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#### Article

# *Ex Situ* and *In Situ* Analyses of the Mechanism of Electrocatalytic Hydrogen Peroxide Production by $Co_xZn_{1-x}O$ (0 < x < 0.018) Materials in Alkaline Media

Joselyn Del Pilar Albadalejo, Suheily Alonso-Sevilla, Nicohl I. Cintrón, Xinran Feng, Angel D. García, Dinorah D. Martínez-Torres, Astrid M. Rodríguez, Natalia I. Román-Montalvo, José I. Torres, Yao Yang, Armando Peña-Duarte, Rahul Singhal, Louise M. Debefve, Christopher J. Pollock, Carlos R. Cabrera, Héctor D. Abruña, and Mitk'El Benedikt Santiago-Berríos\*



onset potentials near 649 mV, followed by the two-electron ORR mechanism. *Ex situ* X-ray absorption spectroscopy experiments at the Co K-edge demonstrated the presence of Co(II) ions at tetrahedral sites within the ZnO lattice.

**KEYWORDS:** oxygen reduction reaction, zinc oxide, metal oxide, in situ X-ray spectroscopy, ex situ X-ray spectroscopy, metal oxide–electrolyte interface

## INTRODUCTION

Hydrogen peroxide  $(H_2O_2)$  is an alternative energy carrier to oil, natural gas, and hydrogen fuel for sustainable energy applications.<sup>1–5</sup> However, current  $H_2O_2$  production is energyintensive, as it is manufactured by the catalytic oxidation of hydrogen with atmospheric oxygen using anthraquinone as the catalyst. The four-step process includes hydrogenation on a palladium catalyst between hydrogen and anthraquinone, which produces anthrahydroquinone as an intermediate. This multistep process involving a Pd catalyst could be improved by performing direct electrocatalytic production. The direct electrochemical production of  $H_2O_2$  provides a cost-effective in-house generation alternative<sup>5,6</sup> but requires a high performing catalyst with good selectivity and stability.

Oxide-based diluted magnetic semiconductors are a class of materials in which the properties of a semiconductor host are modified by the magnetic effects of a dopant impurity. Transition-metal dopants, such as Fe, Mn, Co, Ni, and V, hybridize with the semiconductor host *via* sp-d exchange

interactions, giving rise to new properties, thus allowing band gap tuning, which in turn increases the electrocatalytic properties.<sup>7</sup> This effect has been observed in Co-doped zinc oxide.<sup>8–10</sup> Zinc oxide (ZnO) is an n-type direct semiconductor with a wide band gap energy of 3.37 eV at room temperature and large exciton energy of 60 meV.<sup>11</sup> Doping of Co<sup>2+</sup> in ZnO has been shown to produce an intense UV absorption peak at 3.84 eV and weak bands in the visible region (1.8–2.4 eV) owing to the incorporation of cobalt into the tetrahedral sites.<sup>9,12,13</sup> Furthermore, Co-doped ZnO has been reported to catalyze the oxygen reduction reaction (ORR) in alkaline media when combined with reduced graphene oxide.<sup>14</sup>

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Herein, we study the electrocatalytic activity of carbon-free  $Co_xZn_{1-x}O$  (0 < x < 0.018) materials toward the two-electron ORR pathway to produce hydrogen peroxide ( $H_2O_2$ ). We report the effect of Co-doping concentration on the intrinsic ORR catalytic activity by studying the valence state changes in Co K-edge X-ray absorption spectroscopy (XAS) during the production of  $H_2O_2$  under *in situ* conditions.

## 2. METHODOLOGY

**2.1. Materials.** All materials were obtained from Fisher Scientific and used as received. A typical synthesis used zinc nitrate hexahydrate  $[Zn(NO_3)_2 \cdot 6H_2O]$  (98% extra pure, ACROS Organics), cobalt(II) nitrate hexahydrate  $[Co-(NO_3)_2 \cdot 6 H_2O]$  (99%, pure, ACROS Organics), sodium hydroxide (NaOH), and 95% pure ethanol (190 proof). The solutions were prepared with deionized water (18.2 M $\Omega$  cm, Nanopure Diamond, Barnstead).

2.2. Methods. 2.2.1. Synthesis of ZnO and Co-Doped ZnO Nanoparticles. Pure ZnO was prepared by bringing 50 mL of 0.45 M zinc nitrate to a constant temperature of 65  $^\circ \text{C}$ and adding 50 mL of 0.9 M NaOH solution dropwise (using deionized water as the solvent). Upon addition, a white precipitate was formed. The reaction was then cooled to room temperature, stirred for 30 min, and maintained undisturbed for 2 h. The white solid was filtered and washed with 200 mL of deionized water and 200 mL of 95% ethanol. Finally, the precipitate was dried at room temperature in a desiccator for 24 h before annealing at 300 °C for 3 h. Co-doped ZnO materials were synthesized in a similar manner by adding 0.90 M NaOH dropwise to 50 mL of a stock solution containing varying concentrations of cobalt nitrate and 0.45 M of zinc nitrate. A light blue to deep green suspension (with the precipitate product) was obtained. The greenish solution was characteristic of a higher cobalt content. The aqua green precipitate was stirred at room temperature for 30 min and maintained undisturbed for 2 h upon reaching the room temperature. The precipitate was vacuum-filtered and washed three times with 200 mL of distilled water and finally with 200 mL of ethanol, 95%. The concentration of the doped materials was determined using energy-dispersive X-ray fluorescence, showing the following concentrations on cobalt content per weight: 0.255% (Co<sub>.003</sub>Zn<sub>.997</sub>O), 0.554% (Co<sub>.006</sub>Zn<sub>.994</sub>O), and  $1.560\%(Co_{.018}Zn_{.982}O).$ 

2.2.2. ZnO and Co-Doped ZnO Characterization. Powder X-ray diffraction (XRD) of as-synthesized samples was performed using a Rigaku Miniflex X-ray diffractometer (Cu  $K\alpha$  line 1.5418 Å: power of 40 kV and 40 mA). The sample was pulverized and packed into the sample holder. Diffractograms were recorded at a scan rate of  $2^{\circ}$ /min from 20 to  $80^{\circ}$  of the  $2\theta$  angle. Raman spectroscopy was performed using a Renishaw inVia micro-Raman system using a 488 nm laser and a 2400 lines/mm grating. The samples were deposited on a quartz sample holder, forming a uniform pulverized film. We recorded the Raman spectra from 300 to 650 cm<sup>-1</sup> in a dark room. A FEI Tecnai G2F20 TEM/STEM system, 200 kV, with an Oxford X-Max detector (at the Cornell Center for Materials Research Shared Facilities) was used to record the micrographs. The samples were prepared by placing a drop of dispersed catalyst on the surface of a carbon-coated copper grid and dried at room temperature. Diffuse reflectance was measured using a Shimadzu UV-vis NIR 3600 spectrophotometer using a reflectance sphere attachment. For elemental analysis, we used an energy-dispersive X-ray fluorescence

(XRF) spectrometer. Approximately 1.0 g of sample was put on a polypropylene XRF cuvette covered with a polypropylene TF-240 film (4  $\mu$ m thickness). The Co<sub>x</sub>Zn<sub>(1-x)</sub>O sample spectra were acquired using a Rigaku NEX DE VS benchtop EDXRF spectrometer. This equipment has a primary Ag anode X-ray tube and a high-performance fast silicon drift detector. The operational parameters for the X-ray tube were 35 kV and 40  $\mu$ A. The measurement time at the XRF chamber was at 100 s per sample in an air atmosphere.

2.2.3. ORR Activity. Electrochemical measurements were performed in a 1.0 M KOH solution using a Gamry Reference 600 potentiostat/galvanostat. All electrochemical measurements were performed using 5 mg of catalyst per milliliter of 0.05% Nafion/ethanol ink. The catalyst was dispersed in the Nafion/ethanol solution by sonicating for 30 min. A 5  $\mu$ L aliquot of ink was loaded onto a rotating glassy carbon electrode, followed by thermal evaporation under infrared light. A graphite rod was used as the counter electrode, and Ag/AgCl (3 M KCl) was used as the reference electrode. ORR electrocatalysis was performed using a rotary disk electrode in oxygen-saturated 1.0 M KOH solution. Linear sweep voltammetry was performed at 5 mV/s and at constant 1600 rpm. Electrochemical potentials are reported versus the reversible hydrogen electrode (RHE), taking into account the pH of the solution (around pH = 14). Background current was measured in nitrogen-saturated KOH solution.

2.2.4. Rotating Ring Disk Electrode Experimental Methods.  $Co_{.006}Zn_{.994}O$  material catalyst inks were prepared by mixing 1 mg of the  $Co_{.006}Zn_{.994}O$  material with 1 mL of DI water, 1 mL of isopropanol, and 10 mL of Nafion solution. The mixture was homogenized under ultrasound for 1 h. Afterward, 2 mL of the prepared  $Co_{.006}Zn_{.994}O$  ink was added on a cleaned electrode surface and dried at room temperature for 30 min. The hydrodynamic rotating ring disk electrode (RRDE) analysis was completed by running the  $Co_{.006}Zn_{.994}O$ -modified glassy carbon disk and a Pt ring in 1 M KOH. The potential was swept between 200 and -1000 mV versus Ag/AgCl/sat. KCl at a scan rate of 10 mV/s. The ring potential was fixed at 1600 rpm.

2.2.5. Ex Situ XAS Experiments. Ex situ Co K-edge XAS experiments were carried out at the beamline for materials measurements (BMM) 6-BM at the National Synchrotron Light Source II (NSLS II) facility at Brookhaven National Laboratories. The reference used for this type of analysis was a Co metal foil (7709 eV). For this analysis, we chose the sample Co<sub>.006</sub>Zn<sub>.994</sub>O (the sample that showed the highest activity toward ORR, vide infra) and ground it with a mortar and pestle until finely milled. The powder was then evenly spread onto a Kapton tape until achieving a homogeneous film. The Co K-edge absorption spectra were collected in transmission mode and later analyzed using the DEMETER and Larch program packages<sup>15,16</sup> and following standard procedures described elsewhere.<sup>17</sup> The analysis of the data was performed by subtracting the background obtained from the same set of data. Determination of the pre-peak and analysis of the X-ray absorption near edge structure (XANES) spectra were performed using the pseudo-Voigt model to determine the pre-peak energy. The cobalt K-edge position was determined by performing a linear combination of different measurements from the same experimental conditions and applying the regression model. Extended X-ray absorption fine structure (EXAFS) data were analyzed using the cif files acquired from

the Materials Project Web site. We used CoO (mp-19079) and ZnO (mp-2133) cif files to fit the data obtained from BNL.

2.2.6. In Situ XAS Experiments. In situ XAS data were collected at the photon-in photon-out X-ray spectroscopy (PIPOXS) beamline at the Cornell High Energy Synchrotron Source (CHESS) under the ring conditions of 50 mA at 6 GeV. The beam was provided by a 52-pole Cornell Compact Undulator and was energy-selected using a cryogenically cooled Si(111) monochromator. Harmonic rejection and focusing were achieved using a pair of cylindrically bent Rh-coated focusing mirrors. The sample (preparation detailed *vide infra*) was housed at room temperature in a custom electrochemical cell<sup>18,19</sup> and was placed at 45° relative to the incident beam; data were collected from 7550 to 7850 eV in fluorescence mode using a four-element vortex detector. Incident beam energy was calibrated using the first inflection point of a Co metal foil (7709.0 eV).<sup>18,19</sup>

For a typical experiment, the sample was prepared by modifying a carbon cloth working electrode with a thin film of  $Co_{.006}Zn_{.994}O$ . A piece of carbon paper with 200  $\mu$ m thickness was cut to dimensions of 1 cm  $\times$  8 cm. The ink was prepared by sonicating 10 mg of the sample in 1 mL of Nafion 5% alcohol solution for 15 min. To achieve a thin layer of the sample on top of the carbon cloth, 200  $\mu$ L of the ink was dropcasted in an area of 1 cm  $\times$  1 cm at one end of the carbon cloth. This ensured that the sample correctly occupied the window of the electrochemical cell. The carbon paper was placed under a heating lamp for a few minutes until the ink completely dried. The electrochemical cell was made of PEEK<sup>18</sup> and was fully assembled with the prepared electrode and filled with a 0.1 M KOH solution. Before any electrochemical measurement, the electrochemical cell was treated with nitrogen gas for 30 min to remove oxygen from the system. An Ag/AgCl reference saturated NaCl (ag) electrode and a carbon counter electrode were then inserted to the cell after all air was removed.

#### 3. RESULTS AND DISCUSSION

**3.1. Structural Characterization of ZnO and Co<sub>x</sub>Zn**<sub>(1-x)</sub>**O Samples.** The XRD patterns of  $Co_xZn_{(1-x)}O$  samples (Figure 1) show a hexagonal wurtzite structure, characteristic of the zinc oxide framework.<sup>10,20,21</sup> Figure 1 shows the characteristic wurtzite diffraction peaks located at 31.8, 34.6, and 36.4°, which correspond to the Miller indexes 100, 002, and 101 for pure ZnO. As can be observed, the diffraction peaks of the doped materials are shifted toward lower  $2\theta$  angles.<sup>22</sup> The *d*-spacing of peaks well matched with the Miller indexes of the wurtzite structure, as determined by the standard CCDC database.<sup>22</sup> The samples are highly crystalline, and no trace of impurities was detected by XRD.

The lattice parameters for pure ZnO and cobalt-doped ZnO were calculated from the XRD data. The calculated lattice parameters of pure ZnO obtained from the experimental data were a = b = 3.03 Å, and c = 5.19 Å.<sup>22</sup> As cobalt ions are incorporated within the unit cell (see Table 1), the lattice parameters increase up to a = b = 3.13 Å, and c = 5.33 Å. These changes in the lattice parameters are less than 5%, and we did not detect metal agglomerates or secondary phases in the XRD analysis.

The phase purity and possible defects in the synthesized materials were studied using Raman spectroscopy. The wurtzite structure of ZnO, which corresponds to the hexagonal Bravais lattice, has been solved in the previous literature using



**Figure 1.** Powder XRD diffractograms of ZnO and those of ZnO doped with Co ions at different loading levels. Upon the intercalation of cobalt ions into the ZnO framework, we observed shifts toward lower  $2\theta$  angles due to the intercalation of the foreign ions into the unit cell.

Table 1. Lattice Parameters as Obtained from the XRD Data from Figure  $1^a$ 

lattice constants				
a = b	с	sample		
3.032	5.187	ZnO		
3.122	5.318	Co.003Zn.997O		
3.112	5.313	Co <sub>.006</sub> Zn <sub>.994</sub> O		
3.127	5.327	Co.018Zn.982O		
3.289	5.307	ZnO ref		
<sup>a</sup> The reference is mp-2133 from the Materials Project Web site. <sup>22</sup>				

a  $C_{6\nu}$  point group by using symmetry with an irreducible  $\Gamma = 2A_1 + 2B_1 + 2E_1 + 2E_2$ .<sup>23–26</sup> Figure 2a shows the Raman spectra of ZnO and  $Co_xZn_{(1-x)}O$  samples. As observed by Gandhi,<sup>23</sup> the  $A_1(LO)$  vibrational mode at 550 cm<sup>-1</sup> increases with increasing Co concentration, shadowing the second  $E_1(LO)$  vibrational mode, which becomes a shoulder at higher concentration ratios. Meanwhile, the  $E_2(high)$  vibrational mode around 445 cm<sup>-1</sup> decreases in intensity upon increasing the cobalt concentration.<sup>26</sup> These changes in the Raman spectra are in agreement with those reported in the literature, suggesting that cobalt ions occupy tetrahedral holes within the unit cell, confirming only a single phase within the sample.<sup>23,27</sup>

Transmission electron microscopy (TEM) data of the samples (Figure 3) were analyzed to investigate the uniformity and the doping effects of the cobalt species. The image of Co<sub>.003</sub>Zn<sub>.997</sub>O showed particles with sizes smaller than 250 nm; they possessed different morphologies and a tendency to form rods. However, the samples with higher cobalt concentrations showed particles with sizes smaller than 100 nm. All samples are highly crystalline, confirming the data obtained from XRD (Figure 1). The *d*-spacing for  $Co_{.003}Zn_{.997}O$ ,  $Co_{.006}Zn_{.994}O$ , and Co<sub>018</sub>Zn<sub>982</sub>O was calculated from the lattice plane fringes using the image processing software ImageJ. The calculated dspacing was found to be 0.28 nm for all three samples, which corresponds to the (100) crystal plane in wurtzite ZnO. The vertical aggregates of the particles will contribute to the appearance of "pockets" of cobalt in Figure 3g; however, this is an effect of particle stacking.



Figure 2. Raman spectra of ZnO and  $Co_x Zn_{(1-x)}O$  at different Co doping levels. The inset shows the region of the A1 and E1 vibrational modes around 550 cm<sup>-1</sup>.



Figure 3. High-resolution TEM micrographs of  $Co_{.003}Zn_{.997}O$  (a),  $Co_{.006}Zn_{.994}O$  (b), and  $Co_{.018}Zn_{.982}O$  (c). Elemental mapping (d-g) of  $Co_{.006}Zn_{.994}O$ .

Elemental mapping of zinc, cobalt, and oxygen of  $Co_{.006}Zn_{.994}O$  (Figure 4d–g) shows an evenly distributed composition within the sample.

**3.2. Diffuse Reflectance Spectroscopy.** The effect of cobalt ion incorporation on the band gap energy of doped zinc oxide materials was studied using diffuse reflectance spectroscopy. Figure 4 shows the diffuse reflectance spectra and the Tauc plots of the prepared materials. The diffuse reflectance spectra show new bands around 560, 600, and 660 nm that are not present in pure ZnO, indicating an effect by the cobalt

dopant within the ZnO matrix. Similar results were observed by Lu and co-workers and in other studies as well.<sup>28–30</sup> From the Tauc plots and by performing the Kubelka–Munk analysis, we determine the band gaps of the doped materials, taking into account the linear portion of the curve. As the concentration of cobalt increases in the ZnO wurtzite structure (Table 1), we observe a decrease in band gap energy from 3.2 eV (pure ZnO) to 1.98 eV for Co<sub>.018</sub>Zn<sub>.982</sub>O, thus further confirming the cobalt doping of ZnO (Table 2).<sup>8,9</sup>

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Figure 4. Diffuse reflectance spectra and corresponding Tauc plots of  $Co_x Zn_{(1-x)}O$  materials at different cobalt concentrations.

Table 2. Band Gaps of the Doped Materials, as Determinedfrom the Tauc Plot in Figure 4

sample	band gap determined in the Tauc plot, eV
Co.003Zn.997O	2.86
Co.006Zn.994O	2.73
Co.018Zn.982O	1.98

**3.3. RRDE Results and Analysis.** Figure 5a (bottom lines) shows the linear sweep voltammetry for the ORR kinetics of the  $Co_xZn_{1-x}O$  material, determined with the RRDE technique in  $O_2$ -saturated 0.1 M KOH. The disk current ( $I_{disk}$ ), at potentials between 600 and 0 mV, is attributed to  $O_2$  reduction. The  $I_{disk}$  and  $I_{ring}$  values are determined for the samples  $Co_{.003}Zn_{.997}O$  (gray),  $Co_{.006}Zn_{.994}O$  (blue), and  $Co_{.018}Zn_{.982}O$  (red), respectively. The  $E_{onset}$  potentials of the ORR appear near 649, 640, and 638 mV versus RHE, and a partial diffusion-limited behavior is observed between 352 and 469 mV versus RHE for all the samples.<sup>27</sup>  $Co_xZn_{1-x}O$  diffusion-limited current increases as the potential progresses to more negative values between 352 and 0 mV versus RHE.

The ring current  $(I_{ring})$  is plotted in Figure 5a (top lines) with data collected simultaneously during the hydrodynamic RRDE study.  $I_{ring}$  is associated with the H<sub>2</sub>O<sub>2</sub> formation–

degradation process. The  $H_2O_2$  selectivity (%  $H_2O_2$ ) and the electron transfer number (*n*) were calculated as follows<sup>5,31</sup>

$$\% H_2 O_2 = 200 \left( \frac{I_{\text{ring}}/N}{I_{\text{disk}} + I_{\text{ring}}/N} \right)$$
(1)

$$n = \left(\frac{4I_{\rm disk}}{I_{\rm disk} + \frac{I_{\rm ring}}{N}}\right) \tag{2}$$

where  $I_{\text{ring}}$  is the ring current,  $I_{\text{disk}}$  is the disk current, and N is the collection efficiency.

Figure 5b evidenced *n* values of 3.2, 3.0, and 2.8 for the samples  $Co_{.003}Zn_{.997}O$ ,  $Co_{.006}Zn_{.994}O$ , and  $Co_{.018}Zn_{.982}O$ , respectively. The  $H_2O_2$  production is of about 40, 50, and 60% at a potential window between 600 and 350 mV *versus* RHE is shown in Figure 6c. The RRDE analysis reflects that  $Co_xZn_{1-x}O$  produces a high fraction of hydrogen peroxide intermediate at potentials between 600 and 350 mV *versus* RHE; the sample  $Co_{.006}Zn_{.994}O$  produced the highest concentration of peroxide (60%). Moreover, as the applied potential is swept below 300 mV *versus* RHE, the hydrogen peroxide percentage began to decrease, reaching just 49% at 20



**Figure 5.** Data collected during the hydrodynamic RRDE study of  $Co_xZn_{1-x}O$  for the ORR as a function of  $E_{disk}$  vs RHE. (a) Plot of the disk current,  $I_{disk}$ , and ring current,  $I_{ringy}$  for the samples  $Co_{.003}Zn_{.997}O$  (gray),  $Co_{.006}Zn_{.994}O$  (blue), and  $Co_{.018}Zn_{.982}O$  (red). (b) Number of electrons (*n*) involved in the ORR. (c) Concentration of hydrogen peroxide (% w/w). The RRDE analysis was completed by testing the  $Co_xZn_{1-x}O$  ink on a glassy carbon disk and Pt ring in 0.1 M KOH. The scan rate was 10 mV/s, the Pt ring potential was fixed at 234 mV vs Ag/AgCl/4M-KCl, and the RRDE rotation speed was 1600 rpm.



Figure 6. XANES (a) and EXAFS  $k^{2*}\chi$  (b) with the corresponding Fourier transforms (c) for Co<sub>.006</sub>Zn<sub>.994</sub>O. The statistical analysis of the materials appears in Table 2.

mV versus RHE. It could be suggested that the  $Co_xZn_{1-x}O$  material starts promoting the reactions  $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$  and  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ , simultaneously increasing the formation of water over peroxide as the potential is scanned toward more negative values.

3.4. Ex Situ XAS Experiments. Comprehensive XAS measurements have been analyzed in detail elsewhere.<sup>8</sup> For the focus of this study, we wanted to understand in detail the geometric structure and chemical nature of cobalt before performing any in situ measurements. The XANES region provides information on the oxidation state of the metal ions, while EXAFS gives quantitative information about the metalligand bond lengths. The XANES spectrum appears in Figure 6, showing the Co K-edge. The Co K-edge was determined at  $7721 \pm 1$  eV, which can be consistent for Co(II) species, as discussed elsewhere.<sup>32</sup> The presence of a pre-peak at 7709.26  $\pm$  0.08 eV, characteristic of 1s-3d electronic transitions, is identified.<sup>32</sup> The features centered at 7738 and 7740 eV (marked with \*) provide further evidence for Co(II) substitution into the ZnO wurtzite structure, as described elsewhere.<sup>8,10</sup>

The *k*-weighted and the Fourier-transformed EXAFS demonstrate a signature character of the material's wurtzite structure in accordance with previous studies.<sup>8,9,12,13,25,28,33,34</sup> Further analysis using the Larch<sup>20</sup> and Athena software<sup>21</sup> allowed for the quantification of the interactions between Co and its nearest neighbors (see Table 3)<sup>15,16</sup> Each shell was analyzed by using CoO and ZnO cif files separately to determine the parameters that appear in Table 3.

The data from Table 3 confirm that the cobalt species in the ZnO wurtzite structures is located at tetrahedral sites, as its four atoms coordinated at the metal site.<sup>22</sup>

**3.5.** *In Situ* XAS Measurements. We performed steadystate measurements by applying a constant potential and collected the X-ray fluorescence at the cobalt K-edge. We

Table 3. EXAFS Analysis Using CoO and ZnO Cif Files (mp-19079 and mp-2133) to Fit the Data<sup>a</sup>

shell	distance (Å)	coordination number	$\sigma$ (Å)
Co-O	$1.9 \pm 0.2$	$4.27 \pm 0.03$	$0.005 \pm 0.003$
Co-Zn	$3.33 \pm 0.04$	$8.47 \pm 0.02$	$0.02 \pm 0.01$
<sup><i>a</i></sup> The cif files	were obtained	from the Materials Pro	oject database. <sup>22</sup>

focused our attention on X-ray fluorescence as the concentration of cobalt ions was too low to be detectable in transmission mode. The obtained XANES spectra in Figure 7 are measured at different applied potentials under nitrogen, which resemble the XANES spectra previously presented in Figure 6. The XANES spectra show that the intensity of the K edge is barely changed upon more reductive potentials. Upon  $O_2$  saturation, we observe ORR activity. However, in the XANES spectra in Figure 7 (right), we do not see a change in the energy of the cobalt K-edge as a function of the applied potential, indicating that the bulk Co oxidation state remains unchanged on the timescale of the experiment.

#### 4. DISCUSSION

The synthesis of zinc oxide doped with low concentrations of cobalt intake was analyzed in this study. The characterization of the doped materials determines its purity; furthermore, we analyzed the electrocatalytic properties toward the formation of hydrogen peroxide. Our RRDE studies demonstrated that the mechanism favors the formation of hydrogen peroxide species at the electrode surface, suggesting that they follow the same mechanism as Suntivich and collaborators suggested for perovskite metal oxides.<sup>35</sup> However, when we perform *in situ* XAS at different constant potentials in the presence and absence of oxygen, we do not observe a dramatic change in the oxidation state of the cobalt species. This might suggest that cobalt might not be accessible for the hydrogen peroxide



**Figure 7.** Left: XANES spectra of a carbon cloth electrode modified with  $Co_{.006}Zn_{.994}O$  at different constant potentials in the *in situ* electrochemical cell saturated with nitrogen. Spectra are vertically offset for clarity and normalized to the maximum of the white line absorption. Right: XANES spectra of the same modified carbon cloth with  $Co_{.006}Zn_{.994}O$  at different constant potentials. Spectra are normalized to the maximum of the white line feature and are vertically offset to allow for better comparison. The vertical dashed lines are provided as a visual aid and are centered at the first edge inflection and maximum of the white line for the 0.1 V spectrum.

formation at the electrode surface and also suggest that zinc sites are more responsible to bind with hydroxyl groups before the electrochemical reaction takes place. This possibility could indicate that there is a synergy between zinc and cobalt sites to catalyze the hydrogen peroxide formation.<sup>10</sup> Rong and coworkers observed synergy in cobalt oxides materials doped with zinc ions, while studying the photocatalysis of water oxidation. In their study they observed that water oxidation can be promoted using Zn centers as water absorption sites and cobalt centers as water oxidation sites. We believe that could be a similar situation at the electrode surface. The Zn centers are hydroxyl group absorption sites, and cobalt centers lower the over potential facilitating hydrogen peroxide production at the electrode surface. Future in operando experiments will determine if a synergy within the unit cell facilitates the ORR mechanism by positioning the hydroxyl groups within nearzinc sites.

## 5. CONCLUSIONS

We investigated the electrocatalytic H<sub>2</sub>O<sub>2</sub> production of zinc oxide doped with different concentrations of cobalt ions. Three doping concentrations, 0.25% (Co.003Zn.997O), 0.55% (Co.006Zn.994O), and 1.56% (Co.018Zn.982O), were obtained using a co-precipitation method. The material's selectivity toward H<sub>2</sub>O<sub>2</sub> production was assessed using RRDE measurements. The  $E_{\text{onset}}$  potentials of the ORR appear near 649, 640, and 638 mV versus RHE for Co<sub>.003</sub>Zn<sub>.997</sub>O, Co<sub>.006</sub>Zn<sub>.994</sub>O, and Co<sub>.018</sub>Zn<sub>.982</sub>O respectively. These potentials represent a 14% improvement over those potentials previously reported for similar materials.<sup>26</sup> The highest selectivity toward hydroperoxide production was observed for Co.006Zn.994O, with 60% H<sub>2</sub>O<sub>2</sub> produced. This finding suggests that there is a maximum doping level that can promote selective ORR via a two-electron mechanism. Cobalt ion incorporation into the ZnO lattice was confirmed by an increase in lattice parameters along with

changes in Raman vibrational modes  $A_1$  (LO) and  $E_2$  (high). A shift in optical band gap from 3.2 eV (ZnO) to 2.86, 2.73, and 1.98 eV for samples  $Co_{.003}Zn_{.997}O$ ,  $Co_{.006}Zn_{.994}O$ , and  $Co_{.018}Zn_{.982}O$ , respectively, is produced as a result of cobalt doping. The XRD patterns of all three samples showed no secondary phases. *Ex situ* XAS analysis confirms that cobalt ions hold a 2+ oxidation state and are located in tetrahedral sites within the wurtzite structure. In order to address the cobalt participation in  $H_2O_2$  production, we performed *in situ* XAS measurements by applying electrochemical potentials and monitoring the cobalt K-edge energy. We did not observe any changes in the cobalt K-edge energy.

## AUTHOR INFORMATION

#### **Corresponding Author**

Mitk'El Benedikt Santiago-Berríos – School of Science and Technology, Universidad Ana G. Méndez, San Juan, Puerto Rico 00926, United States; orcid.org/0000-0003-0827-1502; Email: msantiago326@uagm.edu

## Authors

- Joselyn Del Pilar Albadalejo Department of Chemistry, University of Puerto Rico, Mayagüez, Puerto Rico 00681, United States
- Suheily Alonso-Sevilla School of Science and Technology, Universidad Ana G. Méndez, San Juan, Puerto Rico 00926, United States
- Nicohl I. Cintrón School of Science and Technology, Universidad Ana G. Méndez, San Juan, Puerto Rico 00926, United States
- Xinran Feng Department of Chemistry and Chemical Biology, Baker Laboratory and the Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York 14853, United States
- Angel D. García School of Science and Technology, Universidad Ana G. Méndez, San Juan, Puerto Rico 00926, United States
- Dinorah D. Martínez-Torres Department of Chemistry and Biochemistry, University of Texas at El Paso, El Paso, Texas 79968, United States; School of Science and Technology, Universidad Ana G. Méndez, San Juan, Puerto Rico 00926, United States
- Astrid M. Rodríguez School of Science and Technology, Universidad Ana G. Méndez, San Juan, Puerto Rico 00926, United States
- Natalia I. Román-Montalvo School of Science and Technology, Universidad Ana G. Méndez, San Juan, Puerto Rico 00926, United States
- José I. Torres School of Science and Technology, Universidad Ana G. Méndez, San Juan, Puerto Rico 00926, United States
- Yao Yang Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States; orcid.org/0000-0003-0321-3792
- Armando Peña-Duarte Department of Chemistry and Biochemistry, University of Texas at El Paso, El Paso, Texas 79968, United States; Department of Physics, University of Puerto Rico, San Juan, Puerto Rico 00926, United States; orcid.org/0000-0002-4286-5278
- Rahul Singhal Department of Physics and Engineering Physics, Central Connecticut State University, New Britain, Connecticut 06050, United States; orcid.org/0000-0002-5017-9091

- Louise M. Debefve Cornell High Energy Synchrotron Source, Wilson Laboratory, Cornell University, Ithaca, New York 14853, United States
- Christopher J. Pollock Cornell High Energy Synchrotron Source, Wilson Laboratory, Cornell University, Ithaca, New York 14853, United States; o orcid.org/0000-0001-5736-513X
- Carlos R. Cabrera Department of Chemistry and Biochemistry, University of Texas at El Paso, El Paso, Texas 79968, United States; Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico 00926, United States; orcid.org/0000-0002-3342-8666
- Héctor D. Abruña Department of Chemistry and Chemical Biology, Baker Laboratory and the Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York 14853, United States; © orcid.org/0000-0002-3948-356X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaem.1c04030

#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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