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Electrocatalytic Water Oxidation by Single Site and Small Nuclearity Clusters of Cobalt

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Cobalt oxides are an earth abundant material that exhibits high electrocatalytic activity for the oxygen evolution reaction (OER) across a wide pH range. Recent studies suggest that OER catalysis can proceed through an active site comprised of one or two cobalt atoms but that multiple adjacent cobalt centers are preferred to stabilize high valent cobalt oxo-intermediates by delocalization. Utilizing molecular precursors to prepare single, isolated cobalt atoms (SS-Co) and small clusters of Co₃O₄ we find that OER proceeds more efficiently on Co₃O₄. Using electrochemical impedance spectroscopy (EIS), these results were rationalized at an atomic level. The EIS results support a hypothesis that charge transfer related to the formation of reaction intermediates proceeds more easily on Co₃O₄ than on SS-Co, which is attributed to the difficulty in forming Co(IV) = O and unlikely nucleophilic attack by water to form Co(II)-OOH.

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Conversion of solar energy into a useful chemical fuel for later use represents a major scientific goal in the evolution toward a society fully powered by renewable energy.¹ Several potential fuel targets exist including hydrogen from proton reduction; methane, methanol and higher order carbon species from carbon dioxide reduction; and ammonia via nitrogen reduction. To achieve meaningful rates of fuel production, any of these potential reduction reactions must be coupled to an oxidative reaction that generates both electrons and protons. The most sensible candidate to provide these electrons and protons is water, which can be decomposed via the oxygen evolution reaction (OER):

In all proposed systems, the OER occurs at the anode and is coupled to the reductive reaction occurring at the cathode. Ideally, the potential needed to drive the OER and its partner reaction is generated via a photovoltaic process. In a photoelectrochemical cell with the catalysts directly coupled to the light absorber, the efficiency of the catalyst, in particular the OER catalyst is paramount. A key figure of merit for a catalyst used in a photoelectrochemical cell is the amount of overpotential required to achieve a desired current density (typically $\sim 10 \text{ mA cm}^{-2}$).² In addition, because photoelectrochemical cells operate at lower current densities than electrolyzers, a larger amount of catalyst is needed and so cost becomes a key consideration. Finding OER catalysts that are both active and cost effective is a major challenge. Iridium and ruthenium OER catalysts are highly active across a wide pH range but are costly.³⁻⁹ By contrast, some lower cost non-noble metals also show activity for OER. Fe_xNi_{1-x}OOH catalysts exhibit low overpotentials for OER ($\sim 300 \text{ mV}$ for 10 mA cm^{-2}) in base.¹⁰⁻¹³ Natural photosynthesis utilizes a manganese oxo cluster¹⁴ and manganese oxides show some facility for OER, albeit at large overpotentials.¹⁵⁻¹⁸ Some copper complexes also demonstrate electrocatalytic OER behavior at high pH.^{19,20}

As an alternative to noble metal catalysts, cobalt oxides are a promising potential OER catalyst material. As a first-row transition metal, cobalt is abundant and relatively inexpensive and many studies have demonstrated moderate to low overpotentials for OER across a

wide pH range.²¹⁻²⁶ Cobalt OER catalysts are particularly interesting in the context of hybrid microbial/inorganic solar fuels systems where the biocompatibility of cobalt is critical.^{27,28} Investigations into the mechanism of OER on cobalt oxides are essential to the development of new cobalt OER catalysts. In general, mechanistic studies suggest that water oxidation on cobalt oxide can proceed through both mononuclear and dinuclear pathways.²⁹⁻³³ At neutral pH, a dinuclear (dicobalt) pathway for oxygen formation appears to be preferred, which in principle could involve intermolecular coupling of adjacent oxyl radicals, or the coupling of hydroxyl and oxo ligands on neighboring cobalt centers to form a hydroperoxo intermediate.^{29,30} By comparison, a mononuclear pathway, involving nucleophilic attack of water or hydroxide onto a cobalt oxo species, is reported to be slow at neutral pH because of the difficulty in deprotonating the water molecule.²⁹ At basic pH, our recent mechanistic work utilizing an oxo cobalt cubane complex suggests that O-O bond formation occurs exclusively by hydroxide attack onto a terminal Co(V) oxo.³¹ It is important to note; however, that even though the latter mechanism proceeds through a single terminal oxo species, all four cobalt centers in the cubane appear to play a role in supporting the formal, high oxidation state of Co(V), so in this case multiple cobalt atoms are required for efficient catalysis.

With the recent development of single atom catalysts (SACs), a new frontier in heterogeneous catalysis research has opened. The most spectacular demonstrations of SACs, isolated metal atoms supported on a substrate, offer unprecedented catalytic selectivity, activity, and stability. For example, oxygen reduction on single-atom Pt supported on TiN and TiC demonstrates selectivities as high as 80% for H₂O₂ production, whereas Pt nanoparticles achieve no better than 25% selectivity for H₂O₂.³⁴ Despite the potential of SACs, there are only a limited number of reports on electrocatalysis using SACs,³⁵ and strategies for preparing SACs remain a major research focus.³⁶ Previous work from our group demonstrated that deposition and subsequent thermal decomposition of a molecular precursor, Co[N(SiMe₃)₂]₂, could be used to prepare cobalt structures ranging from single, isolated cobalt atoms (SACs) to small clusters with a Co₃O₄ spinel structure on a range of oxide supports.^{37,38} These supported catalysts were also shown to be active for photocatalytic water oxidation. In this study, the same molecular precursor was utilized to prepare single-site cobalt (SS-Co) and small cobalt oxide clusters (Co₃O₄) on high surface area indium tin oxide (ITO) electrodes for electrocatalytic OER. By comparing OER

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catalysis on isolated cobalt atoms to catalysis on the Co_3O_4 clusters, marked differences in kinetics and activity were observed. Unlike molecular OER catalysts anchored to an electrode, SS-Co and Co_3O_4 are directly coupled to ITO electrodes allowing direct interrogation of the energetics of the respective catalysts using electrochemical impedance spectroscopy (EIS). These differences in electrocatalytic OER activity are correlated between the two catalyst types with differences in the faradaic resistance related to the formation of surface intermediates.

Experimental

$\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ was prepared according to the literature using standard air-free Schlenk techniques.³⁹

Preparation of electrodes.—Mesoporous films of indium tin oxide (ITO) nanoparticles on fluorine-doped tin oxide (FTO) were prepared using the method of Michaux et al.,⁴⁰ except that the electrodes were not annealed in 5% H_2 . Briefly, 1 g of ITO (< 50 nm particles, Sigma Aldrich) was mixed with 1 g of acetic acid and 3.3 mL of ethanol. After sonication in a bench top sonicator, the suspension was sonicated using an ultrasonic horn and then the ethanol was removed via rotary evaporation. FTO glass substrates were cleaned by sequential sonication in soapy water, water, and ethanol and then dried with a stream of nitrogen. ITO films were deposited on the clean FTO substrates by doctor-blading, using 1 layer of Scotch Magic Tape as a spacer layer. The as-deposited films were then sintered in air at 450°C. Cross-sectional SEM determined a sintered film thickness of approximately 5 μm . Typical film geometric areas were 1.3 to 1.5 cm^2 .

$\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ was deposited on the electrodes from toluene in a glove box. To ensure reproducibility of deposition, the deposition was performed in a vial that had been previously exposed to a high concentration of $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$, and any exposed FTO glass was covered by Kapton tape. The cobalt complex was allowed to graft for 1 hour before the electrodes were rinsed with toluene and dried with a stream of nitrogen. The electrodes were then heated to 300°C in air to decompose the precursor. Short wires were attached to the FTO electrode using silver epoxy and then covered with Loctite Hysol 1-C, which was allowed to dry overnight at 80°C.

To determine cobalt loading, the above procedure was followed and the cobalt-functionalized ITO was removed by mechanical scraping. The film was then dissolved in aqua regia and analyzed by inductively coupled plasma spectroscopy (Perkin Elmer Optima 7000 DV ICP-OES) using a gallium standard.

Electrochemical characterization.—All electrochemical measurements were performed in a 0.1 M pH 7 potassium phosphate buffer in air using a Bio-Logic SP300 potentiostat. Oxygen was continuously bubbled into the solution over the course of the measurement. Applied potentials were referenced to a Ag/AgCl (sat. KCl) reference electrode (0.197 V vs. NHE). A piece of platinum mesh was used as the counter electrode. All electrochemical potentials were corrected for the uncompensated resistance (R_u) determined using high frequency impedance measurements. Values for R_u were $\sim 20 \Omega$ in 0.1 M potassium phosphate buffer. The turnover frequency was calculated by measuring the current for a fixed period of time at $\eta = 300$ mV and 500 mV and correcting for background current from the ITO, measured using an identical, bare electrode. The corrected current was converted into C/s and then divided by the total number of cobalt centers on the electrode as determined by ICP-OES.

Impedance measurements were made from 100 kHz to 100 mHz. Prior to each impedance measurement, the sample was held at a constant overpotential for 10 minutes to ensure stability. At each frequency, the potentiostat waited the length of two periods before recording the average of two measurements. For each loading, a total of three to four unique samples was measured. The values of the various parameters were determined from a fit of the equivalent circuit to the experimental data. In cases where we had determined the value of

a parameter in a different manner, the fit was constrained around that value. Each fit passed a logarithmic Kramers-Kronig analysis with residuals less than 2% to ensure a quality fit.

Results and Discussion

Characterization of the electrodes.—To prepare single-site and nanoparticulate cobalt OER catalysts, $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ was utilized as a molecular precursor because it reacts vigorously to eliminate $\text{HN}(\text{SiMe}_3)_2$ in the presence of protic reagents. This reactivity can be exploited to graft cobalt on oxide surfaces by allowing the $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ to react with an oxide surface under anhydrous conditions. The strongly basic $\text{N}(\text{SiMe}_3)_2^-$ deprotonates a surface hydroxyl group to form a mono-amido cobalt(II) species anchored to the oxide surface. This species can then be thermally decomposed to give an inorganic cobalt site, the nuclearity of which is controlled by the precursor concentration.

In order to provide sites to graft $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$, mesoporous, nanoparticulate films of ITO were chosen as the electrode. This type of high surface area ITO electrode is widely utilized to heterogenize molecular OER catalysts. The surface area and pore size distribution of the ITO electrodes were characterized with BET measurements and determined to have a surface area of 32.26 $\text{m}^2 \text{g}^{-1}$ for the sintered, doctor-bladed ITO films, with an average pore width of 48.4 nm, though the distribution of pore sizes was broad.

Typical preparations of high surface area ITO electrodes first sinter the ITO films in air and then anneal them in H_2 . Annealing partially reduces the ITO and increases its conductivity. However, after grafting the $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ the thermal decomposition at 300°C reoxidized the ITO. Using a transmission line measurement approach, the sheet resistance (R_s) for the unannealed ITO film was found to be 2376 Ω . Though the sheet resistance is high, the bulk resistivity was moderate at 1.19 Ωcm . Considering that the catalyst-functionalized films were 5 μm thick and approximately 1.5 cm^2 , the overall resistance of the films was about 40 m Ω . At a current density of 10 mA cm^{-2} , the ohmic drop across the film would be less than 1 mV. Thus, to avoid any modification to the catalyst structure, $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ was grafted on unreduced ITO and not subsequently annealed in 5% H_2 .

Previous work from our group studied the deposition of $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ on various high surface area oxide supports and determined that the nuclearity of the final cobalt catalyst depended on the loading of the molecular precursor.^{37,38} At loadings less than 0.25 Co/nm^2 , extended X-ray absorption fine structure (XAFS) measurements indicate that the cobalt(II) species are predominantly single, isolated atoms, whereas small nuclearity clusters of Co_3O_4 form at loadings higher than 0.65 Co/nm^2 . To understand the different electrocatalytic OER behavior of single-site and clusters of cobalt(II), deposition conditions were utilized that gave loadings of $0.16 \pm 0.03 \text{ Co/nm}^2$ and $1.34 \pm 0.07 \text{ Co/nm}^2$, as determined by ICP-OES.

Electrochemical performance.—The electrochemical behavior of the electrodes was characterized at pH 7. Figure 1 shows representative cyclic voltammograms for electrodes with 0.16 and 1.34 Co/nm^2 as a function of OER overpotential ($E_{\text{H}_2\text{O}/\text{O}_2} = 618 \text{ mV vs. Ag/AgCl}$). In the electrodes with the higher cobalt loadings, a redox couple can be clearly seen near $\eta = 281 \text{ mV}$ ($E_{1/2} = 709 \text{ mV vs. Ag/AgCl}$). Integration of that feature gave an average of $5 (\pm 2) \times 10^{16}$ electrons per cm^2 and assuming a one electron process (i.e., Co(II/III)) that gives an average of $1.6 \pm 0.5 \text{ Co/nm}^2$, which suggests that all cobalt deposited within the ITO electrode is electroactive. Electrodes functionalized with cobalt exhibited an onset of catalytic current between 350–400 mV of overpotential, whereas ITO electrodes without cobalt exhibited no catalytic current. The SS-Co electrodes reached a current density of 1 mA cm^{-2} at an average overpotential of $532 \pm 5 \text{ mV}$, whereas Co_3O_4 electrodes reached the same current density at an overpotential of $499 \pm 7 \text{ mV}$.

To better understand the differences between the SS-Co and Co_3O_4 electrodes, the per-cobalt turnover frequencies (TOF) at both 300 and 500 mV of overpotential were calculated. At 300 mV, TOFs of

Figure 1. Representative cyclic voltammograms of SS-Co and Co_3O_4 in 0.1 M pH 7 potassium phosphate buffer ($E_{\text{H}_2\text{O}/\text{O}_2} = 618$ mV v. Ag/AgCl, scan rate 10 mV s^{-1}). Inset: Zoom of the region from $\eta = 0$ to 500 mV to show the Co(II/III) couple at $E_{1/2} = 709$ mV v. Ag/AgCl.

0.07 ± 0.02 s^{-1} for SS-Co and 0.007 ± 0.001 s^{-1} for Co_3O_4 were obtained. Those TOF values are in good agreement with previous studies in the literature that found per cobalt TOFs between 0.02 and 0.0008 for OER on Co_3O_4 .¹ The TOFs were also determined at 500 mV of overpotential and were 0.28 ± 0.03 s^{-1} and 0.12 ± 0.04 s^{-1} for SS-Co and Co_3O_4 , respectively. Ahn et al. photocatalytically determined TOFs for SS-Co and Co_3O_4 using tris(2,2'-bipyridine)ruthenium(III) and sodium persulfate and observed values roughly two to three orders of magnitude lower.³⁷ These lower TOFs can be attributed to differences in the method of catalysis; in the photocatalytic system, the chromophore needs to absorb a photon, reduce the persulfate, and then oxidize the OER catalyst, which is an inherently slower chain of events than oxidation of an active site on an electrode. Also, the samples in that study were prepared on a mesoporous silica support that may have also slowed diffusional contact between the chromophore, persulfate and catalyst. Wang and coworkers observed TOFs of ~ 0.27 s^{-1} for isolated cobalt ions grafted onto doped graphene.⁴¹ It is important to emphasize that the TOF values determined here are based on total cobalt. With the SS-Co samples, all the cobalt can participate in the electrocatalysis and thus likely reflect the TOF of a mononuclear OER mechanism. In the case of the Co_3O_4 electrodes, most of the cobalt is locked within the core of the nanoparticle so that our values represent a lower limit for the TOF of surface active sites that perform the OER catalysis. Esswein and coworkers demonstrated that OER activity on Co_3O_4 increases with surface area to volume ratio, demonstrating the importance of surface cobalt.⁴² That the TOFs for SS-Co and Co_3O_4 differ by only a factor of ~ 2 at 500 mV overpotential despite nearly an order of magnitude difference in the loading of cobalt suggests that OER catalysis is significantly more active on a Co_3O_4 surface, which is in agreement with the observations of Frei and coworkers.²⁹

The Tafel behavior of the SS-Co and Co_3O_4 electrodes can offer a better insight into the relative mechanisms of OER catalysis (Figure 2). For the SS-Co electrodes, the observed Tafel slope was 118 ± 4 mV dec^{-1} . A Tafel slope of 120 mV dec^{-1} in OER catalysis implies that the first electron transfer is the rate-limiting step.⁴³ On Co_3O_4 electrodes, the Tafel slope was 105 ± 2 mV dec^{-1} . By comparison, slopes of ~ 40 – 60 mV dec^{-1} are usually reported for cobalt oxide electrodes, though most studies are performed in base and/or utilize amorphous electrocatalysts.^{32,44–47} A slope of 100 mV dec^{-1} is not typically associated with a specific rate-limiting step but is not

Figure 2. Representative Tafel plots for SS-Co and Co_3O_4 in 0.1 M pH 7 potassium phosphate buffer ($E_{\text{H}_2\text{O}/\text{O}_2} = 618$ mV v. Ag/AgCl, scan rate 10 mV s^{-1}). Solid line is the linear fit for the Tafel slope. Only 10% of the data is displayed for clarity.

unprecedented in the OER literature. NiO_x thin films prepared using molecular precursors likewise exhibited Tafel slopes of 104–105 mV dec^{-1} .⁴⁸ Crystalline CoWO_4 exhibits a Tafel slope of ~ 110 mV dec^{-1} , whereas amorphous CoWO_4 has a slope of 60 mV dec^{-1} .⁴⁹ $\text{Fe}_{1.75}\text{Mn}_{0.25}\text{P}$ nanorods are reported to have slopes of 100 mV dec^{-1} that decrease with increasing Mn concentration.⁵⁰ García-Osorio et al. recently suggested a similar Tafel slopes on PbO_2 was related to the formation of hydroxyl radicals.⁵¹ While a specific rate-determining step on the Co_3O_4 electrodes cannot be suggested, the marked difference in Tafel behavior between SS-Co and Co_3O_4 electrodes suggests that there may be differences in OER mechanism, for example different rate limiting steps, between the two catalyst preparations. It is also important to note that mass transport through the mesoporous ITO electrode could affect the observed Tafel behavior.

Electrochemical impedance.—Electrochemical impedance spectroscopy (EIS) is a powerful in situ analytical technique to simultaneously extract kinetic and structural data about OER catalysts. Our previous work utilized EIS to probe the energetics of OER on $\text{Ni}_x\text{Fe}_{1-x}\text{OOH}$ catalysts¹² but, to the best of our knowledge, this is the first report of EIS measurements on a single-site OER catalyst. Lyons and co-workers,^{52,53} Cahan and Chen,^{54,55} and Harrington and Conway⁵⁶ largely developed the conceptual basis for the analysis of OER catalyst by EIS. In their model, OER catalysis is described by a resistive circuit element (R_p) in series with an RC loop (R_s and C_ϕ). Unlike in the hydrogen evolution reaction, these circuit elements do not describe a single charge transfer process but rather each handles multiple steps within the overall catalytic reaction. The polarization resistance, R_p , relates to the reaction rate and handles the charge transfer resistance of the various steps within the OER up to and including the rate-determining step. The other resistance, R_s , broadly incorporates the ease of forming surface intermediates on the catalyst and, together with R_p , gives the faradaic resistance, simply defined as $R_{\text{far}} = R_s + R_p$. Charge relaxation associated with the formation of surface intermediates is described by the loop given by R_s and C_ϕ . This model is typically then extended with elements describing the catalyst double layer and conductivity of the catalytic film. In this case, however, a slight modification of these additional elements to account for the deposition of the catalyst within a porous electrode is needed.

As a starting point, a transmission line (Figure 3) is used to develop the equivalent circuit model. An electron first travels through the ITO experiencing a resistance to transport (R_{ITO}). The charge in the FTO then has two possible pathways. One pathway is OER catalysis,

Figure 3. Equivalent circuit model for EIS measurements of catalyst functionalized, mesoporous ITO. Catalyst is either SS-Co or Co_3O_4 .

which is described above. The other pathway is via charge transfer at ITO/electrolyte interface, which is described by an RC circuit ($R_{\text{ITO/Elec}}$ and $C_{\text{ITO/Elec}}$). Also included is a resistance to account for the solution resistance (R_{sol}) as well as an additional RC loop before the other circuit elements to describe the interface between the ITO and the underlying electrode. The values of this RC loop do not change with potential or catalyst loading, suggesting that this additional loop may be related to the use of a silver epoxy to prepare a contact to the electrode. Overall, this equivalent circuit model draws from the work of Cueto-Gómez et al.⁵⁷ and of Bisquert and coworkers^{58,59} on other applications using porous electrodes.

Figures 4 and 5 show representative Nyquist plots for Co_3O_4 and SS-Co electrodes as a function of applied overpotential, along with fits to the equivalent circuit presented in Figure 3. At low overpotentials, we were not able to resolve full semicircles due to the frequency range of the experiment. The flattening of the semicircles in the Nyquist plots at higher overpotentials shows evidence of dispersive capacitances,⁶⁰ requiring the use of constant phase elements (CPE) instead of an ideal capacitor. The CPE is defined as:

$$\frac{1}{Z_{\text{CPE}}} = Q(\omega)^{\alpha}$$

where Z_{CPE} is the impedance of the CPE. If $\alpha = 1$, then the CPE describes an ideal capacitor and $Q = C$, whereas if $\alpha = 0$ then CPE describes an ideal resistor with $Q = R$.⁶¹ The values of α for C_{ϕ} and $C_{\text{ITO/Elec}}$ ranged from 0.9 to 1, indicating capacitive behavior. Typical values for R_{ITO} were on the order of 10–20 Ω , which agree with our earlier estimates (*vide supra*), whereas this study observed values for

Figure 4. Nyquist plots of a representative Co_3O_4 electrode at pH 7 ($E_{\text{H}_2\text{O}/\text{O}_2} = 618 \text{ mV v. Ag/AgCl}$). Inset: wider scale showing the full Nyquist plots for $\eta = 300, 400$, and 450 mV .

Figure 5. Nyquist plots of a representative SS-Co electrode at pH 7 ($E_{\text{H}_2\text{O}/\text{O}_2} = 618 \text{ mV v. Ag/AgCl}$). Inset: wider scale showing the full Nyquist plots for $\eta = 300, 400$, and 450 mV .

R_{sol} between 5–10 Ω . Hernández-Pagán et al.⁶² determined a solution resistivity of $\sim 50 \Omega \text{ cm}$ for 0.1 M potassium phosphate buffer. Though not explicitly positioned, the Ag/AgCl reference electrode used in this study was typically positioned less than 1 cm from the working electrode, so a value for R_{sol} of 5–10 Ω is reasonable.

As shown in Figure 1, ITO is a poor electrocatalyst for OER catalysis, which is reflected in the EIS data. Typical values for $R_{\text{ITO/Elec}}$ were at least one order of magnitude larger than R_{far} and at high overpotentials as much as three orders of magnitude larger (6–75 k Ω). From $\eta = 400$ –600 mV, the value of $C_{\text{ITO/Elec}}$ remained essentially constant at $\sim 5.4 \text{ mF s}^{\alpha-1} \text{ cm}^{-2}$ for Co_3O_4 electrodes and $\sim 3.5 \text{ mF s}^{\alpha-1} \text{ cm}^{-2}$ for SS-Co, with a typical error of $\pm 1 \text{ mF s}^{\alpha-1} \text{ cm}^{-2}$. This is consistent with expectations, as $C_{\text{ITO/Elec}}$ is expected to be independent of the catalyst nuclearity and, because of the large values of $R_{\text{ITO/Elec}}$, to be largely unaffected by a change in overpotential. Measurements of the electrochemically active surface area from cyclic voltammograms around the open-circuit potential give a double layer capacitance of $2 \pm 0.3 \text{ mF cm}^{-2}$, which is in good agreement with the values determined by EIS. The full ITO electrode may not be sampled at open-circuit, which may explain any differences.

The most significant differences between the Co_3O_4 electrodes and SS-Co electrodes are observed in R_s and R_p . At low overpotentials, there are no meaningful differences between either Co_3O_4 or SS-Co electrodes for either resistance; however, with increasing overpotential there is significant divergence (Figure 6). At overpotentials greater than 500 mV, R_s is an order of magnitude lower for Co_3O_4 than for SS-Co electrodes, whereas R_p is two to three times lower for Co_3O_4 . As previously noted, R_s broadly deals with the formation of surface intermediates whereas R_p reflects the facility of charge transfer. While EIS measurements cannot provide specific information on the catalytic mechanism, we can rationalize our results in the context of previous mechanistic work on cobalt-catalyzed OER. Zhang et al. suggest that efficient OER on cobalt oxide proceeds via a dinuclear mechanism because two Co(IV) = O intermediates can form and, after the subsequent nucleophilic addition of water to one oxo site, form a hydroperoxide group (Figure 8A).^{29,30} The formation of the O-O bond in hydroperoxide is facilitated by the adjacent Co(IV) = O site, which accepts a proton from water to form Co(III)OH . Subsequent oxidation forms a superoxide and results in the release of oxygen. For OER to proceed on a single cobalt atom, addition of water to Co(IV) = O must proceed without an adjacent site to facilitate the deprotonation of that water molecule (Figure 8B). While Co(V) = O is expected to be electrophilic, Co(IV) = O should be nucleophilic, making water attack unfavorable. In addition, the cobalt site must switch from Co(IV) to Co(II) . Based on this model, surface intermediates are expected to form more readily on Co_3O_4 when compared to

Figure 6. A) R_s and B) R_p versus overpotential SS-Co electrodes (blue circles) and Co_3O_4 (black squares) at pH 7 ($E_{\text{H}_2\text{O}/\text{O}_2} = 618 \text{ mV v. Ag/AgCl}$).

SS-Co. More facile charge transfer is also expected as the oxidation states only change by ± 1 throughout the catalytic mechanism. This picture is consistent with our EIS results, which demonstrate that formation of intermediates and charge transfer is more facile on Co_3O_4 than SS-Co. Difficulty in forming surface intermediates is also consistent with the larger Tafel slope of $\sim 120 \text{ mV dec}^{-1}$ that suggested a slower rate-limiting step. This may be related to the difficulty in forming $\text{Co(IV)} = \text{O}$ as our work in cobalt cubane model systems demonstrates how important delocalization over multiple cobalt sites is to the formation of $\text{Co(IV)} = \text{O}$.⁶³ No significant differences were observed in C_ϕ between the two catalyst loadings (Figure 7), though this may be due to charge relaxation facilitated by the presence of the conductive ITO.

Conclusions

In this study, electrocatalytic OER on two distinct catalytically active sites was compared. On the isolated cobalt atoms, OER most likely proceeds through a mononuclear mechanism, which is thought

Figure 7. C_ϕ versus overpotential SS-Co electrodes (blue circles) and Co_3O_4 (black squares) at pH 7 ($E_{\text{H}_2\text{O}/\text{O}_2} = 618 \text{ mV v. Ag/AgCl}$).

to be disfavored. By comparison, on the Co_3O_4 electrodes, OER can proceed through the preferred dinuclear (or mononuclear) mechanism. The difference between these mechanisms is clearly observed in the electrochemical and impedance data. SS-Co electrodes exhibited an overall lower OER activity than the Co_3O_4 electrodes, though a higher TOF on a per-cobalt basis. This higher TOF on SS-Co electrodes tell an incomplete story, however, because most of the cobalt atoms on the Co_3O_4 are presumably in the core of the particle and not available for catalysis. Thus, our measured TOF values represent a lower limit and it is likely that OER on Co_3O_4 is significantly more efficient than on SS-Co.

The EIS data for SS-Co and Co_3O_4 electrodes allowed these differences to be rationalized at an atomic level. The data was successfully fit to an equivalent circuit model that described not only the OER catalysis but also charge transport through the ITO support and charge transfer at the ITO/electrolyte interface. The resistances that give the faradaic resistance, R_s and R_p , exhibited a marked difference between SS-Co and Co_3O_4 samples. On Co_3O_4 , surface intermediates are more readily formed and charge transfer is more facile than on SS-Co, which is consistent with the proposed differences in mechanism between the two types of catalytic site.

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Figure 8. Proposed rate-limiting step in OER catalysis on A) Co_3O_4 and B) SS-Co.

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