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Z. Chen, I. Waluyo

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Investigation of Water Dissociation and Surface Hydroxyl Stability on Pure and Ni-Modified CoOOH by Ambient Pressure Photoelectron Spectroscopy

Zhu Chen¹, Coleman X. Kronawitter², Iradwikanari Waluyo³ and Bruce E. Koel^{1*}

¹Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544

²Department of Chemical Engineering, University of California at Davis, Davis, CA 95616

³Photon Science Division, National Synchrotron Light Source II, Brookhaven National
Laboratory, Upton, NY 11973

Abstract

Water adsorption and reaction on pure and Ni-modified CoOOH nanowires was investigated using ambient pressure photoemission spectroscopy (APPEs). The unique capabilities of APPEs enable us to observe water dissociation and monitor formation of surface species on pure and Ni-modified CoOOH under elevated pressures and temperatures for the first time. Over a large range of pressures (UHV to 1 Torr), water dissociates readily on the pure and Ni-modified CoOOH surfaces at 27 °C. With an increase in H₂O pressure, a greater degree of surface hydroxylation was observed for all samples. At 1 Torr H₂O, ratios of different oxygen species indicate a transformation of CoOOH to CoO_xH_y in pure and Ni-modified CoOOH. In temperature dependent studies, desorption of weakly bound water and surface dehydroxylation were observed with increasing temperature. Larger percentages of surface hydroxyl groups at higher temperatures were observed on Ni-modified CoOOH compared to pure CoOOH, which indicates an increased stability of surface hydroxyl groups on these Ni-modified surfaces.

INTRODUCTION

The interaction of water with surfaces plays a key role in many applications including heterogeneous catalysis, environmental science, and electrochemistry. This interaction, which can involve H_2O molecules, hydronium (H_3O^+) ions, and hydroxide ions (OH^-), is especially important for the water electrolysis half reactions—the hydrogen evolution reaction (HER)¹⁻³ and the oxygen evolution reaction (OER)—which must be driven efficiently for many emerging renewable energy technologies.⁴⁻⁷ In the case of OER, a complex reaction mechanism that involves four electron transfer steps and multiple surface intermediates is believed to be the reason for the observed slow kinetics associated with most electrocatalysts.⁸⁻¹¹ As a result, a large overpotential is required to obtain high rates of reaction, which makes OER the bottleneck reaction in many energy

conversion devices, including water splitting cells¹²⁻¹⁴ and metal-air batteries.^{5, 15-16}

Metal oxide and (oxy)hydroxide catalysts are commonly utilized to effect low overpotentials for OER in alkaline conditions. A volcano-type relationship is frequently reported for these catalysts, where optimal activity is observed when the interaction between the catalyst surface site and a key surface-bound intermediate is neither too strong nor too weak.¹⁷⁻¹⁹ As a result, scaling relationships based on the calculated free energy of formation of surface intermediates have been established and are used as descriptors for predicting and explaining trends in the OER activity of different catalysts.²⁰ Cobalt-based oxides and (oxy)hydroxides represent a promising and interesting group of OER catalysts. These catalysts have demonstrated excellent OER activities that are comparable to the most active precious metal catalysts in alkaline conditions.²¹⁻²⁴ A typical reaction

mechanism proposed for the OER half reaction at oxide catalysts is shown in Eq. (1-4), where * denotes a surface site.^{11, 25-26}

Based on this general mechanism, different rate-determining steps are proposed for cobalt oxide and (oxy)hydroxide catalysts of different compositions and structures. For example, Chen et al. has predicted that Eq. (2), the second deprotonation step prior to the formation of O^* , is the rate determining step, and stabilization of such product species reduces the OER overpotential for Co_3O_4 .²⁶ However, either Eq. (1) or (3), the formation of either OH^* or OOH^* , respectively, has been proposed to be the potential-limiting step depending on the crystal surface orientation of CoOOH .²⁷ Using *operando* FTIR spectroscopy, Frei and coworkers

discovered that OER on Co_3O_4 is facilitated by a dual site mechanism.²⁸ There are two types of surface active sites on Co_3O_4 : a kinetically fast site consisting of two Co^{III} -OH surface species bridged by an O atom, and a slow site associated with formation of isolated $\text{Co}^{\text{IV}}=\text{O}$ surface species.²⁸ These results illustrate the strong influence that different surface groups (i.e., OH^* and O^*) have on OER activity. Recent studies using Raman spectroscopy²⁹ and X-ray absorption³⁰ techniques have also revealed a strong correlation between the structure of Co-based catalysts and their OER activities.

In a recent study, we showed based on electrochemical impedance analysis that Ni incorporation into CoOOH reduces the interfacial charge transfer resistance and improves the stability of surface groups.³¹ Our results were in excellent agreement with results from DFT calculations by the Nørskov group regarding the positive influence of Ni doping in CoOOH towards

its OER activity²⁷. However, there was no direct evidence correlating Ni doping with the stability of surface species. A straightforward way to obtain this information would be to monitor and compare the proportion of surface oxygen species at different temperatures on pure and Ni-modified CoOOH. To this end, ambient pressure photoemission spectroscopy (APPEs) is an excellent technique because it provides information on the water/solid interface at a molecular level, with high surface and chemical sensitivity, but does not rely on an ultrahigh vacuum (UHV) measurement environment. Previous X-ray photoelectron spectroscopy (XPS) studies of H₂O adsorption on Co(0001)³² and oxidized cobalt³³ surfaces under UHV conditions have been reported, however, the adsorption and interaction of adsorbates at near-ambient pressure can differ greatly. One example is the appearance of interactions between surface hydroxyl groups (OH_{ad}) and

adsorbed water molecules (H₂O_{ad}) on oxide³⁴⁻³⁶ and semiconductor³⁷⁻³⁹ surfaces, which was only observed under near-ambient pressure (1 to 10 Torr H₂O). As a result, studying the water/solid interface of pure and Ni-modified CoOOH under such relatively high H₂O pressures can provide a better understanding of this interface, especially with respect to the surface composition and concentrations of surface-bound OH and H₂O species at conditions closer to the environment encountered during practical catalysis. Herein, we report the use of APPEs to investigate the interactions of adsorbed water and hydroxyl species with pure and Ni-modified CoOOH catalyst surfaces at different temperatures and H₂O pressures to provide direct comparisons of water and hydroxyl group stability on the surface of these oxyhydroxides, a type of oxide catalyst shown previously to be active for OER.^{22, 24,}

^{31, 40-44}

EXPERIMENTAL SECTION

Synthesis of pure and Ni-modified CoOOH

Pure and Ni-modified CoOOH materials were synthesized according to a previously reported procedure.³¹ Briefly, 5 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, >99.99%) and 2.5 mmol of NH_4NO_3 (Aldrich, >99.0%) were added to a mixture of de-ionized water (35 mL) and 30 wt.% ammonia (5 mL, Aldrich) and pre-heated to 85 °C for 1 h. A degreased stainless steel mesh was added to the pre-heated Co precursor solution and incubated at 85 °C for 12 h. The resultant material consisted of $\text{Co}(\text{OH})_2$ nanowires attached to the stainless steel mesh and this was then subjected to chemical oxidation in 6 M NaOH (Aldrich, 99.99%) and 30 wt.% H_2O_2 at 45 °C for 8 h to form CoOOH nanowires on the stainless steel mesh. Nickel incorporation was performed through wet-impregnation of the as-prepared $\text{Co}(\text{OH})_2$ sample in 1 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution

followed by chemical oxidation to form Ni-modified CoOOH nanowires on the stainless steel mesh. Prior to APPES experiments, Ni concentration was determined by XPS (Thermo K-Alpha Plus) using a monochromatic Al K- α source operated at 150 W. Additional physical and electrochemical characterizations of the pure and Ni-modified CoOOH were performed prior to the APPES experiments and the details of these experiments are outlined in the Supporting Information. A

Ambient pressure X-ray photoelectron spectroscopy

The APPES experiments were performed at the undulator beamline 23-ID-2 (CSX-2) of the National Synchrotron Light Source II at Brookhaven National Laboratory. The endstation consist of a load-lock connected to a chamber for XPS measurements at near-ambient pressures. The base pressure of the APPES chamber was 2×10^{-9} Torr. The sample was heated by a button heater that

was capable of reaching a sample temperature of 900 °C, which was monitored by a chromel-alumel (K-type) thermocouple attached to a Ta plate that was placed between the sample and the button heater. Briefly, X-rays were incident on the sample through a 100 nm thick SiN_x window, which separated the XPS chamber at high pressure from the synchrotron beamline in UHV. The photoelectrons emitted from the sample were collected by a small aperture (0.3-mm dia.), which is the entrance to the differentially-pumped hemispherical electron analyzer (Phoibos 150, Specs). The sample was placed in close (ca. 500 μm) proximity to the analyzer entrance aperture in order to minimize elastic and inelastic scattering of photoelectrons in the gas phase. The angle between the incident X-rays and the emitted photoelectrons was set at 70°. The incident angle of the X-ray beam and the emission angle of photoelectrons were 50° and 20°,

respectively, with respect to the surface normal. All APPES spectra were collected using a photon energy of 1100 eV. This was chosen to include the Co and Ni 2p regions as well as to avoid overlapping of the XPS core level emission lines with the Auger emission from Ni and Co. Water vapor, after being degassed by multiple freeze-pump-thaw cycles of Milli-Q water, was introduced into the XPS chamber to achieve different pressures ($P_{\text{H}_2\text{O}}$) using a high precision variable leak valve. The binding energy scale was calibrated by aligning the Fermi energy level of the APPES survey spectrum of the pure and Ni-modified CoOOH catalysts in isothermal or isobaric conditions. Co 2p, Ni 2p, and O 1s XPS spectra were decomposed into components having a convoluted Gaussian (70%)—Lorentzian (30%) lineshape after a Shirley background subtraction. The Co 2p_{3/2} and Ni 2p_{3/2} were fitted with corresponding principle peaks, multiplet splitting

components, and shake-up satellites. The O 1s XPS spectra were fitted with four peaks corresponding to oxide (O^{2-}) and hydroxide (OH_L) that are part of the crystal structure, adsorbed hydroxyl (OH_{ad}), and adsorbed water (H_2O_{ad}). Two additional O 1s peaks were required for fitting spectra obtained at water pressures above 0.1 Torr and these correspond to species involved in OH_{ad} - H_2O_{ad} hydrogen bonding interactions and gas-phase water molecules (H_2O_{vap}). In the

peak fitting procedure, four parameters were considered: peak position, full-width-at-half-maximum (fwhm), Lorentzian-Gaussian (L/G) -ratio, and intensity. Three of these parameters (position, fwhm, and L/G ratio) for each component were constrained to be constant for all spectra of the same element, unless clear changes were discernible in the raw XPS spectra.

Figure 1. Physical and electrochemical characterizations of pure and Ni-modified CoOOH nanowires. Left: scanning electron micrographs. Middle: Raman spectroscopy. Right: linear sweep voltammetry. The inset in the right panel displays Nyquist plots from electrochemical impedance analysis.

RESULTS AND DISCUSSION

Our objective was to understand how hydroxylation and H_2O adsorption proceed on pure and Ni-modified CoOOH surfaces by measurements as a function of $P_{\text{H}_2\text{O}}$ at constant temperatures (isotherms) and as a function of temperature at constant $P_{\text{H}_2\text{O}}$ (isobars). All oxygens in pure and Ni-modified CoOOH materials are oxides. These catalysts do not contain peroxide moieties and CoOOH does not refer to hydroperoxide groups bound to a Co cation. The morphology, crystal structure, and electrochemical characterizations of pure and Ni-modified CoOOH samples are summarized in Figure 1. The pure and Ni-modified CoOOH samples clearly exhibit nanowire morphologies and their Raman spectra are consistent with crystalline β - CoOOH ³¹. These nanowires are highly active OER catalysts and the Ni-modified CoOOH clearly demonstrates greater activity compared to pure CoOOH . The

current density of Ni-modified CoOOH (11.5 mAcm^{-2}) measured at 1.53 V vs. RHE is 2.2 times greater than that of pure CoOOH (5.3 mAcm^{-2}). Additionally, the impedance analysis shown in the inset in the right panel of Figure 1 indicates that Ni-modified CoOOH has smaller charge transfer resistance and can better stabilize surface species compared to the pure CoOOH sample based on the smaller Nyquist-plot diameter. A more detailed analysis of the physical and electrochemical characterization is given in the Supporting Information. These promising electrochemical results for the promoting effect of Ni incorporation for OER activity provides excellent motivation for our APPES studies to better understand water chemistry on the surface of pure and Ni-modified CoOOH .

Isothermal Experiments. First, we consider APPES isothermal experiments at 300K. The Co 2p APPES spectra (Figure 2A) are

decomposed into multiple components showing a principle peak located at 780.1 eV binding energy (BE) as well as multiplet splitting and shake-up satellite peaks at higher binding energies.⁴⁵ The position of the satellite peaks and the overall lineshape of the Co 2p spectra confirm trivalent Co (Co³⁺) as the primary Co species in pure CoOOH, and also Ni-modified CoOOH (as shown below). With increasing P_{H2O}, no significant change to the Co 2p lineshape was observed indicating a similar oxidation state of Co at all levels of P_{H2O} examined. Based on the kinetic energy of the Co 2p photoelectrons, the probing depth is estimated to be 3 nm. The lattice spacing of β -CoOOH in the (0001) direction is 0.44 nm, which contains two layers of Co ions. Thus, the XPS signal from the top layer of Co ions (0.22 nm) is estimated to constitute 20% of the total XPS signal intensity.

The O 1s APPES spectra illustrate a clear picture of H₂O chemistry on CoOOH

(Figure 2B). Under UHV conditions (2×10^{-9} Torr), a broad O 1s peak was observed, which can be decomposed into four components. We attribute the peaks at 529.6 and 530.6 eV to O²⁻ and OH_L, respectively. These binding energies for these species agree well with the values from previous investigations.^{31, 46-48} The concentration ratio of O²⁻ to OH_L is 1:0.75, which is lower than the 1:1 ratio expected for stoichiometric CoOOH and indicates the presence of proton vacancies in the near-surface region (*ca.* 5 nm). A third O 1s component at 531.6 eV BE is attributed to OH_{ad} groups bound at Co³⁺ sites, and a fourth component at 532.6 eV BE is assigned to H₂O_{ad}. The presence of OH_{ad} and H₂O_{ad} observed under UHV conditions prior to explicit H₂O dosing we assume is due to retention of moisture from synthesis and exposure of the sample to moisture in the air prior to and during sample transfer into the UHV chamber. As the water pressure increased from 2×10^{-9} to

1 Torr, the proportion of OH_L and OH_ad increased from 38% to 47% and 10% to 22%, respectively, accompanied by a decreased in the proportion of O^{2-} from 52% to 31%. At $P_{\text{H}_2\text{O}} > 1$ mTorr, two new peaks appeared at 533.7 and 535.3-535.8 eV BE. These two peaks are due to the interactions of $\text{H}_2\text{O}_\text{ad}$ and OH_ad through hydrogen bonding, i.e. $(\text{OH}_\text{ad}-\text{H}_2\text{O}_\text{ad})$,^{34-36, 38-39} and from $\text{H}_2\text{O}_\text{vap}$, respectively.

Figure 2. A) Co 2p and B) O 1s APPES spectra of CoOOH at 27 °C in the presence of different water pressures. The y-scale for

the Co 2p and O 1s XPS spectra at $P_{\text{H}_2\text{O}}=1$ Torr is enlarged by a factor of 2 for clarity.

All results for Ni-modified CoOOH (5.2 at% Ni) at 27 °C at different $P_{\text{H}_2\text{O}}$ are shown in Figure 3. Co 2p spectra of Ni-modified CoOOH are similar to those of pure CoOOH under different $P_{\text{H}_2\text{O}}$ (Figure S3). An additional satellite peak at 6.4 eV above the primary peak indicates the presence of small amount of divalent Co (Co^{2+}) in addition to Co^{3+} . Ni 2p XPS spectra shown in Figure 3A have a principle peak at 855.5 eV BE and multiplet splitting components that are fitted according to Grosvenor et al.⁴⁹ Based on a lineshape analysis, Ni^{2+} and Ni^{3+} are the dominant Ni species in this sample⁴⁹. The changes in the O 1s APPES spectra of Ni-modified CoOOH under different $P_{\text{H}_2\text{O}}$ displayed similar trends as those observed for pure CoOOH (Figure 3B). As the water pressure increased from 2×10^{-9} to 1 Torr, the proportion of OH_L and OH_ad increased

from 34% to 41% and 15% to 26%, respectively, accompanied by a decrease in the proportion of O^{2-} from 51% to 33%. For $P_{H_2O}=1$ mTorr, XPS peaks due to H_2O_{vap} and H_2O_{ad} involved in $OH_{ad}-H_2O_{ad}$ interactions were also observed.

Figure 3. A) Ni 2p and B) O 1s XPS spectra of Ni-CoOOH at 27 °C for several water pressures. The y-scale for the Co 2p and O 1s XPS spectra at $P_{H_2O} = 1$ Torr is enlarged by a factor of 2 for clarity.

The relative proportions of O^{2-} , OH_L , and OH_{ad} for CoOOH and Ni-modified CoOOH

at different P_{H_2O} are shown in Figure 4. We are most interested in these surface species because they are intimately involved with the surface chemistry of H_2O . Additionally, the O 1s peaks due to H_2O_{vap} and H_2O_{ad} associated with $OH_{ad}-H_2O_{ad}$ were omitted from these percentage calculations because the concentrations of these weakly physisorbed species are not dependent upon the surface chemistry of H_2O but scales mainly with P_{H_2O} . As a result, excluding these species presents more accurate trends regarding changes in O^{2-} , OH_L , and OH_{ad} as a function of P_{H_2O} . A clear increase in the OH_L and OH_{ad} surface coverage is observed at higher water pressures, which we attribute to dissociation of water on the surface of CoOOH. We believe H_2O dissociation on pure and Ni-modified CoOOH takes place at oxygen vacancies based on the following reasons. First, the crystal structure of β -CoOOH consists of layers of edge-sharing Co^{3+} oxyhydroxyl octahedra,^{30, 50-51} and a

fully coordinated Co^{3+} cation in this octahedral geometry is unlikely to form additional chemical bonds with H_2O or with components from dissociated H_2O . Alternatively, under-coordinated Co^{3+} that can form due to presence of an oxygen vacancy can interact with H_2O , or components from dissociated H_2O , such as OH. In addition, the presence of oxygen vacancies is confirmed by the Co:O ratio for pure (1:1.8) and Ni-modified (1:1.83) CoOOH. Furthermore, higher reactivities of oxygen vacancies toward water dissociation has been observed on several important oxide catalysts.⁵²⁻⁵⁵ As a result, we propose that a H_2O molecule can dissociate at an oxygen vacancy to form OH_{ad} on Co^{3+} and form OH_{L} with a nearby lattice oxygen atom. A schematic representing the H_2O dissociation process at an oxygen vacancy is shown in Figure S4. H_2O interaction with cobalt oxyhydroxide has not been studied previously by APPES and fundamental

UHV surface science investigations are limited. An investigation of H_2O chemistry on the $\text{Co}_3\text{O}_4(111)$ surface has reported molecular adsorption of water at 110 K and hydroxylation in UHV was only observed when heating the sample to 650 K after an exposure of 150 L H_2O .³³ We observed extensive H_2O dissociation on pure CoOOH nanowires at $P_{\text{H}_2\text{O}} \geq 10^{-5}$ Torr and at 27 °C indicating that surface oxygen vacancies are active towards H_2O dissociation on CoOOH at relatively low temperature. A crude estimation of the oxygen vacancies (using Co:O ratio) and the amount of dissociated H_2O (OH_{L} and OH_{ad} percentages) showed reasonable agreement within an order of magnitude.

Based on DFT calculations by Bajdich et al., the formation of O_2 on the $(01\bar{1}2)$ and (0001) surfaces of CoOOH is thermodynamically limited by the formation of surface OH groups (OH^*).²⁷ Given this

finding, achieving a high density of surface hydroxyl groups should be important for OER on pure and Ni-modified CoOOH catalysts. On the basis of our observation of OH_{ad} formation on the catalyst surfaces in $P_{\text{H}_2\text{O}} \geq 10^{-5}$ Torr, it is likely that surface OH_{ad} groups in aqueous medium will similarly be formed by a chemical process via water dissociation, prior to anodic polarization. As a result, two mechanisms exist for the formation of OH_{ad} on pure and Ni-modified CoOOH—a chemical route by water dissociation and an electrochemical route by the discharge of hydroxyl anions. However, without experimental observations on individual mechanistic steps during reaction, we are unable to determine the exact role of OH_{ad} formation by water dissociation in the oxygen evolution reaction mechanism. Interestingly, for $P_{\text{H}_2\text{O}} \geq 1$ mTorr, the $\text{OH}_\text{L}:\text{O}^{2-}$ ratio is greater than unity for both samples studied. This indicates a low barrier for surface hydroxylation of pure and Ni-

modified CoOOH, where OH_L becomes the dominant oxygen species constituting the material structure. The exact mechanism for the structural change is currently unclear based solely on the APPES results.

Figure 4. Ratios of surface oxygen species associated with A) CoOOH and B) Ni-CoOOH at 27 °C as a function of water pressure. Insets show individual species concentrations.

Isobaric Experiments. The thermal stabilities of surface oxygen species and the structural evolution of pure and Ni-modified CoOOH were investigated as a function of temperature in isobaric experiments at $P_{H_2O}=1$ Torr. All APPEs spectra were collected by heating the sample in 1 Torr H_2O and not at room temperature after cooling down from heating. Based on the Co 2p spectra (Figure 5A), no significant change to the chemical state of Co cations was observed below 220 °C. At higher temperatures, a 0.5 eV shift of the primary Co 2p peak to lower binding energy was observed. Simultaneously, a new satellite peak at 6.5 eV higher BE than the primary peak also appeared. Both observations can be attributed to the formation of Co^{2+} .⁵⁶⁻⁵⁸ At 320 °C, the transformation of CoOOH to spinel Co_3O_4 took place, as indicated by the change in the Co 2p lineshape, and this is consistent with previous reports.⁵⁹ The

changes in the O 1s XPS spectra (Figure 5B) are in good agreement with the changes observed in the Co 2p spectra. As the sample temperature increased to 220 °C, significant intensity decreases occurred in the OH_L and OH_{ad} components, while the proportion of O^{2-} increased. These observations point to surface dehydroxylation of CoOOH, likely following the reaction below,

The H_2O molecules from this reaction are expected to desorb from the surface at $T \geq 120$ °C due to the decrease in the H_2O_{ad} peak intensity (Figure 5B). With further increases in temperature, the O^{2-} component became the dominant surface oxygen species, and this is consistent with the transformation of CoOOH to Co_3O_4 . Upon cooling the sample back to 25 °C, O^{2-} species remained the dominant components with relatively lower proportions of OH_L and OH_{ad} indicating irreversible structural

changes occur due to sample heating in 1 Torr H₂O to 220 °C.

Figure 5. A) Co 2p and B) O 1s XPS spectra of CoOOH taken at different sample temperatures in 1 Torr H₂O.

The temperature dependence of Co 2p XPS spectra (Figure 6A) from Ni-CoOOH in 1 Torr H₂O is similar to that of CoOOH at lower temperatures, but some important distinctions are observed at higher temperatures. For Ni-CoOOH, a small satellite peak at 786.5 eV that represents the formation of Co²⁺ appeared when the

temperature was increased to 120 °C. With further increase in temperature, the intensity of this satellite peak continues to increase, which indicates a significant portion of Co³⁺ cations were converted to Co²⁺ and causes a much different lineshape. Upon cooling to 27 °C, the 786.5 eV satellite peak persists, which indicates an irreversible structural change from CoOOH to CoO_xH_y has occurred, where Co²⁺ cations constitute a significant proportion of Co near the surface. This is in stark contrast with the behavior of pure CoOOH after heating to 320 °C, where we observed that Co₃O₄ was the dominant phase formed. Thus, the incorporation of Ni promotes the formation of Co²⁺ after annealing in 1 Torr H₂O to T ≥ 220 °C. Ni 2p spectra (Figure S5) show little change to the Ni concentration or chemical state in the temperature range and H₂O pressure explored in this study.

Figure 6. A) Co 2p and B) O 1s XPS spectra of Ni-CoOOH taken at different sample temperatures in 1 Torr H₂O.

Analysis of the O 1s spectra (Figure 6B) at increasing temperatures clearly illustrates dehydroxylation of Ni-modified CoOOH, consistent with the observations made from the Co 2p spectra. For Ni-CoOOH at 220 °C, the proportion of OH_L and OH_{ad} is 36% and 26%, respectively, which are much greater than the proportions of these species found for CoOOH at the same temperature. This observation provides additional strong evidence for the greater stabilities of OH_L

and OH_{ad} on the Ni-modified CoOOH surface compared to the CoOOH surface. The relative proportions of oxygen species for CoOOH and Ni-CoOOH at different temperatures are given in Figure 7. Comparing the two samples, the amount of OH_L and OH_{ad} retained by Ni-modified CoOOH at all temperatures is greater than that for pure CoOOH. These results from our isobaric experiments are in excellent agreement with the DFT calculations by Bajdich et al. who predicted improved stability of surface species with Ni incorporation into β-CoOOH.

The greater stability of OH_{ad} on Ni-modified CoOOH has profound implications for water oxidation reactions. Based on the DFT calculations by Selloni and coworkers, H₂O deprotonation to form a surface OH species is energetically costly, and that increasing the surface stability of OH_{ad} is critical in lowering the barrier for its formation.²⁶ As a result, the greater stability

of OH_{ad} on Ni-modified CoOOH , as shown by our isothermal experiments, should be beneficial for OH_{ad} formation. Indeed, our previous characterization of the OER performance of pure and Ni-modified CoOOH showed a better activity for Ni-modified CoOOH . Therefore, our experimental results support the theoretical mechanistic proposal that increased adsorbed hydroxyl stability promotes OER activity.

Figure 7. Ratios of the concentrations of surface oxygen species associated with A) CoOOH and B) Ni-CoOOH as functions of temperature at 1 Torr H_2O . Insets show individual species compositions.

CONCLUSION

In conclusion, we have observed extensive water dissociation on pure and Ni-modified CoOOH catalyst surfaces at 27 °C using APPES in all pressure range from 10^{-7} to 1 Torr. For both catalysts, the transformation of CoOOH to CoO_xH_y at 27 °C in 1 Torr H_2O indicates only a small activation barrier for phase change. Based on APPES isobaric results, Ni incorporation was found to improve the stability of OH_{ad} and promote the formation of Co^{2+} at elevated temperatures. The greater thermal stabilities of OH_{ad} observed for Ni-modified CoOOH compare to the pure CoOOH is consistent with previous DFT calculations. This APPES study has revealed that oxygen vacancies are highly reactive towards H_2O

dissociation and that Ni incorporation can improve OH_{ad} stability. This additional experimental information on the chemistry of water at CoOOH and Ni-CoOOH surfaces provides key insights that contribute to the continued rational design of the structure and chemical composition of catalysts optimized for OER activity.

ASSOCIATED CONTENT

Supporting Information The Supporting Information is available free of charge on the ACS Publications website at DOI:

Detailed procedures for electrochemical characterizations of nanowire catalysts; detailed analysis of Raman spectroscopy; detailed analysis of impedance data; APPEs Co 2p spectra of Ni-modified CoOOH at different $P_{\text{H}_2\text{O}}$; APPEs spectra of Ni 2p of Ni-modified CoOOH at different temperatures.

AUTHOR INFORMATION

Corresponding Author

*E-mail: bkoel@princeton.edu (B.E.K.)

Notes

The authors declare no competing financial interest.

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TOC Graphic