving the metal nitrates in 10% ethanol/deionized water to make a solution with a metal ion concentration of 0.15 M. The concentrations of Fe$^{3+}$ and Co$^{3+}$ ions were varied (La/Fe/Co = 1:0.20:0.80, 1:0.25:0.75, 1:0.30:0.70, 1:0.40:0.60, 1:0.50:0.50, and 1:0.75:0.25). The conventional method for synthesizing La-based perovskite powders is through an EDTA–citrate, ethylene glycol–citrate, or just citric acid complexation. Typically, the metal nitrates are dissolved in one of these mixtures and heated to 60 °C under continuous stirring for 2 h until a thick gel is formed. The gel is then calcinated at high temperatures (700 °C and above) to form the oxide powders.

When we tried the citrate complexation technique (procedure adapted from Milanova et al.17), we diluted the prepared gel in 10% EtOH–deionized water and performed our normal spraying procedure.

A custom glass sprayer (Figure S6) was constructed from a standard 10.00 mL glass pipette by removing the bulb and adding a sidearm for the flow of nitrogen gas. The reagent solution is drawn from a flask through 0.5 mm inner diameter tubing that connects to an internal capillary tube, which has an outer diameter of 0.5 mm on the spray end and 1.5 mm on the tubing end. A small piece of rubber tubing creates a seal between the capillary and the glass sprayer. The measured flow rate of the sprayer was 5–6 mL/min at a pressure of 20 psi.

The solutions were deposited onto 76 mm (3 in.) square SnO$_2$/F (FTO) conductive glass substrates (Hartford Glass). Before spraying, the substrate was washed with detergent (Fisherbrand Versa-Clean, 04-342), rinsed with deionized water, followed by 99% ethanol, and then wiped dry with Kimwipes. The substrate was then rinsed with 99% methanol and wiped again with Kimwipes, followed by a cotton, lint-free cloth. Once cleaned, the substrate was placed in a U-shaped bracket (conductive side facing the sprayer) mounted on an aluminum base plate that is attached to a hot plate. During spraying, the substrate was heated to ∼170 °C by setting the hot plate beneath the aluminum base to 500 °C. The apparatus is constructed with a lab jack and a ruler mounted on a wood track that allows for precise repositioning of the hot plate (Y direction, up and down). The sprayer, 11.5 cm from the substrate and 90° to the substrate surface, is mounted on a Lego trolley that moves back and forth, under computer control, in the X direction. With movement of the trolley in the X direction and movement of the hot plate in the Y direction, repositioning can allow for any part of the substrate to be sprayed.

For electrochemical characterizations, the bottom centimeter of the FTO glass substrates was sprayed with the metal precursor solution. After spraying, the substrates were allowed to slowly cool on the hot plate and then placed in a room-
temperature oven (Ney 2-160 Series 2), which was heated to 500 °C at a rate of 15 °C/min and held for 5–6 h to form the oxides and anneal the films. After cooling slowly, the substrate was cut into ∼1 cm strips (Figure S7). The middle half of the conductive surface was covered with clear finger nail polish (Rimmel 581 Clear) so that nothing but the metal oxide layer was exposed to the electrolyte solution, while still allowing electrical contact at the top of the glass substrate.

### Electrochemical Characterization for ORR.

The synthesized thin films were the working electrodes in a four-electrode electrochemical cell (Figure S7) using 0.1 M Na$_2$SO$_4$ electrolyte and purged with O$_2$ gas for 15 min prior to data collection. The voltammetric experiments were performed at room temperature blanketed with an oxygen atmosphere. SCE was used as the reference electrode and a Pt mesh as the counter electrode. The electrochemical characterization consisted of a linear sweep voltammogram (LSV) from −0.10 to −0.80 V at a scan rate of 6 mV/s, controlled by a Pine Instruments bipotentiostat and recorded with a PASCO Science Workshop (500 Interface) Data Logger using “Data Studio” computer software. The current as a function of applied potential was recorded simultaneously for the two working electrodes under the same conditions. Current densities were determined by dividing the current by the geometric surface area of the electrodes. Three perovskite thin films were prepared for each composition to check the reproducibility of the film quality and performance. All voltammograms were smoothed using Excel’s exponential smoothing routine to average low-frequency oscillations occurring at the low scan rate used. The optimal composition ratio of the LaFeCo$_{1-x}$O$_3$ film was determined by carrying out a comparative $I$–$V$ curve analysis to see which composition would generate the most positive onset potentials for oxygen reduction. Once the composition and molar concentrations were optimized, the optimal film thickness was determined by varying the number of spraying cycles.16,17

The ORR performance of our optimized material, four-layer LaFe$_{0.95}$Co$_{0.05}$O$_3$ film, was measured in oxygen-saturated 0.100 M NaOH (Fisher Chemical, 0.0995–0.1005 M) in a three-electrode cell with the same Pt mesh counter electrode and SCE reference electrode used in all of the other experiments. The SCE was calibrated in the same 0.100 M NaOH electrolyte and cell finding the potential at zero current for the hydrogen oxidation/reduction at our freshly polished (0.3 µm alumina) Pt flag electrode in bubbling hydrogen. The measured potential was −0.990 V, so the potential versus RHE was calculated by adding 0.990 V to the potential measured versus SCE. Ohmic losses were subtracted from the measured potential and plotted as $E = iR$.

### Spectroelectrochemistry.

An absorbance spectrum of the LaFe$_{0.95}$Co$_{0.05}$O$_3$ thin film was measured with an Agilent 8453 diode-array spectrophotometer at several applied potentials using the bare substrate as a blank. The film-coated FTO
working electrode, platinum mesh counter electrode, and SCE reference electrodes were placed in a flat-sided cell filled with 0.1 M Na₂SO₄. The cell was the bottom three-fourths of a Corning polystyrene tissue culture flak with the top machined off. The applied potential was controlled using a Pine Instruments bipotentiostat.

**Materials Characterization.** All measurements were done at Iowa State University’s Materials Analysis and Research Laboratory. The SEM data were collected at 15 kV on an FEI Quanta-250 scanning electron microscope with a field emission gun. All images are from backscattered electrons. The energy-dispersive X-ray spectrum was acquired with an Oxford Aztec energy-dispersive spectrometer system with an X-Max 80 detector having light element capability. Samples were examined at a low-vacuum setting of 80 Pa of water except for the edge image due to charging of the glass substrate. The XRD data were measured on a Siemens D 500 diffractometer with a Cu X-ray tube operated at 45 kV and 30 mA with medium-resolution slits and a diffracted beam monochromator. A Kratos Amicus/ESCA 3400 instrument was used to measure the XPS spectra. The sample was irradiated with 240 W unmonochromated Mg Kα X-rays, and photoelectrons emitted at 0° from the surface normal were energy-analyzed using a DuPont-type analyzer. The pass energy was set at 150 eV and either a Shirley or linear baseline was removed from all reported spectra. Raw data files were processed using CasaXPS.

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