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# Surface Interrogation of $CoP_i$ Water Oxidation Catalyst by Scanning Electrochemical Microscopy

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Supporting Information

**ABSTRACT:** Despite exhaustive spectroscopic investigations on the $CoP_i$ oxygen-evolving catalyst over the past several years, little is known about the surface cobalt sites and intermediates in direct contact with water that are responsible for the actual catalysis. Many studies thus far have been limited to *ex situ* characterizations or bulk film measurements, often in the absence of solvent. Here we describe an investigation of the $CoP_i$ catalyst by surface interrogation scanning electrochemical microscopy (SI-SECM). This method should allow us to selectively study surface atoms separately from the bulk in a solvent-filled environment. By SI-SECM, independent titrations of surface $Co^{III}$ and $Co^{IV}$ were performed, yielding a direct measurement of the surface active-site density of a $CoP_i$ electrode (11 Co/nm$^2$). The pseudo-first-order reaction rate constants of $Co^{III}$ and $Co^{IV}$ with water were determined to be 0.19 and >2 s$^{-1}$, respectively, through time-dependent titration measurements.

Recent research efforts have been concentrated on the development and understanding of oxygen evolution reaction (OER) electrocatalysts, due to the heightened interest in artificial photosynthesis.[1,2] The water oxidation half-reaction has often been identified as a bottleneck in artificial photosynthetic devices,[3,4] and much research has been focused in the development of inexpensive and efficient electrocatalysts from abundant elements.[5−12] In particular, cobalt-based water oxidation catalysts have been studied extensively, with recent interest sparked by work on the $CoP_i$ catalyst.[10] Thin electrocatalyst films generated anodically from an aqueous $Co^{2+}$ solution in a phosphate medium have been heavily investigated. An *ex situ* EPR study identified the presence of a $Co^{IV}$ intermediate,[13] and studies based on steady-state log *i* vs *E* curves (Tafel plots) proposed a proton-coupled electron-transfer step in the mechanism, with the phosphates in the OER material serving as proton acceptors.[14,15] Near and extended structures of the $CoP_i$ catalyst were identified by X-ray absorption spectroscopy.[16,17] While these spectroscopic studies and other *ex situ* approaches have revealed much about $CoP_i$, they are generally limited to bulk film measurements that provide little information about the surface cobalt sites and intermediates in direct contact with water that are responsible for the actual electrocatalytic activity.

Surface-selective *in situ* spectroscopy or transient electrochemical methods with a catalyst electrode allow for direct detection of the reaction intermediates in a water-filled environment. In this regard, surface interrogation scanning electrochemical microscopy (SI-SECM) provides a good approach for the direct quantification and time-resolved detection of surface active sites and intermediates on the $CoP_i$ catalyst.[18,19] The SI-SECM technique utilizes an independent (tip) electrode near a target (substrate) electrode in the same solution and therefore enables *in situ* interrogation of the solvent-accessible surface active sites, independent of the underlying bulk.[18,19] Despite these advantages, the technique has been applied in only a few studies of photocatalysts.[20,21]

In this Communication, we describe an SI-SECM investigation of the $CoP_i$ catalyst surface in water during catalysis. Amperometric titrations of the $Co^{III}$ and $Co^{IV}$ oxidation states were performed, allowing the direct measurement of the water-accessible surface cobalt density of the $CoP_i$ catalyst. We were also able to obtain, through time-dependent studies, the pseudo-first-order reaction rate constants of $Co^{III}$ and $Co^{IV}$ in the OER.

In a typical SI-SECM experiment, two size-matched ultramicroelectrodes (UMEs) are used at close proximity, such that the analyte generated by one electrode (tip or substrate) is quantitatively detected at the other electrode without leaving the tip−substrate gap.[18] In this study, two gold UMEs, substrate and tip, of radius $a$ = 12.5 $\mu$m were used, as shown in Figure 1. The tip and substrate electrodes were aligned and approached to a distance of 1.7 $\mu$m, at which point quantitative detection of tip-generated analyte was achieved at the substrate (Figure 1; for details on alignment and approach of the electrodes, see the Supporting Information). The $CoP_i$ catalyst film was deposited onto the substrate electrode according to a published procedure (a cyclic voltammogram of the $CoP_i$ catalyst on substrate electrode is shown in Figure S1).[10,22] Two different redox mediators were employed as titrants: 1,1′-ferrocenedimethanol ($FcDM^{+/0}$, $E$ = 0.22 V vs Ag/AgCl) and $K_2IrCl_6$ ($IrCl_6^{2-/3-}$, $E^\circ$ = 0.68 V vs Ag/AgCl). The potentials reported herein are referenced to a Ag/AgCl (1 M $Cl^-$) electrode.

Titration of surface $Co^{III}$ and $Co^{IV}$ was first attempted by cyclic voltammetry (CV) of FcDM at the tip of the SI-SECM. At open-circuit potential (OCP), the cobalt atoms in the $CoP_i$ film are in their 2+ oxidation states.[10,16] The substrate electrode was pulsed to positive potentials (400 mV to 1 V, $t_{step}$ = 20 s) to generate $Co^{III}$ and $Co^{IV}$ at the surface and then returned to OCP. Following a $t_{delay}$ of 2 s, the tip was scanned from 0.45 to 0.05 V, reducing $FcDM^+$ to FcDM (CVs presented in Figure 2). At substrate potential of $E_{Subs}$ = 400 mV, at which no oxidation of cobalt occurs, a typical negative feedback CV was obtained. This

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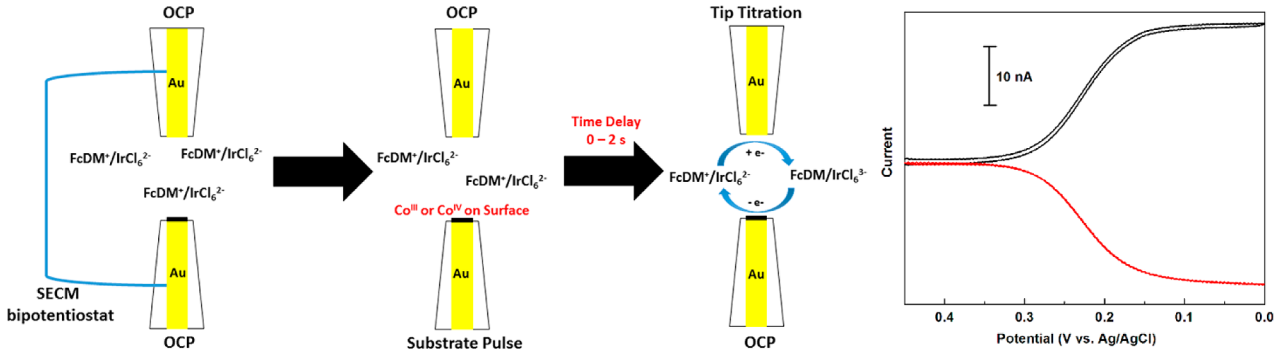


**Figure 1.** Schematic representation of the SI-SECM experimental setup. A positive feedback response exhibiting quantitative substrate detection of the tip-generated analyte ($FcDM^+$ reduction at tip) is shown on the right (tip current shown in black and substrate current in red). Both the tip and the substrate were composed of Au UMEs of $a$ = 12.5 $\mu$m, and the tip−substrate gap was 1.7 $\mu$m. The redox mediator concentrations employed in the experiments were 1.2 and 1.1 mM for FcDM and $IrCl_6^{2-}$, respectively.

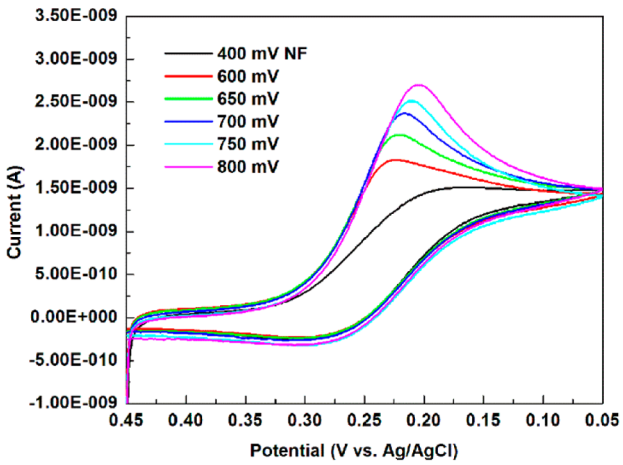


**Figure 2.** Cyclic voltammograms at the tip due to titration of surface $Co^{III}$ (bottom, scan rate 50 mV/s). It is worth noting that the potentials on the $x$-axis are those of the tip during detection, and each voltammogram was obtained at different substrate potentials ($E_{Subs}$), which are displayed in the inset labels. Growth in the feedback current as a function of $E_{Subs}$ indicates that higher concentrations of $Co^{III}$ were formed at more anodic $E_{Subs}$.

behavior is similar to that experienced when the tip was placed in proximity of an insulator, where no chemical feedback occurs. At higher $E_{Subs}$, however, positive feedback occurred, as seen in Figure 2 (schematically in Figure 1), giving rise to currents greater than that of the negative feedback case due to the oxidation of the tip-generated FcDM (titrant) by $Co^{III}$ and $Co^{IV}$ at the substrate. This titration current relaxed to the negative feedback level upon consumption of the surface analyte. As displayed in Figure 2, the titration current increased as a function of $E_{Subs}$, indicating that larger amounts of $Co^{III}$ formed on the surface at higher $E_{Subs}$. The current ceased to grow beyond $E_{Subs}$ ≈ 800 mV (Figure S3). Because $Co^{IV}$ has been spectroscopically observed in a water oxidation cycle of $CoP_i$,[13,16] it is difficult to conclude that no further oxidation of cobalt occurs beyond $E_{Subs}$ = 800 mV. Rather, $Co^{IV}$ probably reacted with water much more rapidly than the time required for detection by the CV technique (ca. 4 or 6 s including $t_{delay}$).

Chronoamperometry (CA) was used at the tip in order to detect the fast-reacting $Co^{IV}$ species. When a $t_{delay}$ of 0 s was chosen, the CA technique had a much shorter time resolution compared to that of CV, limited only by the switching time inherent to the bipotentiostat (estimated to be on the order of 100 ms) and the diffusion time between electrodes. Surface interrogation of $CoP_i$ by CA yielded a continued increase in the titration current at higher $E_{Subs}$ beyond 800 mV, as expected (Figure 3). The currents measured by amperometry were integrated over time to yield charge, representing the Coulombic density of analyte or surface cobalt density on $CoP_i$. As shown in Figure 3, a plateau and inflection of slope (at $E_{Subs}$ ≈ 800 mV) was observed in the charge density vs $E_{Subs}$ plot, which we attributed to the first one-electron oxidation of $CoP_i$ to $Co^{III}$. It is worth noting that, for surface titrations such as the one described here, the titration end points are generally not as sharply defined as those of solution-based titrations due to the distribution of chemical activities of surface species. The potential range of this observed $Co^{III/II}$ event was consistent with literature values for cobalts on $CoP_i$ and $Co_3O_4$.[5,15] The concentration of species that had reacted with FcDM at the plateau in the charge density vs $E_{Subs}$ plot represents the density of surface cobalts that are accessible to reduction by water. The density of cobalts measured by $Co^{III/II}$ titration was 11 Co atoms/nm$^2$ (from ca. 180 $\mu$C/cm$^2$; see SI for detailed calculations). This surface cobalt density is higher than previously reported values calculated from crystal packing (typically 3−7 nm$^{-2}$);[5,6] however, considering the roughness and porosity of the film,[10] an observed density higher than that of a close-packed flat surface is reasonable. A direct measurement of water-accessible cobalt atoms on the surface of the $CoP_i$ (or any other solid catalysts) is of importance, because the catalyst's performance, often expressed as the turnover frequency (TOF), has only been estimated thus far due to the lack of active-site density information.[5,6,14,22] As reported previously,[5,6,14,22] it is commonly understood that the vast majority of the metal atoms in an oxide film such as the $CoP_i$ film serve a structural function unrelated to surface catalysis. The true TOF of surface cobalt atoms on a $CoP_i$ film is calculated next.

In bulk $CoP_i$ films, $Co^{III}$ was believed to be long-lived, with a lifetime much greater than several seconds;[13,16] however, the time-dependent analysis of surface $Co^{III}$ in its reaction with water revealed otherwise. In these experiments, $t_{delay}$ was varied from 6 to 18 s, and the respective titration currents were measured. Because water was the only reagent to react with $Co^{III}$ during $t_{delay}$ (reduced redox mediator generated after $t_{delay}$), a pseudo-first-order rate constant for $Co^{III}$ in its reaction with water could be obtained by plotting ln [Co] vs $t_{delay}$ (Figure S4, calculation details in SI). A relatively high rate constant of 0.19 s$^{-1}$ was obtained, corresponding to a half-life of 3.6 s. There have been reports in the literature on water oxidation by $Co^{III}$,[23,24] and


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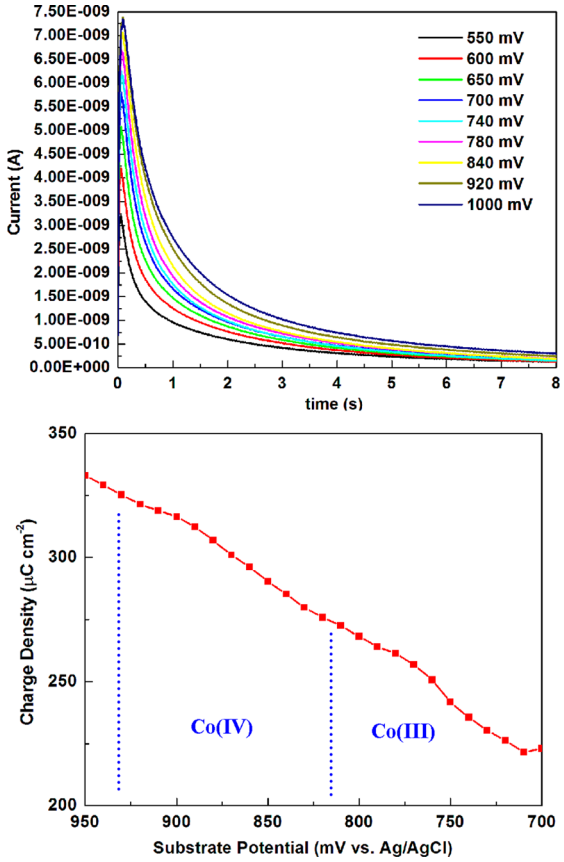


**Figure 3.** Chronoamperograms obtained from $CoP_i$ surface titration by FcDM (top, tip pulsed from OCP to 0.05 V). Continued growth of the titration feedback current suggests formation of a higher density of oxidizing equivalents on the $CoP_i$ surface. Charge density as a function of $E_{Subs}$ is plotted in the bottom frame. General potential regions for $Co^{III}$ and $Co^{IV}$ are depicted. It is worth noting that the charge densities displayed here are distributions of surface cobalt activities that are not quantized to $Co^{III}$ and $Co^{IV}$. A plateau and inflection of slope arfe characteristic of titration of a redox equivalence, and the first plateau was attributed to $Co^{III/II}$. The increase in the charge density beyond the first plateau (ca. 810 mV) is believed to be from the oxidation of $Co^{III}$ to $Co^{IV}$.

accordingly we observed fast reduction of surface $Co^{III}$ by water, which we believe leads to oxygen evolution. However, it is also known that prolonged catalysis does not occur at $Co^{III}$ formation potentials on $CoP_i$ and $Co_3O_4$.[5,10] These seemingly contradictory observations coexist due to slow hole-transfer kinetics through the $CoP_i$ film, as evidenced by a model study[25] in which an anomalously slow charge-transfer rate constant between $Co^{II}$ and $Co^{III}$ of $1.53 \times 10^{-3}$ $M^{-1}\cdot s^{-1}$ was observed. Therefore, without invoking a higher oxidation state, $Co^{III}$ on the surface that reacted with water cannot undergo further turnover, and the underlying $Co^{III}$ is effectively isolated by the now reduced surface $Co^{II}$. The valence-trapped $Co^{III}$ within the film is much longer lived and has been detected by spectroscopy, as mentioned earlier. A direct measurement of the reaction rate between $Co^{III}$ and water could be obtained because SI-SECM is a surface-selective, in-solvent technique; this measurement would not have been achievable by most spectroscopies operating in the absence of solvents or with a certain penetration depth into the bulk. An unexpectedly fast reaction kinetics between $Co^{III}$ and water is notable because, since the discovery of the $CoP_i$ catalyst, the majority of research efforts has been focused on characterizing the $Co^{IV}$ species, while $Co^{III}$ species are often overlooked. The findings in this work should suggest the importance of studying $Co^{III}$ as an active species in water oxidation, possibly lending some explanation to reported negative shifts in the onset potential when a thin film (ca. monolayer) of cobalt catalysts was employed.[26]

The next observed titration equivalent, centered at $E_{Subs}$ = 900 mV, was assigned to feedback from surface-generated $Co^{IV}$. The reaction of $Co^{IV}$ with water was faster, such that quantitative detection of $Co^{IV}$ by CA was not possible—the charge density of $Co^{III/II}$ and $Co^{IV/III}$ exhibited a ratio of ca. 2.5:1, indicating significant decay of $Co^{IV}$ in the switching time delay of the bipotentiostat (estimated to be on the order of 100 ms). Moreover, because $Co^{III/II}$ and $Co^{IV/III}$ are not well resolved in $E_{Subs}$ (plateau potential window very small, ca. 30−40 mV; Figure 3), a better resolved separate titration of $Co^{IV}$ was attempted by using $IrCl_6^{3-}$ as the titrant.

The reduction potential of $IrCl_6^{3-/2-}$, ca. 700 mV vs Ag/AgCl, does not reduce $Co^{III}$. Therefore, use of $IrCl_6^{3-/2-}$ was expected to largely filter out the titration current arising from $Co^{III}$ and enable a selective titration of $Co^{IV}$. Detection of surface $Co^{IV}$ was attempted by the CV technique analogous to that performed with FcDM (results displayed in Figure S5). As expected with the time scale of the CV experiment, no positive feedback current was observed. This result also suggested that oxidation of $IrCl_6^{3-}$ by $Co^{III}$ was negligible. The CA detection mode was implemented to observe the fast-reacting $Co^{IV}$ species. The titration currents from the CA experiments are shown in Figure 4. Negligible feedback current due to titration was observed at $E_{Subs}$ less than ca. 725 mV. Currents due to titration of $Co^{IV}$ by $IrCl_6^{3-}$ appeared at $E_{Subs}$ = 750 mV and increased with more positive $E_{Subs}$ until reaching saturation at $E_{Subs} \approx 900$ mV (Figure 4). When the titration currents were integrated over time to yield charge density and plotted as a function of $E_{Subs}$, a plateau was observed at 900 mV. Therefore, a separate titration of $Co^{IV}$ independent from $Co^{III}$ was achieved with the $IrCl_6^{3-}$ mediator; however, due to the inherent time delay in the switching of the bipotentiostat, detection of $Co^{IV}$ was less than quantitative. The charge density at the plateau of $Co^{IV/III}$ was ca. 120 $\mu C/cm^2$, whereas that of $Co^{III/II}$ was ca. 180 $\mu C/cm^2$, indicating that about one-third of the generated $Co^{IV}$ underwent reaction with water during the switching time delay. Attempts were made to estimate the rate constant and half-life of $Co^{IV}$ in contact with water by selecting delay times of 500 ms and 2 s in titration measurements (Figure S6). Less than one-third of charge compared to that of the smallest delay was obtained at $t_{delay}$ = 500 ms, and a complete negative feedback response was observed at $t_{delay}$ = 2 s. From this set of data, a conservative estimate of $k_{Co(IV)} > 2$ $s^{-1}$ can be obtained, corresponding to a half-life smaller than 0.4 s.

Another method for the acquisition of the reaction rate constant is by calculation of TOF from the surface density data obtained as described above. At an overpotential of 410 mV, where most cobalt-based catalysts are evaluated, a current of ca. 11 nA (see Figure S1) was observed from a 12.5 $\mu$m radius $CoP_i$ electrode. From the previously measured water-accessible cobalt density (11 Co atoms/$nm^2$), the per-metal TOF was obtained to be 3.2 $s^{-1}$ (see SI for detailed calculations), whcih is in good agreement with the estimated lower limit rate constant of 2 $s^{-1}$, and also in accordance with the TOF value for $Co_3O_4$ recently estimated through rapid-scan FTIR (>3 $s^{-1}$).[27] Prior to this recent work, the TOFs for $CoP_i$ and $Co_3O_4$ were estimated in the literature to be in the range of 0.007−0.02 $s^{-1}$,[5,6,14,22] and many researchers have expressed concerns about the large uncertainty


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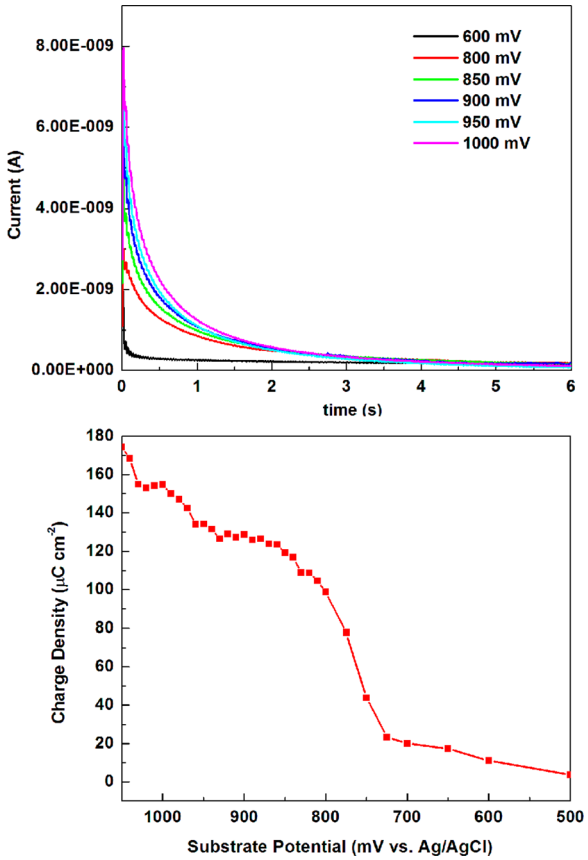


**Figure 4.** Chronoamperograms obtained from $CoP_i$ surface titration by $IrCl_6^{3-}$ (top, tip pulsed from OCP to 0.5 V). Selective titration of $Co^{IV}$ was achieved. Charge density as a function of $E_{Subs}$ is plotted in the bottom frame. The $Co^{IV/III}$ transition seems to occur at ca. 750 mV, consistent with literature precedents.

in the estimated values. With the direct measurement of surface-accessible cobalt density in this Communication, the TOF of a $CoP_i$ catalyst film can be much more reliably calculated. Similar work may be extended to other heterogeneous photo- and electrocatalysts and assist in the elucidation of the per-atom catalytic performance.

In this Communication, we have described a SI-SECM investigation of the $CoP_i$ oxygen-evolving catalyst. By use of this surface-selective technique in a solvent-filled environment, we were able to directly measure, for the first time, the density of water-accessible catalytically active sites on a $CoP_i$ surface. The implication of this direct measurement is an accurate calculation of the TOF of the catalyst, leading to a better understanding of its activity. Also, $Co^{III/II}$ and $Co^{IV/III}$ transitions were separately titrated at the surface. Time-dependent measurements revealed pseudo-first-order rate constants for $Co^{III}$ and $Co^{IV}$ in their reactions with water at 0.19 and >2 $s^{-1}$, respectively. An unexpectedly fast kinetics of surface $Co^{III}$ with water suggests a possibility of $Co^{III}$ assuming an important role as an active species in the next generation of catalysts.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures, and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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