Dynamic Surface Reconstruction Unifies the Electrocatalytic Oxygen Evolution Performance of Nonstoichiometric Mixed Metal Oxides

Samji Samira, II Jiyun Hong, II John Carl A. Camayang, Kai Sun, Adam S. Hoffman, Simon R. Bare,* and Eranda Nikolla*

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ABSTRACT: Compositionally versatile, nonstoichiometric, mixed ionic–electronic conducting metal oxides of the form $A_{n+1}B_nO_{3n+1}$ ($n = 1 \rightarrow \infty$; $A$ = rare-earth-/alkaline-earth-metal cation; $B$ = transition-metal (TM) cation) remain a highly attractive class of electrocatalysts for catalyzing the energy-intensive oxygen evolution reaction (OER). The current design strategies for describing their OER activities are largely derived assuming a static, unchanged view of their surfaces, despite reports of dynamic structural changes to 3d TM-based perovskites during OER. Herein, through variations in the A- and B-site compositions of $A_{n+1}B_nO_{3n+1}$ oxides ($n = 1$ (ABO$_3$) or $n = \infty$ (ABO$_{3\text{∞}}$); $A$ = La, Sr, Ca; $B$ = Mn, Fe, Co, Ni), we show that, in the absence of electrolyte impurities, surface restructuring is universally the source of high OER activity in these oxides and is dependent on the initial oxide composition. Oxide surface restructuring is induced by irreversible A-site cation dissolution, resulting in in situ formation of a TM oxyhydroxide shell on top of the parent oxide core that serves as the active surface for OER. The rate of surface restructuring is found to depend on (i) composition of A-site cations, with alkaline-earth-metal cations dominating lanthanide cation dissolution, (ii) oxide crystal phase, with $n = 1$ A$_3$BO$_4$ oxides exhibiting higher rates of A-site dissolution in comparison to $n = \infty$ ABO$_3$ perovskites, (iii) lattice strain in the oxide induced by mixed rare-earth- and alkaline-earth-metal cations in the A-site, and (iv) oxide reducibility. Among the in situ generated 3d TM oxyhydroxide structures from $A_{n+1}B_nO_{3n+1}$ oxides, Co-based structures are characterized by superior OER activity and stability, even in comparison to as-synthesized Co-oxidehydroxide, pointing to the generation of high active surface area structures through oxide restructuring. These insights are critical toward the development of revised design criteria to include surface dynamics for effectively describing the OER activity of nonstoichiometric mixed-metal oxides.

KEYWORDS: surface restructuring, oxygen evolution reaction, perovskites, Ruddlesden–Popper oxides, alkaline electrolyzers, cationic dissolution, structure–performance correlations

1. INTRODUCTION

The electrolysis of water, one of the earliest discoveries in electrochemistry dating back to the 18th century, provides a sustainable pathway toward storing electrical energy from renewable sources in the form of chemical bonds. Among the two half-cell reactions involved in water splitting, the anodic oxygen evolution reaction (OER), also known as water oxidation, requires electric potentials significantly higher than the thermodynamic limit (overpotentials of >0.30 V) to achieve desirable electrochemical rates, making it a prime source of inefficiency. This effect extends beyond water electrolysis, since OER is also critical for the synthesis of commodity chemicals from the electroreduction of CO$_2$, electrical energy storage in alkali-metal–O$_2$ batteries, and potentially oxygen generation for use in oxygen concentrators for life-saving medical emergencies. Strategies to overcome these challenges while achieving desirable OER rates at low overpotentials have included (i) tailoring the adsorption energetics of oxygenated intermediates by engineering the electronic structure of metal redox-active centers via doping (e.g., Ru$_{1-x}$NiO$_3$, Ni$_{1-x}$Fe$_x$O$_{3\text{∞}}$, etc.), follow which an OER adsorbate evolution mechanism (AEM) involving four concerted proton coupled electron transfer (PCET) steps, (ii) synthesizing high-surface-area nanostructures that are preferentially terminated by catalytically relevant facets using advanced synthetic methods, and (iii) tuning the reaction mechanism toward nonconcerted proton electron transfer.

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steps with an inherently lower barrier for OER, via triggering of anionic redox processes in the oxides (extent of 3d−O 2p band overlap at the Fermi level) leading to the participation of lattice oxygen in the catalytic cycle.18−24 On the basis of these strategies, vast classes of electrocatalysts have been investigated for OER under both acidic and alkaline conditions. Precious-metal-based oxides, such as IrO2, have been largely considered as standard electrocatalysts for OER in acidic environments (2H2O → O2 +4 H+ +4 e−).2,11 Conversely, alkaline water electrolyzers allow for a wider range of nonprecious-metal-based electrocatalysts (i.e., earth-abundant 3d transition metal (TM) systems) for OER (4OH− → O2 +2H2O+4 e−) due to their relatively higher stability under these conditions.3,11,25,26 Specifically, 3d TM-based oxyhydroxides have been shown to exhibit high activity for OER in alkaline electrolytes.33,37 Although immense opportunities exist to tune the catalytic properties of these oxides for targeted reactions, their performance is still limited by lack of effective design criteria. Generally, the bulk electronic structure of the B-site cations in these oxides has been correlated to their electrocatalytic activity for the OER under the assumption that the overall initial state of the oxide surface remains unchanged under electrochemical conditions.10,19,15 Recent reports have suggested that significant irreversible dynamic changes occur to the surface structure of these oxides during OER, affecting their electrocatalytic performance.38−41 These surface structural changes and subsequent effect on performance have largely been linked to the presence of Fe in the oxide structure and/or the electrolyte solution.38−40 However, to date, there is a limited understanding of the effect of the initial oxide composition on oxide restructuring during OER in the absence of Fe in the oxide structure and/or the electrolyte solution.38−40

Figure 1. Characterization of as-synthesized, pristine oxides highlighting LSCoO-75 as an example. (a) HAADF-STEM micrograph of an LSCoO-75 particle. (b) Atomic resolution HAADF-STEM micrograph for the region highlighted in blue in (a) showing the metal cations and (ABO3) (AO) stacking, consistent with a first-series R-P structure shown as an inset (cyan, green, and blue spheres represent La, Sr, and Co cations, respectively). (c) EELS mapping of LSCoO-75 showing the uniform distribution of La, Sr, Co, and O throughout the oxide particle. (d) [001] projected atomic resolution HAADF-STEM micrograph of the near-surface region highlighted in magenta in (a), confirming the high crystallinity of the oxide in the surface atomic layer (~4 Å) as evidenced by the continuous lattice fringes. The inset represents the FFT pattern corroborating its phase-pure tetragonal symmetry. (e) Atomically resolved EELS mapping of La, Sr, and Co in LSCoO-75 for the same region in (d) at a resolution of 1.0 Å per pixel. (f) Averaged corresponding EEL spectra of the surface atomic layer (~4 Å) validating the presence of La, Sr, and Co cations and lattice oxygen anions.
of Fe cations, hindering the development of universal criteria for describing the OER activity of nonstoichiometric, mixed ionic−electronic conducting metal oxides. Herein, controlled electrochemical studies and detailed characterization (e.g., inductively coupled plasma-mass spectrometry (ICP-MS), scanning transmission electron microscopy (STEM), and X-ray absorption spectroscopy (XAS)) were employed to develop an understanding of the effect of the initial composition and crystal phase of nonstoichiometric mixed-metal oxides on the dynamics of their surface reconstruction and consequently electrochemical performance for OER in purified 0.1 M KOH (Fe content <1 ppb). Two different extrema of the crystal phase of $A_{n+1}B_nO_{3n+1}$ oxides were investigated: (i) $n = 1$ A$_2$BO$_4$ type Ruddlesden−Popper (R-P) and (ii) $n = \infty$ ABO$_3$ perovskite phases. The A-site composition was varied from pure to mixed lanthanide/alkaline-earth-metal cations, while the B-site 3d TM cations were varied from Mn to Fe, Co, and Ni. Cation dissolution and the electronic and geometric structure changes of the oxide surface under electrochemical conditions were characterized and correlated to the initial oxide composition using XAS, ICP-MS, and STEM imaging coupled with energy electron loss spectroscopy (EELS). The factors that influenced in situ oxide surface restructuring during OER and their implications in the electrochemical performance of the oxides were identified.

2. RESULTS AND DISCUSSION

2.1. Characterization of as-Synthesized (Pristine) Oxides

A sol−gel approach was used to synthesize the $A_{n+1}B_nO_{3n+1}$ ($n = 1$ and $n = \infty$) nonstoichiometric, mixed ionic-electronic conducting metal oxides reported here (details in Methods).\textsuperscript{27,42} Initially, the first series ($n = 1$) R-P phases (Figure S1a) with a nominal composition of La$_0.5$Sr$_{1.5}$BO$_4$ (LSBO-75, where 75 represents the percent concentration of Sr cations in the A-site of the oxide; B = Mn, Fe, Co, Ni) were synthesized to determine the effect of the B-site 3d TM cation on their electrocatalytic performance. The composition of the A-site was fixed at a La:Sr ratio of 1:3 to facilitate variations among pure B-site 3d TM cations. Phase-pure tetragonal structures belonging to the I4/mmm space group were obtained for all LSBO-75 compositions, as confirmed by powder X-ray diffraction (XRD) (Figure S1b). A negative shift in the highest potential for OER is observed for Mn and Fe as compared to Co and Ni, which is consistent with a lower onset potential and a higher catalytic activity for Fe. The current density achieved at a potential of 1.7 V is shown in Figure 2a for the first cycle normalized per geometric surface area of the electrode. The inset shows the current density achieved at a potential of 1.7 V. (b) Tafel analysis of LSBO-75 oxides in the kinetic regime for the first OER cycle. (c) Percentage dissolution of metal cations into the electrolyte from LSBO-75 oxides after oxide pretreatment between 1.25 and 1.50 V vs RHE for 20 cycles (prior to first-cycle OER polarization), as measured by ICP-MS. The inset represents the percent dissolution of metal cations after 100 OER CVs between 1.1 and 1.7 V. (d) Parity plot showing the change in intrinsic activity (defined as the measured current normalized per oxide BET surface area) at a peak potential of 1.7 V for LSBO-75 oxides over 100 OER CVs. The x axis represents the initial intrinsic activity (at the end of the first cycle), while the y axis is the measured intrinsic activity after 100 CVs. The dashed line represents the expected behavior for an unchanged and stable catalyst. The inset shows the ratio of the number of moles of oxygen evolved on the basis of the measured current to the total number of moles of cation dissolution into the electrolyte after 100 OER CVs.
intensity (103) peak was observed as the B-site varied from Ni to Mn, consistent with an increase in the cell volume with an increase in the ionic radius of the B-site cation from Ni (Ni$^{3+}$ low spin (LS): 0.56 Å; Ni$^{4+}$: LS 0.48 Å) to Mn (Mn$^{3+}$ LS: 0.58 Å; Mn$^{4+}$ high spin (HS): 0.645 Å; Mn$^{4+}$: 0.53 Å), as shown in Figure S1.\textsuperscript{1,12} STEM micrographs in Figure 1a (LSCO-O-75) and Figure S2 (LSBO-75 (B = Mn, Fe, Ni)) show that the sol–gel synthesis led to polyhedral-shaped particles of 138 ± 58 nm in diameter for all considered LSBO-75 oxides. The similarities in the particle morphology and size distribution of the LSBO-75 oxides were reinforced by their similar Brunauer–Emmett–Teller (BET) physical surface areas of 3–5 m$^2$/g (Table S1). The metal cation and oxygen anion distribution in LSCO-O-75 was imaged via high-angle annular dark field (HAADF, Figure 1b) and annual bright field (ABF, Figure S3) in STEM, respectively. These studies clearly showed continuous lattice fringes with a $d$ spacing of ∼3.6 Å, validating the crystalline tetragonal structure of LSCO-O-75 belonging to the $I4/mmm$ space group.

Uniform distributions of La, Sr, and Co cations and lattice oxygen anions throughout the LSCO-O-75 particles were verified via EELS mapping using STEM (Figure 1c). The observed uniform distribution of all ions is in line with the appropriate stoichiometric atomic ratios of La (16.2 ± 1.4 atom %), Sr (51.1 ± 1.1 atom %), and Co (32.6 ± 1.6 atom %) cations in LSCO-O-75 obtained via energy dispersive X-ray spectroscopy (EDS) (Figure S4). Atomic resolution HAADF-STEM imaging of the near-surface region of the oxide particles (Figure 1d and Figure S5) showed continuous lattice fringes with a $d$ spacing of 3.6 Å along the [001] zone axis, consistent with that of the bulk. EELS mapping of the same surface region of LSCO-O-75 (Figure 1e,f) measured a homogeneous distribution of the metal cations, indicating the absence of surface phase segregation of any of the metal cations. These studies confirmed that as-synthesized, pristine oxides were characterized by a high degree of crystallinity and uniformity in cationic distribution within the oxide particles prior to electrochemical testing.

### 2.2. Electrochemical Performance: Effect of Oxide B-Site Composition

The intrinsic OER activities of as-synthesized, pristine LSBO-75 (B = Mn, Fe, Co, Ni) oxides were investigated using drop-casted, composite electrodes on a glassy-carbon substrate in a three-electrode setup, with a rotating-disk electrode (RDE) acting as the working electrode. All electrochemical measurements were performed in purified 0.1 M KOH electrolyte with a minimal amount of Fe (<1 ppb) to circumvent Fe artifacts on the measured electrochemical performance.\textsuperscript{1,4,44} The Fe content was confirmed to be <1 ppb using ICP-MS before and after all electrochemical studies reported here. All electrochemical measurements were also subjected to a $iR$ correction. The oxide particles were supported on high-surface-area graphitic carbon to minimize any artifacts in electrochemical performance due to their electronic conductivity.\textsuperscript{1,24,25} The oxide loading on the working electrode was also kept consistent in all these studies. More details regarding electrolyte purification, $iR$ correction, oxide loading, and preparation of drop-casted composite electrodes can be found in Methods. Prior to the polarization studies, the pristine oxides were pretreated using continuous cycling between 1.25 and 1.50 V vs the reversible hydrogen electrode (RHE) to remove any surface-adsorbed species, consistent with previous reports.\textsuperscript{2,4} All the potentials reported herein and in the Supporting Information are referenced to the RHE.

Representative first-cycle linear sweep voltammograms (LSVs) and cyclic voltammograms (CVs) measured at a scan rate of 10 mV s$^{-1}$ for all composite LSBO-75 electrodes in O$_2$-saturated purified 0.1 M KOH (Fe content <1 ppb) at a rotation speed of 1600 rpm are shown in Figure 2a and Figures S6–S9. No substantial redox transitions prior to OER were observed for LSBO-75 oxides, except for LSNiO-75 at potentials of 1.42 and 1.31 V (Figure S6). This redox feature corresponds to the redox couple associated with the Ni$^{2+/3+}$ transition.\textsuperscript{12,24,27} Among the LSBO-75 oxides considered, LSCO-O-75 exhibited the highest activity, as evidenced by achieving a current density of 10 mA cm$^{-2}$ at the lowest potential of 1.61 ± 0.01 V, followed by LSFeO-75, LSNiO-75, and LSMnO-75 (Figure 2a). To estimate the intrinsic activity of the oxide electrocatalysts, their initial BET specific surface areas were used to normalize the measured electrochemical rates, due to challenges associated with the estimation of electrochemical active surface area of composite electrodes containing oxide particles.\textsuperscript{5,44} We found that normalization of the electrochemical rates by the initial oxide specific surface areas did not change the trend above, validating the uniform distribution and dominant electrocatalytic activity of the oxides in the composite electrodes (Figure S7). The OER kinetics were investigated using Tafel analysis in the kinetic regime, as shown in Figure 2b. The kinetic regime was identified via variations in the rotation speed of the working electrode (Figure S8; additional details can be found in the Supporting Information). Consistent with the activity trend discussed above, LSCO-O-75 demonstrated a >10x higher intrinsic rate at a typical OER potential of 1.63 V (Figure 2b) in comparison to the other oxides. LSBO-75 (B = Fe, Co, Ni) oxides were characterized by similar Tafel slopes (96 ± 6 mV dec$^{-1}$), suggesting a similar first-cycle OER mechanism on these oxides. Conversely, a much higher slope of 193 ± 3 mV dec$^{-1}$ was obtained for LSrMoO-75 (Figure 2b), potentially due to the change in mechanism or strong adsorbate interactions with this oxide surface.\textsuperscript{37,48}

The source of the differences in activity of these LSBO-75 oxides during the first OER cycle correlated to cation dissolution during electrochemical pretreatment. ICP-MS analysis of the electrolyte solution post oxide electrochemical pretreatment, but prior to the polarization studies, showed that all LSBO-75 oxides exhibited irreversible cation dissolution (Figure 2c). No detectable cation dissolution from these oxides was measured in the same electrolyte prior to electrochemical pretreatment, confirming that this process was electrochemically driven. This is possibly due to the electrochemical oxidation of lattice oxygen under oxidative potentials, leading to the destabilization of the cations in the oxide. Sr dissolution was dominant in all LSBO-75 oxides during pretreatment (Figure 2c) with no detectable levels of La dissolution being measured (detection limit for La: 1.2 ppb). Preferential Sr dissolution was attributed to (i) the larger ionic radius of Sr$^{2+}$ (1.44 Å) in comparison to the La$^{3+}$ (1.36 Å) cations\textsuperscript{8} and (ii) the higher solubility of Sr$^{2+}$ cations in alkaline electrolytes due to their preferential coordination with OH$^{-}$ ions.\textsuperscript{4,44} The amount of Sr dissolution during pretreatment was also found to increase with a decrease in the ionic radius of the B-site cation, as it varied from Mn (Mn$^{3+}$ low spin (LS): 0.58 Å; Mn$^{4+}$ high spin (HS): 0.645 Å; Mn$^{4+}$: 0.53 Å), to Co (32.6 ± 1.6 atom %), and Sr (51.1 ± 1.1 atom %).
Mn$^{3+}$ high spin (HS): 0.645 Å; Mn$^{4+}$: 0.53 Å) in LSMnO-75 to Ni (Ni$^{3+}$ LS: 0.56 Å; Ni$^{4+}$ LS: 0.48 Å) in LSNiO-75 (Figure S1b). This points to the fact that an increase in the oxide cell volume induced by an increase in the ionic radius of the B-site cation resulted in the stabilization of the Sr cations in the oxide, consequently lessening the extent of its dissolution in LSMnO-75 in comparison to LSNiO-75.

The amount of Sr dissolution during pretreatment also correlated to the reducibility of the oxide, which is an indicator of the strength of the metal–oxygen bonds in the oxide. We have previously reported that this class of nonstoichiometric, mixed ionic–electronic conducting metal oxides became more reducible (characterized by weaker metal–oxygen bonds) as the B-site varied from Mn to Ni across the 3d TM cations. This suggested that an increase in oxide reducibility as the B-site varied from Mn to Ni in LSBO-75 oxides correlated with an increase in Sr dissolution, potentially due to the facile formation of oxygen defects in the structure, leading to destabilization of the Sr cations in the oxide. B-site cation dissolution was also observed, but to a lesser extent, with Mn and Fe dissolution being significantly higher than that of Co and Ni cations from these LSBO-75 oxides during pretreatment (Figure 2c). This is consistent with the high solubility of Mn and Fe cations due to their favorable coordination with OH$^-$ ions forming stable Mn/Fe–OH species in solution.

The long-term performance of the LSBO-75 oxides during the OER was determined via repeated CVs at a scan rate of 10 mV s$^{-1}$ in a potential window of 1.1–1.7 V (Figure 2d and Figures S10–S13). Continuous CVs allow a simulation of intermittent device operation capturing effects from electrolyzer startup and shutdown cycles. It was observed that LSCoO-75 and LSNiO-75 exhibited a ∼29% and ∼35% enhancement in the electrochemical rates over 100 OER CVs, respectively (Figure 2d and Figure S10–S13). Consistent performance was observed for LSCoO-75, LSNiO-75, and LSSrO-75 oxides during the OER.

**Figure 3.** Electrochemical performance and cationic dissolution of $\text{A}^{n+1}\text{CoO}_{3n}^{{n+1}}$ ($n = 1$, ∞) oxides in O$_2$-saturated purified 0.1 M KOH (Fe content <1 ppb) at 10 mV s$^{-1}$ and a rotation speed of 1600 rpm. (a) Percentage metal cation (La, Sr, and Co) dissolution into the electrolyte from $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$, SrCoO$_3$, LaCoO$_3$, LSCoO-75, and LSCoO-25 oxides after oxide pretreatment between 1.25 and 1.50 V as measured by ICP-MS. (b) Tafel analysis after the first cycle for $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$, SrCoO$_3$, LaCoO$_3$, and LSCoO-25 in comparison with LSCoO-75. (c) Parity plot showing the change in the intrinsic activity of $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$, SrCoO$_3$, LaCoO$_3$, LSCoO-75, and LSCoO-25 oxides over 100 OER CVs at a potential of 1.7 V. The x axis represents the initial intrinsic activity (defined as the measured current normalized per oxide BET surface area) at the end of the first cycle, while the y axis is the measured intrinsic activity after 100 CVs. The dashed line represents the expected behavior for an unchanged and stable catalyst. (d) Percentage Sr$^{2+}$ metal cation dissolution into the electrolyte from $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$, SrCoO$_3$, and LSCoO-75 oxides after 100 CVs between 1.1 and 1.7 V as measured by ICP-MS.
with the pretreatment trends, Sr dissolution continued to occur on LSCO-75 and LSNiO-75 during these 100 cycles (Figure 2c, inset). It is worth noting that the Tafel slopes of LSCO-75 and LSNiO-75 did not change with cycling, suggesting no significant change in the OER mechanism over the 100 OER cycles (Figure S12). Conversely, LSMnO-75 and LSFeO-75 exhibited a loss in activity over cycling, as shown in Figure 2d and Figures S10–S13, consistent with the loss of active Mn and Fe cations from these oxides (Figure 2c, inset). This also resulted in Tafel slope changes for LSMnO-75 and LSFeO-75 oxides over OER cycling (Figure S12). This clearly alludes to dynamic changes in the nature and/or number of surface-active cationic centers in LSBO-75 oxides triggered by cation dissolution with exposure to oxidative potentials.

To determine the effect of cation dissolution and lattice oxygen evolution (oxidation) on the measured electrochemical rates, the ratio of the total moles of oxygen evolved (based on the current generated) to the total moles of cation dissolution from the oxides observed over 100 CVs (\( n_{\text{oxygen}}/n_{\text{cation dissolution}} \)) was calculated (Figure 2d, inset; details regarding these calculations can be found in the Supporting Information).\(^{50,51}\) This ratio (\( n_{\text{oxygen}}/n_{\text{cation dissolution}} \)) is an indicator of the Faradaic efficiency toward OER from water oxidation, as well as the inherent stability of the oxides.\(^{50,51}\) In the case when lattice oxygen evolution associated with cation dissolution dominates the measured electrochemical rates, this ratio would be on the order of \( 10^{-5} - 10^{-4} \).\(^{50,51}\) The calculated \( n_{\text{oxygen}}/n_{\text{cation dissolution}} \) ratios for LSMnO-75 and LSFeO-75 were 1.1 \( \times 10^3 \) and 1.7 \( \times 10^1 \) over 100 OER cycles, respectively, suggesting that the measured electrochemical rates on these oxides were dominated by lattice oxygen evolution (oxidation).

The observed poor electrocatalytic activity of Mn- and Fe-based oxides is in line with previous reports on TM oxyhydroxides.\(^{48,49}\) LSNiO-75 exhibited an \( n_{\text{oxygen}}/n_{\text{cation dissolution}} \) ratio of 2.5 \( \times 10^2 \) over 100 OER cycles, suggesting that OER from water oxidation dominated the measured currents in this case, albeit at low rates (Figure 2d, inset). This ratio (\( n_{\text{oxygen}}/n_{\text{cation dissolution}} \)) was found to be significantly higher for LSCO-75 (\( \sim 1.5 \times 10^3 \)) over 100 cycles, validating its high catalytic activity and stability toward OER from water oxidation, as well as its superior performance among the 3d TM cations discussed above. It was observed that \( n = 1 \) R-P phases of LSCO-75 and LSCO-25 exhibited a tetragonal symmetry belonging to the \( I4/mmm \) space group (Figure S14), while LCCoO-75 exhibited an orthorhombic symmetry belonging to the \( Bmnb \) space group.\(^{2} \) The \( n = \infty \) perovskite phases of LaCoO\(_4\), La\(_{0.25}\)Sr\(_{0.75}\)CoO\(_4\), and SrCoO\(_3\) exhibited rhombohedral (space group \( R\bar{3}c \)),\(^{3} \) cubic (space group: \( Pm\bar{3}m \)),\(^{19} \) and tetragonal (space group: \( I4/mmm \))\(^{53} \) symmetries, respectively. ICP-MS analysis of the electrolyte solution after the initial pretreatment of these oxides showed mainly alkaline-earth-metal cation dissolution (Figure 3a). La (detection limit 1.2 ppb) and Co (detection limit 0.2 ppb) cation concentrations in the electrolyte were negligible and fell within the detection limits of the ICP-MS. This suggested that, independent of the alkaline-earth-metal cation concentration in the A-site and the crystal phase (R-P vs perovskite phase) of the oxide, La and Co cations remained on the electrode under the considered electrochemical conditions. In general, the following Sr dissolution trend was observed: LSCO-75 \( \gg \) La\(_{0.25}\)Sr\(_{0.75}\)CoO\(_4\) \( > \) SrCoO\(_3\) \( > \) LSCO-25 (Figure 3a). The measured cationic dissolution after electrochemical pretreatment clearly suggested changes to the oxide structure even prior to the first cycle of OER activity measurement, similarly to the LSBO-75 (\( B = \text{Mn, Fe, Ni} \)) oxides discussed above. It was observed that the initial concentration of Sr in the A-site of oxides belonging to the same crystal phase (i.e., \( n = 1 \text{ R-P} \)); LSCO-75 vs LSCO-25) directly affected the extent of Sr dissolution, with the higher concentration of Sr in LSCO-75 resulting in higher dissolution (Sr dissolution 9.9%) than in the case of LSCO-25 (Sr dissolution 2.5%). Interestingly, for \( n = \infty \) perovskites, the oxide with pure Sr A-site exhibited lower Sr dissolution in comparison with the mixed La/Sr A-site perovskite (SrCoO\(_3\) (2.9%) vs La\(_{0.25}\)Sr\(_{0.75}\)CoO\(_3\) (3.7%)), potentially due to the lattice strain induced by the differences in the ionic radii of La\(_{3+}\) (1.36 Å) and Sr\(_{2+}\) (1.44 Å) cations in the mixed A-site oxide (La\(_{0.25}\)Sr\(_{0.75}\)CoO\(_3\)).

The resulting first-cycle OER kinetics of these reconstructed oxides after pretreatment were studied using Tafel analysis. A Tafel slope of 97 \( \pm 5 \) mV dec\(^{-1} \) was observed for all Sr-containing \( A_x\text{Co}_y\text{O}_{3+1} \) (\( n = 1 \) and \( n = \infty \)) oxides in the first OER cycle, as shown in Figure 3b. This clearly validated the similar nature of the OER mechanism on all these oxides. Conversely, the Sr-free perovskite LaCoO\(_3\) exhibited the highest Tafel slope of 121 \( \pm 5 \) mV dec\(^{-1} \) and the lowest electrochemical rates normalized per oxide surface area. The following intrinsic activity trend was observed: LSCO-75 \( \gg \) La\(_{0.25}\)Sr\(_{0.75}\)CoO\(_4\) \( > \) SrCoO\(_3\) \( > \) LSCO-25 \( > \) LaCoO\(_3\), which correlated directly with the amount of Sr dissolution from the A-site of these oxides (Figures 3a,b). Interestingly, replacing Sr\(^{2+}\) cations in LSCO-75 with other alkalai-earth-metal cations such as Ca\(^{2+}\) at the same concentration (LSCO-75 and LCCO-75, respectively) did not significantly affect the OER performance. LCCO-75 achieved 10 mA cm\(^{-2} \) at 1.63 \( \pm \) 0.01 V in the first OER cycle similar to LSCO-75 (Figure S16), suggesting similar dissolution behavior and effect on oxide reconstruction for both of these alkalai-earth-metal cations.

To probe the long-term performance of \( A_x\text{Co}_y\text{O}_{3+1} \) (\( n = 1 \) and \( n = \infty \)) oxides, the change in their current density at 1.7 V over 100 CVs was compared, as shown in Figure 3c. An enhancement in activity was observed for LSCO-75, LSCO-25, La\(_{0.25}\)Sr\(_{0.75}\)CoO\(_4\), and SrCoO\(_3\) over 100 OER CVs (Figure 3c and Figure S17). The Tafel slopes did not change significantly after 100 cycles, suggesting that no significant changes in the OER mechanism occurred with cycling (Figure S17, inset). Conversely, LaCoO\(_3\) exhibited no significant
change (<5%) and an inferior electrochemical performance in comparison to the Sr-containing oxides over 100 OER cycles (Figure 3c). Among the Sr-containing $A_{n+1}Co_nO_3^{n+1}$ ($n = 1$ and $n = \infty$) oxides, an activity trend of $\text{LSCoO-75} > \text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3 > \text{SrCoO}_3 > \text{LSCoO-25}$ was observed after 100 cycles, consistent with the trend reported above for the first OER cycle (Figure 3c). ICP-MS analysis of the electrolyte showed that Sr dissolution continued to occur from these oxides during 100 OER cycles (Figure 3d and Figure S18); however, the highest rate of Sr dissolution occurred within the first five OER cycles (Figure 3d).

The effect of the oxide crystal phase ($A_{n+1}B_nO_3^{n+1}$; $n = 1$ R-P vs $n = \infty$ perovskite) on the electrochemical performance can be deduced by comparing the electrocatalytic performance of LSCoO-75 belonging to the $n = 1$ R-P phase and that of its $n = \infty$ perovskite counterpart, $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$ with the same La:Sr ratio of 1:3 in the A-site. We note that the oxidation states of Co cations in LSCoO-75 and $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$ were also similar. It is clear from Figure 3d and Figure S18 that the main effect from the oxide crystal phase (i.e., $n = 1$ R-P vs $n = \infty$ perovskite) relates to the extent of Sr dissolution as a function of cycling, with the highest rate of dissolution occurring consistently in the first five OER cycles in both cases. The LSCoO-75 R-P oxide exhibited a 3-fold higher amount of Sr dissolution in comparison to its counterpart perovskite, $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$, consequently affecting the rate of oxide restructuring and enhancement in electrocatalytic activity upon cycling (Figure 3c). This could be associated with the presence of rock salt AO layers in the $n = 1$ R-P structure, which served as sacrificial layers, facilitating faster Sr dissolution than in the case of the perovskite phase.

To summarize, the results discussed above showed that all $A_{n+1}Co_nO_3^{n+1}$ ($n = 1$ and $n = \infty$) oxides containing alkaline-earth-metal cations (LSCoO-25, LCCoO-75, LSCoO-75, $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$, and SrCoO$_3$), independent of their crystal phase, resulted in enhanced electrochemical rates accompanied by alkaline-earth-metal cation dissolution over OER cycling. This suggested that alkaline-earth-metal cation dissolution led to oxide restructuring with Co cations (the common feature of these oxides) in the restructured surface being primarily responsible for catalytic turnover. The rate of cationic dissolution in all of these oxides was found to be the highest within the first five OER cycles. The extent of Sr dissolution between the 50th and the 100th cycle was significantly lower (<5%) than that between the 1st and the 50th cycle for LSCoO-75, $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$, and SrCoO$_3$. This indicated significant stabilization of the restructured surfaces after 50 OER cycles. The effect of the crystal phase (i.e., $n = 1$ R-P vs $n = \infty$ perovskite) of the oxides with the same alkaline-earth-metal cation concentration in the A-site mainly controlled the rate of cation dissolution. The $n = 1$ R-P structure exhibited a 3-fold higher extent of Sr dissolution in comparison to the perovskite counterpart due to the presence of sacrificial rock salt AO layers in its structure. We note that the measured electrochemical rates on these oxides at any point were significantly higher than the rate associated with lattice oxygen.
evolution (oxidation) that accompanied cation dissolution. For instance, the ratios of the moles of O\textsubscript{2} evolved per total moles of cation dissolution into the electrolyte ($n_{\text{oxygen}}/n_{\text{cation\_dissolution}}$) for all Sr-containing Co-based oxides with improved electrochemical performance over cycling (i.e., LSCO-0.75, La\textsubscript{0.25}Sr\textsubscript{0.75}CoO\textsubscript{4} and SrCoO\textsubscript{3}) were calculated to be 1.5 $\times$ 10$^{-4}$, 1.7 $\times$ 10$^{-4}$, and 1.8 $\times$ 10$^{-4}$, respectively (details are given in the Supporting Information). This suggested that >98% of the moles of O\textsubscript{2} evolved during electrochemical testing on these oxides were associated with water oxidation.

2.4. Insights into the Active Oxide Surface Structure: Oxide Characterization as a Function of Electrochemical Cycling

STEM studies coupled with EDS and EELS were employed to characterize changes in the structure of $A_{n+1}Co_2O_3n+1$ (n = 1 R-P and n = $\infty$ perovskite) oxides (viz., LSCO-0.75, La\textsubscript{0.25}Sr\textsubscript{0.75}CoO\textsubscript{4} and SrCoO\textsubscript{3}) after OER testing (details are given in Methods). As discussed above, the highest rate of Sr dissolution occurred over the first five OER cycles for all of these oxides (Figure 3d), making this catalyst state appropriate for understanding oxide restructuring (referred to as the spent catalyst). Figure 4a,b shows the [001] projected HAADF-STEM micrograph of the spent LSCO-0.75 (the most active electrocatalyst among the oxides considered), clearly demonstrating restructuring of the surface into an amorphous shell on top of the core crystalline parent oxide backbone. The interface between the crystalline lattice of the oxide core and the amorphous shell was clearly observed using atomic resolution HAADF-STEM, as shown in Figure 4b. The thickness of the amorphous layer was found to be 14 $\pm$ 1 nm, resulting in a 26.2 $\pm$ 2.3% change in the volume of spent LSCO-0.75 particles (assuming a spherical shape). EDS mapping and line scan of spent LSCO-0.75 particles (Figure S19) clearly showed the Co-rich/Sr-deficient nature of this amorphous surface region, in line with Sr dissolution into the electrolyte from ICP-MS analysis (Figure 2). Further, a Sr dissolution of 28 $\pm$ 1.4% into the electrolyte was observed using ICP-MS studies for spent LSCO-0.75, corroborating the change measured using imaging. Similarly, HAADF-STEM micrographs showed the formation of amorphous shells for spent La\textsubscript{0.25}Sr\textsubscript{0.75}CoO\textsubscript{4} (6.5 $\pm$ 0.5 nm thickness) and spent SrCoO\textsubscript{3} (3.5 $\pm$ 0.5 nm thickness) (Figures S20 and S21). This corresponded to a 6.9 $\pm$ 1.3% and 4.8 $\pm$ 1.4% change in the oxide volume for spent La\textsubscript{0.25}Sr\textsubscript{0.75}CoO\textsubscript{4} and SrCoO\textsubscript{3} in comparison to the pristine states, respectively. These changes were in line with the lower amount of Sr dissolution from spent La\textsubscript{0.25}Sr\textsubscript{0.75}CoO\textsubscript{4} (10.2 $\pm$ 0.4%) and SrCoO\textsubscript{3} (7.3 $\pm$ 0.3%), as measured using ICP-MS studies discussed above in comparison to LSCO-0.75 (Figure 3d). The thickness of this in situ generated amorphous shell on the spent oxides was found to scale with the electrochemical activity. It was observed that LSCO-0.75 with an in situ generated 14 $\pm$ 1 nm thick amorphous shell achieved a high current density that was 1.5$x$ and 1.7$x$ greater than that of La\textsubscript{0.25}Sr\textsubscript{0.75}CoO\textsubscript{4} and SrCoO\textsubscript{3}, respectively. Given the similarities in the physical surface areas of the parent oxides, the correlation of the thickness of the amorphous shell to the electrochemical performance points to the porous nature of the shell, with a larger shell thickness leading to the highest exposed active surface area for the OER.

Elemental composition and electronic structure insights into the surface region of the spent oxide particles were obtained using atomic resolution EELS mapping in STEM. Figure 4c validated the Co-rich/Sr-deficient nature of the restructured surface shell in spent LSCO-0.75, consistent with EDS studies. The presence of La was also detected in this near-surface region using an EELS line scan analysis (Figure 4c), potentially in the form of amorphous hydroxylated lanthanum oxide, consistent with the undetectable levels of La in the electrolyte using ICP-MS studies. The effect of this lanthanum phase in the restructured surface of spent samples on their electrochemical activity was insignificant, given the fact that the free SrCoO\textsubscript{3} oxide exhibited a similar enhancement in OER performance during cycling in comparison to (La\textsubscript{1-x}Sr\textsubscript{x})\textsubscript{2}CoO\textsubscript{4-y} (0 $\leq$ x $\leq$ 1; y = 0, 1) oxides. This clearly alludes to the fact that Co cations in the restructured amorphous surfaces of these oxides are primarily responsible for catalytic turnover.

The electronic structure of the Co cations and lattice oxygen anions in the restructured amorphous surface region of spent LSCO-0.75 were analyzed using the Co L-edge and O K-edge EEL spectra (Figure 4d). The averaged O K-edge EEL spectrum of pristine LSCO-0.75 was characterized by a prepeak at $\sim$30 eV, followed by a shoulder at 534.5 eV and a main peak at 537 eV (Figure 4d, inset). The O K-edge prepeak represents the near-edge fine structure and contains information regarding the hybridization of the O 2p and Co 3d orbitals and hence the oxygen vacancy concentration.\textsuperscript{5,55} The prepeak intensity for LSCO-0.75 was suppressed in the spent sample, suggesting the formation of oxygen vacancies in the oxide upon cycling. A similar trend was observed for O 1s X-ray photoelectron spectra (XPS), as shown in Figure S22. This is consistent with electrochemical oxidation of lattice oxygen during surface restructuring.\textsuperscript{58} Such structural changes directly altered the electronic structure of Co cations, in line with a lower valence state of Co cations in spent LSCO-0.75. This is evidenced by a 1 eV downshift in energy of both the Co L$_1$- and L$_2$-edges in the spent sample as compared to pristine LSCO-0.75 in the near-surface region (blue and magenta curves in Figure 4d, respectively). The lowering of the Co valence state in the near-surface region of spent LSCO-0.75 was also confirmed by comparing the Co 2p XPS region to that of the pristine oxide (Figure S22). A similar decrease in the Co valence state in the near-surface region was observed for spent La\textsubscript{0.25}Sr\textsubscript{0.75}CoO\textsubscript{3} and SrCoO\textsubscript{3} using XPS, as shown in Figure S23. The most significant changes in the Co 2p XPS were observed between the pristine and the five OER cycle samples, suggesting that the largest changes in the electronic structure of the oxide surface occurred within the first five OER cycles, consistent with the ICP-MS studies discussed above (Figures S22 and S23). Consistently, XPS of the La 4d region for LSCO-0.75 mainly showed changes between the pristine and after five OER cycle states (Figure S22c) induced by oxide surface restructuring. The key observations from these STEM/EDS/EELS studies of spent oxides were that: (i) an amorphous phase around the parent crystalline core emerged upon OER cycling, (ii) the thickness of this amorphous shell was dependent on the parent oxide composition, and the oxide crystal phase, and (iii) the Co cations in this amorphous shell, generally responsible for catalytic turnover, were characterized by a lower valence state in comparison to the pristine oxide.

To determine the nature of the emerged surface phase in these $A_{n+1}Co_2O_3n+1$ (n = 1 and n = $\infty$) oxides upon electrochemical cycling, XAS studies were employed. The absorption edge energy at the Co K-edge of normalized X-ray absorption near edge structure (XANES) spectra of LSCO-
75, La0.25Sr0.75CoO3, and SrCoO3 suggested that all of these oxides, in their as-synthesized, pristine state, had an average Co oxidation state that was higher than 3+, as indicated by the comparison to the oxidic Co standards (Figure 5a). To

Figure 5. XANES characterization of pristine Co-based mixed metal oxides. (a) Co K-edge normalized XANES spectra of LSCoO-75, La0.25Sr0.75CoO3, and SrCoO3 (in their as-synthesized, pristine states), along with the Co standards. The inset zooms in at the 0.5 edge step to show the difference in edge positions between the samples and the standards. (b) Linear correlation plot generated for the determination of the Co oxidation state, based on the XANES region using a half-edge step method. The Co standards with known Co oxidation states are plotted in black squares and the linear trend line is represented using a black line. The pristine states of LSCoO-75, La0.25Sr0.75CoO3, and SrCoO3 are plotted in red, blue, and green circles, respectively.

Figure 6. XANES and EXAFS characterization of spent LSCoO-75. (a) Co K-edge XANES spectra of LSCoO-75 in pristine (solid black), pretreated (solid red), and spent (solid blue) states. The difference spectra for the pretreated (dotted red) and spent (dotted blue) states are also shown for LSCoO-75. (b) Enlarged pre-edge region of the XANES spectra. EXAFS spectra in \( k^2 \)-weighted (c) \( k \) space and (d) \( R \) space (a \( k \) range of 3.6–11.0 Å\(^{-1} \) were used for Fourier transform) for LSCoO-75.
estimate the average oxidation state of the Co cations, the energy position at half of the edge step was used to develop a correlation based on Co oxides of known oxidation state.\textsuperscript{56–58}

The resulting linear correlation using this method is shown in Figure 5b, and the estimated average Co oxidation states calculated are summarized in Table S2. These results indicate that Co cations in L\textsubscript{40.22}Sr\textsubscript{0.75}CoO\textsubscript{3}, and LSCoO-75 have the highest oxidation state, followed by SrCoO\textsubscript{3}, and LSCoO-75 in descending order.

Changes in the electronic and geometric structure of Co cations in these oxides as a function of electrochemical testing were determined by studying three different states of LSCoO-75: (i) the pristine state, which refers to the as-synthesized oxide subject to no electrochemical treatment, (ii) the pretreated state, which refers to the oxide treated electrochemically in a potential window between 1.25 and 1.50 V to remove surface adsorbed species prior to OER, and (iii) the spent state, which refers to the oxide after five OER cycles. Subtle but clear changes were detected in the XANES spectra of these three states of LSCoO-75, as shown in Figure 6a. The relative changes in the XANES region for LSCoO-75 are highlighted in detail by the difference spectra (dotted lines), obtained by subtracting the spectrum of the pristine oxide from those of the pretreated and spent samples (Figure 6a). The difference spectra for the pretreated and spent samples shared identical features that only differed in their amplitudes, suggesting that the same structural change was occurring at both states. This indicated that just the pretreatment was sufficient to induce electronic structure changes that were relevant to the OER activity, consequently affecting the measured activity of the first OER cycle, in line with ICP-MS studies discussed above (Figure 2). This observation is also consistent in the analysis of the extended X-ray absorption fine structure (EXAFS) region (details below).

In comparison to the pristine XANES spectrum of LSCoO-75, the pretreated and spent spectra showed decreased white-line intensities at 7726 eV and the appearance of a new intensity at 7730 eV, along with other subtle changes in the higher-energy region. Consistently, the pre-edge features (Figure 6b) also changed from the broad peak centered at \(\sim\)7710 eV in the pristine state to a slightly sharper peak that was downshifted in energy by 1 eV for the spent sample. The energy position at the half edge step downshifted by 0.1 eV over the three states (7722.0, 7721.9, and 7721.8 eV for the pristine, pretreated, and spent states, respectively, as shown in Figure S24 and Table S2), indicating a reduction in the average oxidation state of Co cations in spent LSCoO-75 consistent with EELS and XPS studies.

Changes in the local coordination environment for spent LSCoO-75 were also observed in the EXAFS spectra (Figure 6c,d). Major changes in the magnitude of the Fourier transform between the pristine and the spent samples included the presence of the second scattering peak in the 2–3 Å region, as well as the changes in magnitude of the first and second scattering peaks (Figure 6d). One common approach to analyzing subtle changes in XAS spectra is via probing the difference spectrum in R-space EXAFS.\textsuperscript{38,39} The difference between EXAFS spectra of (i) pretreated and pristine and (ii) spent and pristine for LSCoO-75 resembled each other in the overall shape (Figure 7), suggesting that a similar structural change occurred in both states, but to a different degree, in line with the XANES studies. The second peak centered at 2.5 Å in the Fourier-transformed difference spectra for both pretreated and spent samples (Figure 7b) was described by a Co−Co scattering path at 2.88 ± 0.01 Å, as indicated by a good-quality fit in both magnitude and imaginary portions of the EXAFS (Figure S25 and Table S3). This Co−Co path at a radial distance of 2.88 ± 0.01 Å can be assigned to edge-sharing Co−O octahedra, as this distance was significantly different from that of corner-sharing octahedra, evidenced by a Co−Co scattering path at \(\sim\)3.9 Å.\textsuperscript{38,39} The latter scattering path at a distance of \(\sim\)3.9 Å was present in the pristine LSCoO-75 (Table S6), validating the presence of corner-sharing octahedra in the \(\text{A}_2\text{BO}_4\) type R-P phase consistent with its crystal symmetry (Figure S1). The presence of a Co−Co distance of 2.88 ± 0.01 Å in the difference EXAFS spectra clearly hints at the structural reorganization of LSCoO-75 into a new phase after the OER. However, it is limited in identifying the exact phase(s) of the oxide that had formed.

To determine the identity of this emerging phase, an approach to constructing the XAS spectrum purely representing the new phase was adopted. Often used in the analysis of ultrafast X-ray transient absorption spectroscopy (XTA) data, the XTA spectrum obtained on a sample is always a mixture of the ground state and excited state(s).\textsuperscript{37–62} Since the ground-state spectrum is always known and the excited-state population at a certain time point can be obtained from other techniques, the spectrum representing only the excited-state spectrum can be obtained by subtracting the spectrum of the pristine oxide from those of the pretreated and spent samples (Figure 6a). This Co−Co difference spectrum for the pretreated and spent LSCoO-75 (phase uncorrected) for the pretreated and spent LSCoO-75. A k range of 3.6–11.0 Å\(^{-1}\) was used for the Fourier transform. The second shell centered at 2.5 Å is well described by the Co−Co scattering path (fit details are included in Figure S25 and Table S3 in the Supporting Information).
state species can be calculated. The analysis of the XAS data for LSCoO-75 can be approached in a similar manner. STEM imaging in Figure 4 and Figure S19 showed that LSCoO-75 exhibited dynamic changes in the near-surface region resulting in the formation of a Co-rich amorphous shell on top of the parent crystalline core. Thus, LSCoO-75 after pretreatment and OER testing can be represented as a mixture of the new phase and the pristine oxide. This relation can be expressed using eq 1, where x refers to fraction of pristine particle turning into the new phase:

\[
\text{spent} = (1-x)\text{(pristine)} + x\text{(new phase)}
\]

To begin with, the value of x was estimated by the volume change in the spent LSCoO-75 particles, based on the averaged values of particle diameters as well as with the assumption that the particles were spherical (in line with the particle morphology from STEM micrographs in Figures 1 and 4). Using eq 1 and x values ranging from 20 to 30%, several XAS spectra representing the new phase were constructed and evaluated (Figure S26). Figure 8 represents the constructed spectra showing a resemblance to Co–OOH as the emerging phase from oxide surface reconstruction, due to electrochemical pretreatment and OER cycling. The signature XANES features of Co–OOH, which included a pre-edge peak at 7710 eV and the white-line peak at 7730 eV, overlapped with the emerging features in the pretreated and spent LSCoO-75 samples (Figure 8a). This observation suggested the formation of Co–OOH phase after pretreatment and after OER. Having identified the nature of this new phase, a linear combination fitting (LCF) analysis was performed on the XANES spectra of pretreated and spent LSCoO-75 to better estimate the fraction of Co–OOH present (Figure 8a). The LCF spectra and the corresponding results are shown in Figure S27 and Table S4. These results indicated that spent LSCoO-75 was composed of ~25% Co–OOH and ~75% parent oxide, in good agreement with the estimation of the volume change from STEM analysis and ICP-MS studies (Figures 3d and 4). Similarly, an LCF analysis after the initial pretreatment indicated an ~10% change due to the formation of Co–OOH, in line with the amount of Sr dissolution measured using ICP-MS (Figure 2b).

The XANES of constructed spectra with 25% and 10% changes for spent and pretreated states, respectively, showed that the white-line features were well-aligned with that of Co–OOH. The EXAFS regions also exhibited an overall similarity to that of Co–OOH (Figure 8b). EXAFS spectra were adequately described using scattering paths generated from the Co–OOH crystal structure (crystallographic information file (cif) obtained from ref27), as shown in Figure S29 and Table S5. The pretreated spectrum showed coordination numbers (CN) of Co–O and Co–Co scattering paths that were smaller than the bulk values of 6 (Table S5). These numbers are reasonable for a Co–OOH layer that would be only a few nanometers thick in the pretreated state, as indicated by the small amount of Sr dissolution and ~10% change observed in the XANES region. For a thin near-surface layer, a large portion of Co atoms would be present as surface sites, consequently remaining undercoordinated. Conversely, the constructed EXAFS spectrum of spent LSCoO-75, which represented a thicker overlayer (thickness of 14 ± 1 nm based on STEM imaging, Figure 4), led to a CN value approaching the bulk values of 6 (Table S5).

The original EXAFS spectra of the pristine, pretreated, and spent states of the LSCoO-75 were analyzed, as shown in Figure 9a (details of the fits are shown in Figure S30 and Table S6). The spectra for the three states were well described with the four scattering paths generated from bulk LSCoO-75, with the addition of a Co–Co scattering path at 2.87 ± 0.02 Å that was ascribed to Co–OOH (Figure 9a). Good-quality EXAFS fits were obtained with CN values for the LSCoO-75 scattering paths remaining constant over all three states, while the contribution from the Co–Co scattering path at 2.87 ± 0.02 Å gradually increased from the pristine to the pretreated and spent spectra, as shown in Figure 9b. These studies clearly suggest that the Co-rich amorphous shell observed in STEM imaging (Figure 4) can be attributed to the formation of Co–OOH.

Similarly, the Co K-edge XAS spectra of Sr-containing Co-based ABO3 type perovskites, La0.25Sr0.75CoO3 and SrCoO3, were also analyzed for the spent states. Consistent with LSCoO-75, these two samples exhibited structural reorganization after OER, albeit to a lesser extent, as evidenced by subtle changes observed between the pristine and spent samples in the XAS spectra (Figure S31). This observation for the spent states of La0.25Sr0.75CoO3 and SrCoO3 was consistent with the lower amount of Sr dissolution in the electrolyte as measured.
LSCO-75, suggesting that they also restructured into CoLa0.25Sr0.75CoO3 and SrCoO3. The corresponding pristine spectrum and CoOOH, spent CoOOH during the OER. On the basis of the LCF analysis using di state, shown in Figure S32) for both samples resembled the LSCO-75 state. While the CNs of scattering paths from LSCO-75 structure are constant, the CNs of the Co–Co path representing the Co–OOH phase increases from the pristine to the spent state. The details of EXAFS fitting and the parameters are summarized in Table S6.

**Figure 9.** (a) Fourier-transform of k²-weighted EXAFS spectra of pristine, after pretreatment, and spent LSCO-75. The black and red curves represent the raw data and the fit, respectively. The contribution from the Co–Co scattering path at 2.87 ± 0.02 Å (Co–OOH) to the overall EXAFS fit is shown in green. (b) Change in the coordination numbers (CN) of all the scattering paths contributing to the EXAFS fit of each LSCO-75 state. The CNs of scattering paths from LSCO-75 structure are constant, the CNs of the Co–Co path representing the Co–OOH phase increases from the pristine to the spent state. The details of EXAFS fitting and the parameters are summarized in Table S6.

Further, the higher magnitude of change observed for LSCO-75 in comparison to La0.25Sr0.75CoO3 and SrCoO3 supports the hypothesis that A-site containing rock salt layers in n = 1 R–P oxides served as sacrificial layers promoting alkaline-earth-metal dissolution.

**2.5. Electrochemical Performance Compared to as-Synthesized Pure Oxyhydroxides**

To understand the similarities and differences between in situ generated Co–OOH structures (Co–OOH@A(n–1)CoO3 (n = 1 and n = ∞)) and as-synthesized bulk Co–OOH, their OER performances in O2-saturated purified 0.1 M KOH (Fe < 1 ppb) were compared (Figure S34). It was observed that in situ generated Co–OOH@LSCO-75 exhibited a >100× higher OER rate normalized per initial oxide surface area after 5 and 100 OER cycles as compared to as-synthesized Co–OOH (Figure S34f). Similarly, Co–OOH@La0.25Sr0.75CoO3 and Co–OOH@SrCoO3 exhibited >50× and 25× higher rates normalized per initial oxide surface area as compared to as-synthesized Co–OOH after 5 and 100 OER cycles, respectively. The high electrochemical activity of the in situ generated Co–OOH structures from the A(n–1)CoO3 (n = 1 and n = ∞) oxides when compared to as-synthesized Co–OOH supports the hypothesis that these structures expose a high number of active centers on geometrically confined oxide crystalline cores. The exposed active surface correlates with Sr2+ dissolution and can be tuned by modulating the oxide composition. This suggests that the initial oxide specific surface area is an underestimation of the in situ generated exposed active surface. To effectively normalize the rates, a quantification of the OER active surface area of these in situ generated, highly active oxyhydroxide shells on top of the parent nonstoichiometric mixed metal oxide core is needed and requires additional studies, which are beyond the scope of this work.

The stability of the in situ generated Co–OOH@LSCO-75 was also greater than that of as-synthesized Co–OOH. For instance, as-synthesized Co–OOH exhibited a 24.6 ± 1.3% loss in performance over 100 OER cycles, as shown in Figure...
Figure 10. Schematic representation of the electrochemical transformations leading to dynamic surfaces of nonstoichiometric mixed metal oxide electrocatalysts, illustrated using $n = 1$ R-P phase under oxidative OER potentials as an example. A, A’, and B represent rare-earth, alkaline-earth, and 3d transition-metal (TM) cations, respectively. (i) Initial state under no applied potential when the oxide surface cations are in contact with the OH$^-$ ions in the electrolyte. (ii) Dissolution of A’ alkaline-earth-metal cations (e.g., Ca, Sr) and oxidation of O$^{2-}$ lattice anions under oxidative OER potentials, resulting in surface restructuring and formation of an amorphous TM–OOH and A–OOH layer on the parent oxide crystalline core. (iii) The in situ generated TM–OOH surface serves as the catalytically active surface for the OER from water oxidation. General equations describing these transformations are also shown below each schematic.

S34d, in line with Co dissolution from the structure resulting in a loss of active centers in purified electrolytes (Fe < 1 ppb).\textsuperscript{40,49} In contrast, the in situ generated Co-OOH@LSCoO-75 (after 100 cycles under which performance improved by 29%) exhibited an additional 9.4% improvement in electrocatalytic performance over the next 100 cycles (200 overall OER cycles), as shown in Figure S34ef. No detectable levels of Co dissolution (detection limit for Co 0.2 ppb) were observed using ICP-MS for Co-OOH@LSCoO-75 over 200 overall OER cycles, suggesting the stability of Co cations in this structure. Similarly, La$_{0.25}$Sr$_{0.75}$CoO$_3$ and SrCoO$_3$ exhibited enhanced performance over 150 and 300 OER cycles, respectively, with no detectable levels of Co dissolution in the electrolyte solution (Figure S17). To explore the stability limit of the in situ generated Co-OOH@LSCoO-75, this electrocatalyst was tested over 1000 OER cycles. It was observed that Co-OOH@LSCoO-75 remained stable over cycling, as shown in Figure S35, with no detectable Co cation dissolution in the electrolyte. The improved stability of the in situ generated Co–OOH surfaces in comparison to as-synthesized Co–OOH could be due to the close interface with the crystalline parent oxide core. These studies clearly demonstrate that in situ generated Co–OOH surfaces from A$_{n}$Co$_{2}$O$_{3-n}$ (n = 1 and n = $\infty$) oxides are highly active over extended OER cycling, presenting an interesting and promising class of in situ generated active OER catalytic surfaces for OER.

2.6. Discussion on the Mechanism of Oxide Reconstruction

All of the studies reported above clearly demonstrate the irreversible dissolution of alkaline-earth-metal cations from highly OER active nonstoichiometric A$_{n}$B$_{2}$O$_{3-n}$ (n = 1 $\rightarrow$ $\infty$; B = Mn, Fe, Co, Ni) oxide electrocatalysts, albeit to different degrees depending on the initial value of n and oxide composition. On the basis of these studies, Figure 10 illustrates the electrochemical transformations that occur universally on A$_{n}$B$_{2}$O$_{3-n}$ (n = 1 $\rightarrow$ $\infty$) oxides during the OER in alkaline environments. In this schematic, n = 1 R-P phase (A$_2$BO$_4$) is used as the model system; however, the proposed electrochemical transformations extend to A$_{n}$B$_{n}$O$_{3n+1}$ oxides with n $\rightarrow$ $\infty$. Initially during rest, the clean oxide surface is in contact with OH$^-$ ions in the electrolyte (Figure 10(i)) with no thermochemical cation dissolution occurring prior to electrochemical testing. Under electrochemical oxidative potentials (as early as electrochemical pretreatment), lattice oxygen oxidation occurs (2O$_2$ $\rightarrow$ O$_2$ + 4e$^-$), resulting in metal cation dissolution, as illustrated in Figure 10(ii). Cation dissolution is dominated by that of alkaline-earth-metal cations, with B-site transition metal (TM) cation dissolution mainly being observed in the case of highly oxophilic metals, such as Fe and Mn. The rate of A’-site alkaline-earth-metal cation dissolution is dictated by (a) the overall A-site composition, with mixed A-sites leading to faster dissolution due to the mismatch in the ionic radii of the cations (i.e., Sr$^{2+}$ vs La$^{3+}$), (b) the oxide reducibility (metal–oxygen bond strength in the oxide), and (c) the inherent oxide crystal phase (i.e., n = 1 R-P vs n = $\infty$ perovskite). More stable rare-earth-metal cations (i.e., La) in the near-surface region potentially form amorphous A–OOH type species in the presence of abundant OH$^-$ cations, with a limited effect on the electrochemical activity. The nature of the restructured active OER surface is found to be independent of the initial A-site oxide composition or the value of n and is characterized by an amorphous TM oxyhydroxide (TM–OOH) shell on top of the crystalline oxide core (Figure 10(iii)).

3. CONCLUSIONS

In this study, we showed that alkaline-earth-metal cation containing mixed metal oxides (A$_{n}$B$_{n}$O$_{3n+1}$, n = 1 and n = $\infty$) independent of their composition or crystal phase (n = 1 or n = $\infty$) underwent surface restructuring as a consequence of alkaline-earth-metal cation dissolution into the electrolyte during OER, resulting in an in situ generation of an amorphous 3d transition metal (TM) oxyhydroxide shell on top of the parent oxide core. Oxide structural changes during OER were probed as a function of the oxide composition (A = La, Sr, Ca; B = Mn, Fe, Co, Ni) in the absence of meaningful Fe impurities in the electrolyte (Fe content <1 ppb). The extent of
A-site alkaline-earth-metal dissolution from the oxide was linked to (i) the oxide crystal phase, with \( n = 1 \) R-P phases exhibiting higher rates of dissolution as opposed to \( n = \infty \) perovskites, (ii) the oxide reducibility, and (iii) the lattice strain induced by the differences in the ionic radii of the rare-earth- and alkaline-earth-metal cations in mixed A-site compositions. The extent of B-site TM cation dissolution was significantly lower, with highly oxophilic metal cations such as Fe and Mn exhibiting higher dissolution in comparison to Co and Ni. Among all the oxide compositions reported here, alkaline-earth-metal-containing \( \text{A}_{x+1}\text{Co}_{3-x}\text{O}_{n} \) exhibited the highest improvement in OER performance as a consequence of restructuring, leading to electrochemical rates (normalized per physical surface area of the oxide) that were even higher than for as-synthesized bulk CoOOH. The stability of the in situ generated CoOOH surfaces from mixed metal oxide cores was demonstrated under extended OER cycling. The reported insights are critical in understanding the surface dynamics of nonstoichiometric mixed ionic–electronic conducting metal oxides under OER conditions and pave the way for the identification of effective design criteria for describing their OER performance.

4. METHODS

4.1. Synthesis of Oxides

The LSBO-75 oxides used in this study were synthesized via a previously reported citrate-based sol–gel approach.\(^{57,42}\) Appropriate stoichiometric amounts of \( \text{La(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) (Sigma-Aldrich, >99.999%) and \( \text{Sr(NO}_3\text{)}_2 \) (Sigma-Aldrich, >98%) were used as the precursors for the A-site in the LSBO-75 oxides. The precursors for the B-site transition metal were \( \text{Mn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (Sigma-Aldrich, >98%), \( \text{Fe(NO}_3\text{)}_2\cdot2\text{H}_2\text{O} \) (Sigma-Aldrich, >98%), \( \text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (Sigma-Aldrich, >98%), and \( \text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (Sigma-Aldrich). A 2 mmol equiv amount of the oxide composition was synthesized by dissolving appropriate amounts of the metal precursors in Millipore water (>18.2 MΩ cm). Citric acid (Anhydrous, Fisher Scientific, >99.5%) was used as the chelating agent to trap and disperse the metal cations. Subsequently, ethylene glycol was added as a complexing agent to complete this trapping process. The total metal ions: citric acid:ethylene glycol molar ratio was fixed at 1:1:1.5:1. This led to the formation of dissolved cations in a suspension network known as a sol. The pH of the resulting solution was adjusted to 9.0 via the addition of \( \text{NaOH} \) (Sigma-Aldrich, ACS grade) to aid in the complete deprotonation of the chelating agents. The resulting solution was simultaneously stirred and heated at 90 °C on a stir plate (350 rpm) to aid in the evaporation of water, consequently leading to the formation of a three-dimensional network of non-Newtonian type fluid, known as the gel. The formed gel was then transferred into an alumina crucible and burned in a box furnace (Carbolite) at 400 °C (3 °C min\(^{-1}\)) in air to aid in further dehydration and burning of residual hydrocarbons, leading to the formation of a network of metal cations. This precursor was crushed and calcined in either alumina or zirconia boats between 950 and 1100 °C (heating rate 5 °C min\(^{-1}\)) in a box furnace to aid in the formation of the targeted oxides. Specifically, the following temperatures were used to obtain phase-pure structures: (i) \( \text{LSMnO}_x\text{-75} \) (1100 °C; 5 h), (ii) \( \text{LSrFeO}_x\text{-75} \) (950 °C; 5 h), (iii) \( \text{LScCoO}_x\text{-75} \) (950 °C; 6 h), and (iv) \( \text{LSrNiO}_x\text{-75} \) (950 °C; 5 h). A similar method was adopted for the synthesis of \( \text{LSCoO}_x\text{-25} \) with the calcination temperature being 1150 °C (6 h) to achieve phase purity. The Co-based perovskites (\( \text{LaCoO}_x\text{, }\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_x \) and \( \text{SrCoO}_x \)) were synthesized using the same method as described above. \( \text{LaCoO}_x \) was calcined at 750 °C for 5 h, while \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_x \) and \( \text{SrCoO}_x \) were calcined at 950 °C for 5 h to obtain phase-pure structures.

As a control, CoOOH was synthesized using a simple soft-chemistry-based approach as described in a previous report.\(^{30}\) In this method, \( \text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) was used as the precursor salt to initially synthesize Co(OH)_2. A 80 mL portion of 0.05 M \( \text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) solution was prepared in Millipore water. Co(OH)_2 was precipitated by dropwise addition of 50 mL of 0.1 M \( \text{NaOH} \) (Sigma-Aldrich, >97%). The resulting solution was allowed to react at 45 °C for 2 h in an oil bath. Subsequently, the pink precipitate was collected and washed three times with Millipore water using centrifugation (4500 rpm; 3 min). The obtained Co(OH)_2 was resuspended in 40 mL of Millipore water and heated to 45 °C, followed by addition of 10 mL of 8 M \( \text{NaOH} \) solution to ensure complete precipitation of Co cations as Co(OH)_2. The Co cations in the formed Co(OH)_2 solution were oxidized from a +2 to a +3 valence state via addition of 4 mL of 30% \( \text{H}_2\text{O}_2 \) (Sigma-Aldrich). The resulting solution was allowed to react for 18 h at 45 °C. The final brown precipitate was dried overnight at 65 °C prior to crushing using a mortar and pestle.

4.2. Characterization

The phase purity of the as-synthesized, pristine samples was investigated using powder XRD studies, which were acquired using a Bruker D8 diffractometer equipped with a Cu Kα source (\( \lambda = 1.5406 \text{ Å} \)). XRD was obtained in a 2θ range of 20–80° with a step size of 0.01°. Atomic resolution HAADF-STEM and ABF-STEM micrographs and EEL spectra were obtained using a double Cs corrected JEOL 3100R05 electron microscope equipped with a cold field emission gun. An acceleration voltage of 300 keV was used for all these measurements. A Gatan double-tilt sample holder was used to align the particle along the zone axis. On the other hand, EDS mapping was performed using a Talos F200X electron microscope (Thermo Fisher Scientific, USA) equipped with a field emission electron source at an acceleration voltage of 200 keV. Further, Talos F200X electron microscope was equipped with Super-X EDS consisting of four windowless silicon drift (SDD) detectors (area of each detector: 30 mm\(^2\)) to aid in high sensitivity to all elements during elemental analysis. A Thermo Fisher NEXSA X-ray electron spectrometer equipped with a monochromatic Al Kα (1486.6 eV) x-ray source was used for all XPS studies. The samples were taped onto a Cu tape prior to analysis. A pass energy of 50 eV with a step size of 0.1 eV was used for all measurements. The sample was continuously sputtered with Ar+ ions to allow for charge neutralization. All of the spectra were background subtracted using the Shirley background and normalized to allow for comparison.

Brunauer–Emmett–Teller (BET) physical surface areas of these oxides were measured via \( \text{N}_2 \) adsorption/desorption isotherms at 77 K, using a Micromeritics ASAP 2020 adsorption analyzer. All oxide samples were degassed at 350 °C for 90 min prior to analysis. Note that CoOOH was degassed at 80 °C for 12 h due to its lower thermal stability in comparison to the nonstoichiometric mixed metal oxides. An Agilent 7700x ICP-mass spectrometer was used to determine the concentration of metal cations in the electrolyte. ICP-MS samples were prepared by treating the electrolyte (0.1 M KOH) from RDE studies in 65% \( \text{HNO}_3 \) (Omnifit, Millipore Sigma) in a 19:1 volume ratio. This ratio was chosen because it yielded a proton to \( \text{OH}^- \) concentration of \( \sim 6:1 \). The treated electrolyte was then mixed in a 4:6 volume ratio with 2% \( \text{HNO}_3 \) (Sigma) in a 19:1 volume ratio. This ratio was chosen because it yielded a proton to \( \text{OH}^- \) concentration of \( \sim 6:1 \). The treated electrolyte was then mixed in a 4:6 volume ratio with 2% \( \text{HNO}_3 \) solution (prepared by diluting 65% \( \text{HNO}_3 \) in Millipore water) for ICP-MS analysis. Calibration curves for ICP-MS studies were obtained using standard solutions (High-Purity Standards). These calibration studies were also used to establish the detection limits of the ICP-mass spectrometer. Additional details regarding identification of the detection limits of metal cations can be found in the Supporting Information.

Co K-edge XAS measurements were collected at beamline 9-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) at the SLAC National Accelerator Laboratory. Beamline 9-3 is a 16-pole, 2 T wiggler beamline with a vertically collimating mirror for harmonic rejection and a cylindrically bent mirror for focusing. The incident photon energy was selected by the liquid-N\( _2 \)-cooled, double-crystal Si(220) monochromator at a crystal orientation of \( \phi = 90° \). For these XAS measurements, the electrodes were prepared on a carbon paper via air spraying (details below). The electrodes were placed at a 45°
angle to the X-ray source. Ex situ XAS spectra were acquired in fluorescence mode using a passivated implanted planar silicon (PIPS) detector stationed at a 90° angle to the path of the incident X-ray beam. A beam size of 1 mm (v) by 2 mm (h) was used. N2-filled ion chambers were used to measure the incident X-ray intensity and the Co foil, which was simultaneously scanned in transmission mode for energy calibration. Four scans were obtained for each electrode to aid in signal averaging. The obtained raw data were processed using the Athena interface of the Demeter software package. The spectra were energy-calibrated, merged, and then normalized. The EXAFS spectra were extracted in k space and a Fourier transformation was conducted. The FT-EXAFS spectra were fit using the FEFF6 code on the Artemis interface of the Demeter package.

4.3. Electrochemical Measurements

Prior to any electrochemical measurement, all oxides were supported on conductive high-surface-area acid-treated Vulcan XC-72R graphitic carbon (Fuel Cell Store; BET surface area ~250 m² g⁻¹). As-received Vulcan XC-72R carbon was treated with concentrated HNO3 via refluxing at 80 °C for 12 h to remove all traces of metal impurities present in the carbon during its seeded growth synthesis. Acid treatment of the carbon was followed by washing it with copious amounts of Millipore water (~7–8 L) to neutralize the acidity.

Working electrodes of the oxide electrocatalysts were prepared by drop-casting slurries on a glassy-carbon support (Pine Research, 5 mm diameter) prior to electrochemical measurements. The slurries used for the drop-casted, composite electrodes were prepared by ultrasonication of a mixture containing a 5:1 mass ratio of the synthesized oxide and acid-treated graphitic carbon, in a solution of 2:1 volume ratio of Millipore water and 2-propanol (Sigma-Aldrich, >99.9%). 5 wt % Na Nafion solution (Ion Power) was used as the binder in these studies. The slight acidity of the Nafion binder was found to have minimal effect, as the pH of the ensuing slurry was ~7, consistent with previous reports. The glassy-carbon support was polished to a mirror finish progressively using 300 and 50 nm alumina slurries prior to drop-casting the slurry. The disk was also sonicated further in Millipore water and 2-propanol. The glassy-carbon support electrode was then placed in a Teflon tip (Pine Research), which was also cleaned via sonication in Millipore water and 2-propanol. The tip assembly was inverted and then dried by rotational air drying at 1600 rpm. Finally, 10 μL of the slurry was drop-casted on the inverted shaft assembly containing the glassy carbon support, followed by rotational drying of the ink at 700 rpm to aid in the formation of composite electrodes. The final amounts of the oxide catalyst, carbon, and Na Nafion were consistently set for all catalytic systems at 250, 50, and 50 μg cm⁻² geo, respectively.

All of the electrochemical activity measurements reported here were performed in a standard three-electrode system consisting of an RDE as the working electrode. 0.1 M KOH (Sigma-Aldrich, Semiconductor grade, >99.99%) was used as the electrolyte solution for these studies. Fe cationic impurities in the KOH electrolyte were removed using a previously reported method. Briefly, this method involved utilization of Ni(OH)₂ to absorb the Fe impurities in the KOH electrolyte. Ni(OH)₂ was synthesized via a coprecipitation method. Initially, ~750 mg of Ni(NO₃)₂·6H₂O was dissolved in 5 mL of Millipore water and precipitated with 20 mL 0.1 M KOH (>99.99% Semiconductor grade, Sigma-Aldrich). The precipitated Ni(OH)₂ was washed three times with Millipore water (4500 rpm for 5 min each). The synthesized Ni(OH)₂ was suspended in 1 M KOH and mechanically agitated overnight to absorb the Fe impurities. The resulting solution was centrifuged (14000 rpm for 15 min), and the supernatant KOH solution was collected for further analysis. The 1 M KOH solution was diluted to 0.1 M prior to all electrochemical studies. The Fe and Ni concentrations in the 0.1 M KOH solution were measured using ICP-MS and found to be <1 ppb prior to being used as the electrolyte in our studies. The Fe content in the electrolyte was also measured after all electrochemical measurements. The absence of Fe impurities was confirmed via ICP-MS studies, which indicated a Fe content of <1 ppb.

A Hg/HgO electrode in 20 wt % saturated KOH solution (Koslowsk Scientific Company) was used as the reference electrode, while a graphitic rod (Pine Research) was used as the counter electrode. Calibration of the Hg/HgO reference electrode against the RHE was performed using a Pt-coil (Pine Research) counter electrode in H₂-saturated 0.1 M KOH. The potentials in all electrochemical measurements were referenced to the Hg/HgO electrode but reported with respect to the RHE. All electrochemical measurements were corrected for the internal resistance (E – Egeo). The internal resistance was determined using high-frequency impedance studies. An internal resistance of ~50 Ohm was found for all of these studies and was subsequently used for iR correction. A custom-built 40 mL electrochemical cell with four openings to accommodate the gas bubbler, counter electrode, reference electrode, and working electrode was used for all activity measurements. Prior to electrochemical measurements, the oxides were pretreated by cycling 20 times in a potential region between 1.25 and 1.50 V at 100 mV s⁻¹. All CVs and LSVs were obtained at a scan rate of 10 mV s⁻¹ in O₂-saturated purified 0.1 M KOH at 1600 rpm and were obtained in triplicate to ensure reproducibility of the data. The long-term testing experiments (100 cycles) were performed using repeated CVs in a potential range of 1.1–1.7 V at 1600 rpm and a scan rate of 10 mV s⁻¹. In the case of 100-cycle stability testing for LSCoO-75, the electrolyte was replaced after 500 cycles to avoid artifacts in the electrochemical measurements due to changes in the OH⁻ concentration altering the pH. The electrochemical measurements were also benchmarked using commercial IrO₂ (Alfa Aesar, 99.99% purity) as a standard for OER (Figure S36).

The electrodes used for XAS and STEM studies were prepared via air-spraying the same slurry onto a carbon-paper electrode (Fuel Cell Store, Toray 030), as reported previously. We note that, for all of the characterization studies in this section, larger electrodes (1.5 × 1.5 cm²) with a higher oxide loading (loading 500 μg cm⁻² geo) were used to mimic the RDE setup. The ratio of mass of oxide electrocatalyst on the electrode to the volume of electrolyte was kept similar to that of the RDE studies. The oxides were characterized when the amounts of Sr dissolution from these electrodes were similar to the measured values after the first five cycles of the OER on an RDE system.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00359.

Crystal symmetries, XRD patterns, STEM micrographs, physical surface areas, electrochemical performance of oxides, EDS mapping of oxides, ICP-MS analyses, XPS studies, and additional XAS data (PDF)

AUTHOR INFORMATION

Corresponding Authors

Simon R. Bare — Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States; orcid.org/0000-0002-4932-0342; Email: srbare@stanford.slac.edu

Eranda Nikolla — Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan 48202, United States; orcid.org/0000-0002-8172-884X; Email: erandan@wayne.edu

Authors

Samji Samira — Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan 48202, United States; orcid.org/0000-0002-7147-5340
Jiyan Hong — Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

John Carl A. Camanyang — Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan 48202, United States

Kai Sun — Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States

Adam S. Hoffman — Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

Complete contact information is available at:
https://pubs.acs.org/10.1021/jacsau.1c00359

Author Contributions

S.S. and J.H. contributed equally.

S.S. and E.N. conceived the idea. E.N. supervised the overall project. J.C.A.C. assisted S.S. with synthesis and electrochemical, XPS and ICP-MS studies. S.S. and J.H. acquired XAS data with help from A.S.H. and S.R.B. XAS data were analyzed by J.H. with assistance from A.S.H. and S.R.B. STEM imaging and analysis was performed by K.S. and S.S. The manuscript was written by S.S., J.H., S.R.B., and E.N. All authors commented on the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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