

# Water Oxidation Catalysis Beginning with 2.5 $\mu\text{M}$ $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ : Investigation of the True Electrochemically Driven Catalyst at $\geq 600$ mV Overpotential at a Glassy Carbon Electrode

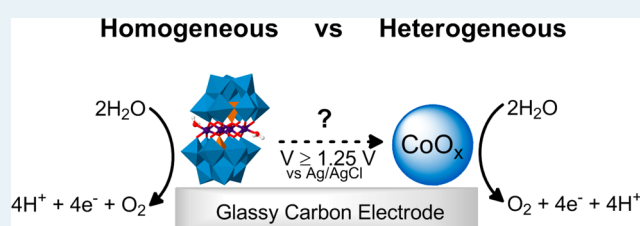
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## Supporting Information

**ABSTRACT:** Evidence for the true water oxidation catalyst (WOC) when beginning with the cobalt polyoxometalate  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  ( $\text{Co}_4\text{-POM}$ ) is investigated at deliberately chosen low polyoxometalate concentrations (2.5  $\mu\text{M}$ ) and high electrochemical potentials ( $\geq 1.3$  V vs Ag/AgCl) in pH 5.8 and 8.0 sodium phosphate electrolyte at a glassy carbon working electrode—conditions which ostensibly favor  $\text{Co}_4\text{-POM}$  catalysis if present. Multiple experiments argue against the dominant catalyst being  $\text{CoO}_x$  formed exclusively from  $\text{Co}^{2+}$  dissociated from the parent POM. Measurement of  $[\text{Co}^{2+}]$  in the  $\text{Co}_4\text{-POM}$  solution and catalytic controls with the corresponding amount of  $\text{Co}(\text{NO}_3)_2$  cannot account for the  $\text{O}_2$  generated from 2.5  $\mu\text{M}$   $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  solutions. This result contrasts with our prior investigation of  $\text{Co}_4\text{-POM}$  under higher concentration and lower potential conditions (i.e., 500  $\mu\text{M}$   $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ , 1.1 V vs Ag/AgCl, as described in Stracke, J. J.; Finke, R. G. *J. Am. Chem. Soc.* **2011**, *133*, 14872) and highlights the importance of reaction conditions in governing the identity of the true, active WOC. Although electrochemical studies are consistent with  $\text{Co}_4\text{-POM}$  being oxidized at the glassy carbon electrode, it is not yet possible to distinguish a  $\text{Co}_4\text{-POM}$  catalyst from a  $\text{CoO}_x$  catalyst formed via decomposition of  $\text{Co}_4\text{-POM}$ . Controls with authentic  $\text{CoO}_x$  indicate conversion of only 3.4% or 8.3% (at pH 8.0 and 5.8) of  $\text{Co}_4\text{-POM}$  into a  $\text{CoO}_x$  catalyst could account for the  $\text{O}_2$ -generating activity, and HPLC quantification of the  $\text{Co}_4\text{-POM}$  stability shows the postreaction  $\text{Co}_4\text{-POM}$  concentration decreases by  $2.7 \pm 7.6\%$  and  $9.4 \pm 5.1\%$  at pH 8.0 and 5.8. Additionally, the  $[\text{Co}^{2+}]$  in a 2.5  $\mu\text{M}$   $\text{Co}_4\text{-POM}$  solution increases by 0.55  $\mu\text{M}$  during 3 min of electrolysis—further evidence of the  $\text{Co}_4\text{-POM}$  instability under oxidizing conditions. Overall, this study demonstrates the challenges of identifying the true WOC when examining micromolar amounts of a partially stable material and when nanomolar heterogeneous metal-oxide will account for the observed  $\text{O}_2$ -generating activity.

**KEYWORDS:** water oxidation catalysis, cobalt polyoxometalate precatalyst, determining the true catalyst, electro-catalysis, homogeneous catalysis, heterogeneous catalysis, multielectron and multiproton transfer catalysis



## INTRODUCTION

Catalytic oxidation of water to oxygen and protons is a central reaction to many sustainable energy storage schemes including water splitting or direct conversion of carbon dioxide into methanol.<sup>1–12</sup> Ideally, water oxidation catalysts (WOCs) should be efficient, long-lived (i.e., stable under the reaction conditions), highly active, and composed of earth-abundant elements.<sup>13–21</sup>

Polyoxometalates (POMs) are of particular interest as WOCs since these discrete metal-oxo compounds can self-assemble (typically at neutral to acidic pHs), are composed primarily of high-valent metals such as tungsten, vanadium, or molybdenum, and can incorporate a variety of redox active transition metal centers including cobalt, ruthenium, or iridium.<sup>22</sup> In addition, since the POM backbone contains metals in their highest accessible oxidation state, they are resistant to oxidative damage. A caveat here is that the POM-

incorporated transition metals are still subject to ligand exchange reactions<sup>23–26</sup> and possibly oxidative transformations.

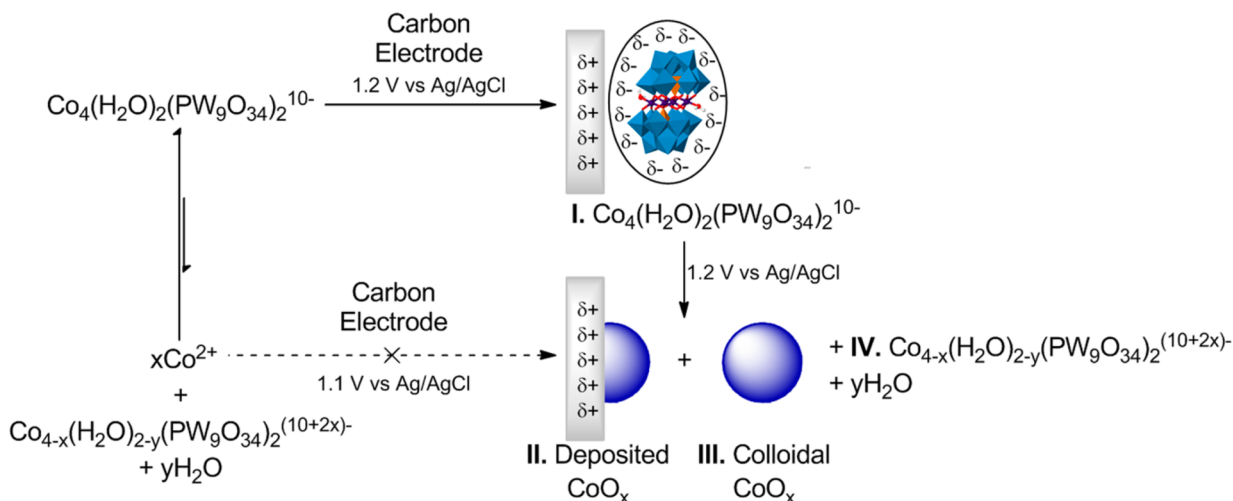
The practical advantages listed above have led to a number of publications describing polyoxometalate WOCs.<sup>27–46</sup> Of particular relevance to the present work is a 2010 *Science* paper which reported the cobalt POM  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  ( $\text{Co}_4\text{-POM}$ ) as a highly active WOC when  $\text{Ru}(\text{bpy})_3^{3+}$  is used as the chemical oxidant.<sup>46</sup> Under the specific conditions of 3.2  $\mu\text{M}$   $\text{Co}_4\text{-POM}$ , 1.5 mM  $\text{Ru}(\text{bpy})_3^{3+}$  oxidant, and pH 8, turnover frequencies of up to 5 ( $\text{mol O}_2 \cdot \text{s}^{-1} \cdot \text{mol Co}_4\text{-POM}^{-1}$ ) and total turnovers of  $>1000$  ( $\text{mol O}_2 \cdot \text{mol Co}_4\text{-POM}^{-1}$ ) were reported.

Subsequently, we reported that under the different conditions of 500  $\mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$ , pH 8, and electrochemi-

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Scheme 1. Plausible WOCs and Their Formation Pathways That Underlie the 4 Hypotheses Tested Herein<sup>a</sup>

<sup>a</sup>Possible catalysts include I.  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$ , II. deposited (i.e., not soluble)  $\text{CoO}_x$ , III. colloidal (i.e., soluble)  $\text{CoO}_x$ , and/or IV. a discrete POM fragment (e.g.  $\text{Co}_3(\text{H}_2\text{O})(\text{PW}_9\text{O}_{34})_2^{12-}$ ). The aqueous  $\text{Co}^{2+}$  to  $\text{CoO}_x$  pathway will be shown to be insignificant under the conditions herein, vide infra.

cally driven oxidation at 1.1 V vs Ag/AgCl, the true catalyst is heterogeneous, electrode-bound  $\text{CoO}_x$  generated from micromolar aqueous  $\text{Co}^{2+}$  which had dissociated from the parent  $\text{Co}_4$ -POM.<sup>47</sup> This conclusion is strongly supported by (1) the isolation and testing of a  $\text{CoO}_x$  film formed during bulk electrolysis at 1.1 V, (2) the decomposition of  $4.3 \pm 0.6\%$   $\text{Co}_4$ -POM measured by UV-vis over a 3 h period, (3) the concomitant increase of  $[\text{Co}^{2+}]$  to  $58 \pm 2 \mu\text{M}$  during that same 3 h period, and importantly, (4) control experiments which showed *identical* water oxidation activity for solutions containing either  $58 \mu\text{M}$   $\text{Co}(\text{NO}_3)_2$  or  $500 \mu\text{M}$   $\text{Co}_4$ -POM during bulk electrolysis at 1.1 V vs Ag/AgCl. Noteworthy here is that  $\text{CoO}_x$  type<sup>48</sup> materials have been studied extensively and form under operating conditions while oxidizing water with moderate overpotentials.<sup>49–55</sup>

However, the key question remained whether the  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  POM could be a catalyst under conditions specifically chosen to favor a discrete  $\text{Co}_4$ -POM WOC including higher electrochemical potential, lower concentration, and more acidic pH conditions where the POM should be more stable.

As depicted in Scheme 1, four hypotheses are considered in the current study under low  $\text{Co}_4$ -POM concentrations, which are closer to those used in the 2010 *Science* paper,<sup>46</sup> and high electrochemical potentials, since that is where  $\text{O}_2$  generation is observed (i.e.,  $2.5 \mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  and 1.1 to 1.4 V vs Ag/AgCl at pH 5.8 or 8.0). The four hypotheses considered herein for the true WOC are as follows: (1) That the starting  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  polyoxometalate is an active WOC; (2) That the starting polyoxometalate is converted into an active  $\text{CoO}_x$  colloidal (soluble) or deposited (insoluble, electrode-bound) WOC at highly oxidizing potentials (i.e.,  $\geq 1.3$  V vs Ag/AgCl); (3) That the polyoxometalate releases cobalt(II) from its core and the dissociated cobalt is then oxidatively converted into a  $\text{CoO}_x$  (colloidal or deposited) WOC (Scheme 1); or (4) That an unknown polyoxometalate or discrete cobalt-oxo(hydroxo) fragment is the true WOC.

Herein, we report  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  electrochemical activity and stability measurements in conjunction with

$\text{Co}(\text{NO}_3)_2$  control experiments which rule out hypothesis (3)— $\text{CoO}_x$  formed from dissociated  $\text{Co}^{2+}$ . However, comparison of the  $\text{Co}_4$ -POM stability,  $\text{O}_2$  evolution activity, and XPS surface analysis with authentic electrodeposited  $\text{CoO}_x$  is consistent with either homogeneous  $\text{Co}_4$ -POM or heterogeneous colloidal  $\text{CoO}_x$  formed from direct oxidative decomposition of the  $\text{Co}_4$ -POM. Indeed, this remaining ambiguity (i) highlights the difficulty in effectively answering the “who is the true catalyst?” question for WOCs when beginning with micromolar concentrations of a metastable material that can lead to nanomolar concentrations of possible catalytic species, and (ii) emphasizes the need for the synthesis, characterization and study of  $\text{CoO}_x$  colloidal WOCs under the precise conditions of a given WOC system such as that examined herein.

## EXPERIMENTAL SECTION

**Materials.**  $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  was synthesized according to published procedures,<sup>46,56</sup> recrystallized, and confirmed via <sup>31</sup>P NMR, UV-vis, and IR spectroscopies which reproduced literature values.<sup>46,47</sup> Other chemicals and solvents were obtained from Sigma-Aldrich or Fisher Scientific and used without further purification. Ultrapure water (resistivity = 18 MΩ-cm) was used to prepare all aqueous solutions and to clean and rinse electrodes.

**Electrochemical Measurements.** A CHI630D potentiostat (CH Instruments), Ag/AgCl (1 M KCl) reference electrode (CH Instruments), and platinum wire counter electrode were used for all electrochemical measurements. Working electrodes were 3 mm diameter glassy carbon disk (CH Instruments), 1 cm<sup>2</sup> glassy carbon plate (Alfa Aesar), boron-doped diamond 3 mm diameter disk (CCL Diamond), or indium tin oxide (ITO) coated glass slides (Delta Technologies). Glassy carbon electrodes were cleaned by polishing with 0.05 μm alumina for 1 min, rinsing with water, sonicating for 30 s, rinsing with water, and drying under air. No attempt was made to remove oxygen from the solutions since  $\text{O}_2$  is produced in most of the electrochemical experiments.

**Cyclic Voltammetry.** The  $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  and 0.1 M sodium phosphate buffer solution was prepared by

diluting the appropriate amount of a 500  $\mu\text{M}$   $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  solution (e.g., 0.010 mL for a final  $[\text{Co}_4\text{-POM}] = 2.5 \mu\text{M}$ ) to 2.00 mL using 0.1 M sodium phosphate buffer. A clean glassy carbon working electrode (3 mm diameter disk) was then pretreated by holding at 1.2 V (vs Ag/AgCl) for 30 s in a pure 0.1 M sodium phosphate electrolyte. The electrodes were then moved to the polyoxometalate solution where cyclic voltammetry was performed; typical scans had a potential range = 0.5 to 1.6 V (vs Ag/AgCl) and a scan rate = 20 mV/s.  $\text{Co}_4\text{-POM}$  solutions were aged 15–60 min prior to recording the voltammogram, aging which did not appear to significantly change the observed CV.

**Determination of  $[\text{Co}^{2+}]_{\text{apparent}}$  by Differential Pulse Cathodic Adsorptive Stripping Voltammetry.** *Bismuth Plating and Stripping Voltammetry Conditions.* Stripping voltammetry was based upon a previously published procedure.<sup>57</sup> Briefly, bismuth was plated onto a clean glassy carbon electrode (3 mm diameter disk) at  $-0.25$  V (vs Ag/AgCl) for 45 s from a solution containing 0.02  $\text{Bi}(\text{NO}_3)_3$ , 0.5 M LiBr, 1 M HCl. The electrodes were then rinsed and placed into the analyte solution. The potential was then held at 1.3 V for 15 s, followed by magnetic stirring for 2 s, and then differential pulse voltammetry. Parameters for the voltammogram were as follows: potential range =  $-0.7$  to  $-1.3$  V (vs Ag/AgCl), potential increments = 0.004 V, step amplitude = 0.05 V, pulse width = 0.1 s, pulse period = 0.2 s, quiet time before initiating scan = 10 s.

A standard curve was generated using  $\text{Co}(\text{NO}_3)_2$  solutions at known concentrations of 0, 50, 250, and 500 nM; the standard solutions also contained 0.10 M sodium phosphate buffer at pH 8.0, and 20  $\mu\text{M}$  dimethylglyoxime.

*Determination of  $[\text{Co}^{2+}]$  in  $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  Solutions under Noncatalytic Conditions.* Polyoxometalate solutions used to determine the  $[\text{Co}^{2+}]_{\text{apparent}}$  initially contained 2.63  $\mu\text{M}$   $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  and 0.105 M sodium phosphate buffer at pH 8.0. Then, 0.10 mL of 400  $\mu\text{M}$  dimethylglyoxime was added to make a 2.50  $\mu\text{M}$   $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$ , 0.100 M sodium phosphate, and 20  $\mu\text{M}$  dimethylglyoxime solution. Dimethylglyoxime was added to either the  $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  or  $\text{Co}(\text{NO}_3)_2$  standards just 5 min before starting the differential pulse voltammogram to minimize any kinetic acceleration effects of dimethylglyoxime binding of  $\text{Co}^{2+}$  on the final amount of  $[\text{Co}^{2+}]_{\text{apparent}}$ .

*Comparison of  $[\text{Co}^{2+}]$  in  $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  Solutions before and after Bulk Electrolysis.* A 2.50  $\mu\text{M}$   $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  solution in pH 8.0, 0.1 M sodium phosphate was prepared. 1.50 mL of that solution was subjected to a 1.4 V vs Ag/AgCl bulk electrolysis as described below in the section “Bulk Electrolysis and Dissolved  $\text{O}_2$  Measurements”. After the electrolysis, 1.00 mL of the solution was transferred to a vial and 5.0  $\mu\text{L}$  of an aqueous 4.0 mM dimethylglyoxime solution was added to the  $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  solution. After 5 min, the cathodic stripping voltammogram was recorded as described above in the “Bismuth plating and stripping voltammetry conditions” section. Next, 1.00 mL of the original 2.50  $\mu\text{M}$   $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  solution in pH 8.0, 0.1 M sodium phosphate (i.e., a portion of the original solution which had not been subjected to bulk electrolysis) was transferred to a vial, and 5.0  $\mu\text{L}$  of an the 4.0 mM dimethylglyoxime solution was added to the polyoxometalate solution. The solution was aged 5 min and then the cathodic

stripping voltammogram was recorded using the “Bismuth plating and stripping voltammetry conditions” described above. The total aging time of the  $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  solution was 24 minutes for the electrolyzed sample and 33 min for the unelectrolyzed sample.

In a variation of the above experiment, a 2.50  $\mu\text{M}$   $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  solution was subjected to three consecutive 60 s bulk electrolysis experiments at 1.4 V vs Ag/AgCl. The 1.0  $\text{cm}^2$  glassy carbon electrode was polished and cleaned between each electrolysis experiment as described in the “Electrochemical Measurements” section above. After the three electrolysis experiments were completed, 1.00 mL of both the electrolyzed and the nonelectrolyzed  $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$  solution were subjected to the cathodic stripping voltammetry procedure described in the previous paragraph. Total aging times for the electrolyzed and unelectrolyzed sample were 41 and 50 min, respectively.

**Bulk Electrolysis and Dissolved  $\text{O}_2$  Measurements.** Bulk water electrolysis was conducted using a two compartment electrochemical cell where the working compartment contained the glassy carbon plate working electrode ( $A = 1.0 \text{ cm}^2$ ), the Ag/AgCl reference electrode, the  $\text{O}_2$  measurement probe, a stir bar, and 1.50 mL of analyte solution. The other compartment contained the platinum wire counter electrode. The oxygen was measured using an Ocean Optics FOXY-R probe connected to a Neofox system. The probe was calibrated using 0% and 20.9% (i.e., air saturated)  $\text{O}_2$  solutions, that is, using 0 and 236  $\mu\text{M}$   $\text{O}_2$  at 20  $^\circ\text{C}$  and correcting for the lower air pressure in Fort Collins, Colorado (pressure values ranged from 0.83 to 0.86 bar during the periods of data collection). The dissolved  $[\text{O}_2]$  was measured beginning 20 s before initiation of the bulk electrolysis. The solution was stirred at 400 rpm throughout the experiment. Between each electrolysis experiment, the solutions were changed and the electrodes were cleaned as described in the “electrochemical measurements” section above. POM solutions were aged for 15–60 min prior to electrolysis; this aging did not result in a measurable change in the  $\text{O}_2$  producing activity of the  $\text{Co}_4\text{-POM}$  solutions, vide infra.

*Deposited  $\text{CoO}_x$  Controls.* Prior to bulk electrolysis and  $\text{O}_2$  measurements,  $\text{CoO}_x$  was deposited onto the glassy carbon working electrode by placing the working, reference, and counter electrodes into a 0.1 mM  $\text{Co}(\text{NO}_3)_2$  plus 0.1 M, pH 8.0 sodium phosphate solution and holding the potential at 0.79 V vs (Ag/AgCl) for a predetermined amount of time. Electrodes were then rinsed with water, dried by wicking away excess water with a kim-wipe, and placed into their respective electrochemical compartments as described in the previous paragraph. The amount of deposited  $\text{CoO}_x$  was estimated by subtracting the current passed during a blank electrolysis (i.e., containing only 0.1 M sodium phosphate buffer) from the current passed during the  $\text{Co}(\text{NO}_3)_2$  plus sodium phosphate electrolysis while assuming 1  $e^-$  was passed per deposited cobalt.

**HPLC.** A Hewlett-Packard 1050 system fitted with a Kromasil C18 column (100  $\times$  4.6 cm, 3.5  $\mu\text{m}$  particles) was used for all HPLC analyses. Mobile phase composition, similar to a previously published procedure for polyoxometalate separations,<sup>58</sup> was 80% water, 20% acetonitrile, 30 mM *n*-butyl ammonium, 10 mM sodium citrate, pH 6.5. The ammonium and citrate portion of the eluent was prepared by dissolving the appropriate amounts of *n*-butyl amine and sodium citrate in water and adjusting the pH with concentrated

HCl. The injection volume was 50  $\mu\text{L}$ , and the flow rate was 1.25 mL/minute. Samples were monitored at 240 and 580 nm.

For comparing electrolyzed and unelectrolyzed polyoxometalate samples, the postelectrolysis solution was analyzed immediately after stopping  $[\text{O}_2]$  data collection (see above), and was followed by HPLC analysis of the otherwise identical, unelectrolyzed sample.

**XPS.** X-ray photoelectron spectra were obtained using a Physical Instruments PHI-5800 spectrometer. Samples were prepared by rinsing with water after completion of a bulk electrolysis experiment, followed by drying under vacuum. Data was collected using a 7 mm aluminum anode during a 15 min measurement time.

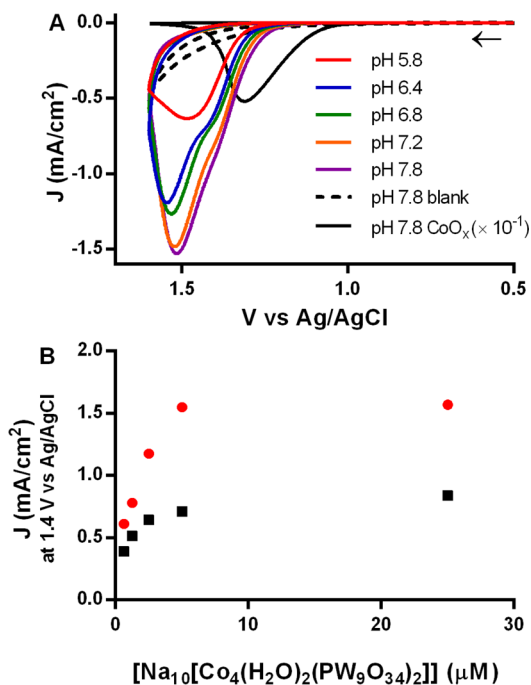
**SEM/EDX.** Scanning electron microscopy and energy dispersive X-ray spectroscopy was conducted using a JEOL JSM-6500F microscope and a Thermo Scientific NORAN system. Sample preparation was the same as for XPS.

## RESULTS AND DISCUSSION

**Electrochemical Studies of  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  Solutions.** Consistent with our prior investigation,<sup>47</sup> cyclic voltammetry of freshly dissolved  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  in aqueous 0.1 M sodium phosphate buffer yields almost no anodic response up to 1.1 V vs Ag/AgCl (e.g., 578 mV of overpotential for the water-to-oxygen oxidation reaction at pH 8).<sup>59</sup> However, at larger overpotentials, one (or two) oxidative wave(s) is observed for the 2.5  $\mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  solutions (Figure 1A) at a glassy carbon electrode.<sup>60</sup> These waves are chemically irreversible regardless of pH, switching potential (see the Supporting Information, Figure S1A), or scan rate (Supporting Information, Figure S1B). Additionally, the first oxidation wave exhibits current saturation at concentrations greater than 5  $\mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  (Figure 1B), which is consistent with adsorption of  $\text{Co}_4$ -POM (or a different active species) to the glassy carbon electrode. This behavior is not surprising given the precedent of POM adsorption to electrodes,<sup>61</sup> as well as the expected Coulombic attraction of a highly positively polarized electrode in conjunction with the large, 10- negative charge on  $\text{Co}_4$ -POM. Although indium tin oxide and boron doped diamond electrodes were also tested, neither of these materials showed measurable activity in 2.5  $\mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  solutions relative to blank experiments (Supporting Information, Figure S2). Therefore, a glassy carbon electrode was used herein for all electrochemical studies of the  $\text{Co}_4$ -POM solutions.

As shown in Figure 2, the anodic wave in the  $\text{Co}_4$ -POM solution shifts by  $-36$  mV/pH unit with increasing pH and  $-93 \pm 3$  mV/decade in the Tafel plots. The combination of these data indicates a fractional dependence of the anodic current on pH. However, these parameters might include contributions from noncatalytic processes, as has been reported previously for cobalt oxide WOCs.<sup>62</sup> For example, Gerken et al. observed that up to 30 min of equilibration time at a given potential is sometimes necessary to make reproducible Tafel plots using  $\text{CoO}_x$  catalysts.<sup>54</sup> Unfortunately, the oxidation currents for the  $\text{Co}_4$ -POM decay rapidly to background levels within minutes, *vide infra*, which prevents study of the present  $\text{Co}_4$ -POM system at long equilibration times. Hence, it follows that the current system is being studied under nonequilibrium conditions.

Cyclic voltammetry and the corresponding current-pH and current-overpotential dependences were used to compare

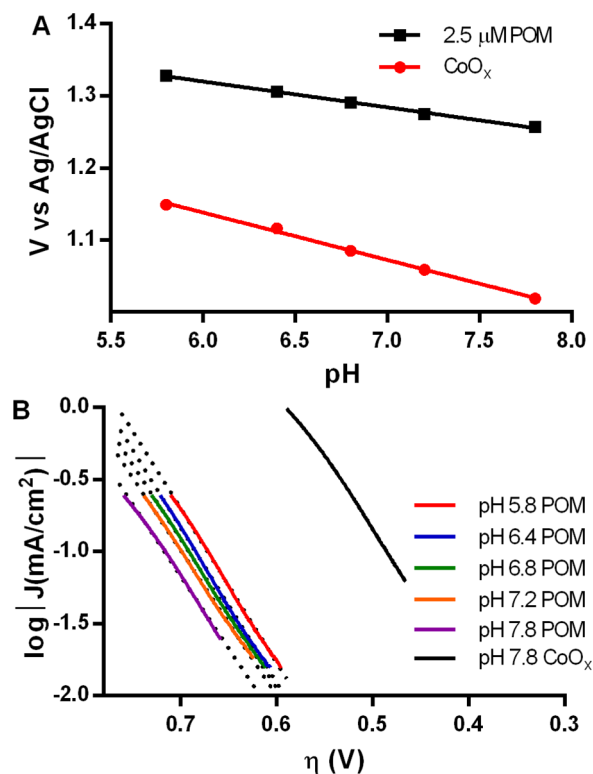


**Figure 1.** (A) Cyclic voltammetry of 2.5  $\mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  as a function of pH after subtraction of the background current at the indicated pH. For comparison, the uncorrected background current at pH 7.8 is shown as a dotted line and a  $\text{CoO}_x$  catalytic film—at  $1/10^{\text{th}}$  of its measured intensity—is shown as a solid black line. The  $\text{CoO}_x$  was deposited from 100  $\mu\text{M}$   $\text{Co}(\text{NO}_3)_2$  plus 0.1 M, pH 8.0 sodium phosphate buffer at 0.79 V for 39 s (i.e., conditions which correspond to passage of  $1.0 \times 10^{-4}$  coulombs/cm<sup>2</sup>, *vide infra*). An arrow indicates the initial scan direction. (B) Saturation of the measured cyclic voltammetry current at 1.4 V with increasing polyoxometalate concentration at pH 5.8 (black squares) and pH 8.0 (red circles). Supporting electrolyte is 0.1 M sodium phosphate buffer. Working, reference, and counter electrodes are glassy carbon (3 mm diameter disk), Ag/AgCl, and Pt, respectively. The scan rate is 20 mV/s.

empirically the  $\text{Co}_4$ -POM solutions with heterogeneous  $\text{CoO}_x$ . Authentic  $\text{CoO}_x$  samples were deposited from 100  $\mu\text{M}$   $\text{Co}(\text{NO}_3)_2$  plus 0.1 M, pH 8.0 sodium phosphate buffer using a procedure similar to that reported by Surendranath et al.<sup>53</sup> where it was assumed that one electron oxidation corresponds to the deposition of one cobalt(III) atom. Using this treatment, the prepared  $\text{CoO}_x$  films in Figures 1 and 2 contain approximately 10 nmols of cobalt.

The resultant electrochemical data when beginning with  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  differs from heterogeneous, deposited  $\text{CoO}_x$  in at least two significant ways. First, the onset for water oxidation by  $\text{CoO}_x$  occurs a few hundred millivolts less positive than the  $\text{Co}_4$ -POM anodic wave (e.g.,  $\sim 240$  mV less oxidizing potentials at pH 7.8 as shown in Figure 1). Second, the pH and Tafel dependences for a  $\text{CoO}_x$  catalyst exhibit slopes of  $-66$  mV/pH unit and  $-104 \pm 7$  mV/decade (Supporting Information, Figure S3), respectively. Cumulatively, these differences offer strong evidence *against* the hypothesis that the true catalyst is heterogeneous  $\text{CoO}_x$  formed from aqueous  $\text{Co}^{2+}$  (either insidious or dissociated from  $\text{Co}_4$ -POM) while under the reaction conditions here.

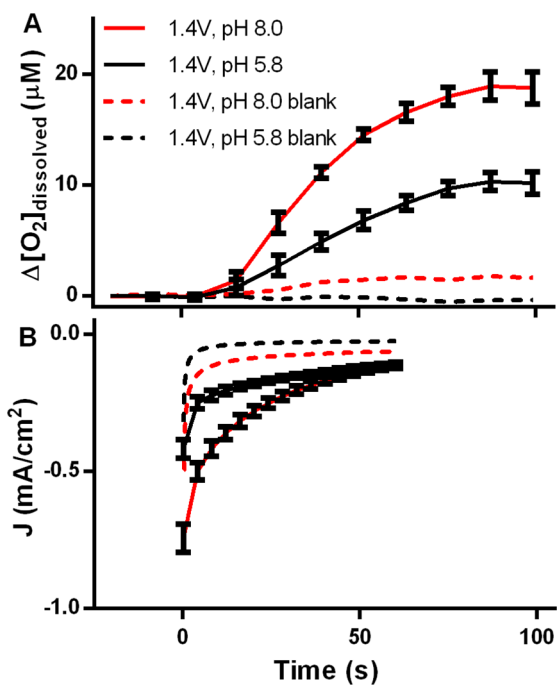
Additionally, repeated cycling of the  $\text{Co}_4$ -POM voltammogram shows no evidence of any  $\text{CoO}_x$  peaks growing in (Supporting Information, Figure S4). Moreover, cyclic voltammetry of the glassy carbon electrodes show only



**Figure 2.** (A)  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  (POM) and  $\text{CoO}_x$  pH dependence of the potential measured at a constant current of 0.1 mA/cm<sup>2</sup> using the cyclic voltammetry data in Figure 1 and Supporting Information, Figure S3. The slopes of the POM and  $\text{CoO}_x$  curves are  $-36$  and  $-66$  mV/pH unit. (B) Tafel plots for  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  (POM) and  $\text{CoO}_x$  derived from the cyclic voltammetry data in Figure 1. Dotted lines indicate the linear fit to the data and where  $1/\text{slope}$  (i.e., the current-overpotential relationship) of the  $\text{Co}_4$ -POM fits varies between  $-93$  and  $-100$  mV/decade and the  $\text{CoO}_x$  fit is a similar  $-101$  mV/decade. The overpotential was calculated using the equation:  $\eta = E - (1.23 - 0.059 \cdot \text{pH}) + 0.236$  V, where  $E$  is the potential versus Ag/AgCl,  $(1.23 - 0.059 \cdot \text{pH})$  is the reversible potential for water oxidation versus NHE, and  $0.236$  is the voltage addition needed to convert the measured potential from Ag/AgCl to NHE.

background activity levels after bulk electrolysis of a 2.5  $\mu$ M  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  at 1.4 V vs Ag/AgCl and then rinsing of the electrodes (Supporting Information, Figure S5). These results contrast our previous study of  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  at 500  $\mu$ M concentration and 1.1 V vs Ag/AgCl which showed clearly that the dominant catalyst is, under those different concentration and electrochemical potential conditions, heterogeneous  $\text{CoO}_x$  formed from  $\text{Co}^{2+}$  which had been released by the parent  $\text{Co}_4$ -POM.

To confirm  $\text{O}_2$  as a reaction product and to determine the faradaic efficiency of the system, bulk electrolysis of  $\text{Co}_4$ -POM solutions was performed at several potentials. Similar to the cyclic voltammetry above, significant water oxidation activity was not observed until 1.3 V vs Ag/AgCl. At a potential of 1.4 V, quantifiable water oxidation activity was observed where  $15.6 \pm 1.2$  and  $28.4 \pm 1.8$  nmol  $\text{O}_2$  were produced at pH 5.8 and 8.0, respectively (Figure 3A). If the POM is assumed to be a WOC, then conversion of this  $\text{O}_2$  generation data into an average turnover frequency when beginning with the  $\text{Co}_4$ -POM yields an approximate TOF = 0.54 and 0.98 mol  $\text{O}_2 \cdot \text{s}^{-1} \cdot \text{mol cobalt}^{-1}$  at pH 5.8 and 8.0. This calculation assumes



**Figure 3.** Bulk electrolysis dissolved  $\text{O}_2$  measurement and current density for a 2.5  $\mu$ M  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  solution (volume = 1.50 mL) in 0.1 M sodium phosphate buffer (pH 8.0 or 5.8) at 1.4 V vs Ag/AgCl on a glassy carbon electrode ( $A = 1.0$  cm<sup>2</sup>). The  $\text{O}_2$  was measured using a fluorescence based detection system (FOXY-R probe from Ocean Optics). Electrolysis was started at  $t = 0$  s. The lag between the start of electrolysis and the detection of oxygen is primarily due to a slow response time of the probe. Error bars indicate the standard deviation of three experiments.

the only active portion of the POM solution is a monolayer in contact with the 1 cm<sup>2</sup> electrode and where the area coverage of one  $\text{Co}_4$ -POM is 1.38 nm<sup>2</sup>—which is the area of the smallest crystallographically determined face.<sup>46</sup> Note, the assumption that only the  $\text{Co}_4$ -POM molecules which are in a monolayer contribute to the catalysis will overestimate the TOF since it is likely that exchange between solution and adsorbed  $\text{Co}_4$ -POMs occurs during the reaction. Further details of this TOF calculation can be found in the Supporting Information. This TOF estimation is provided primarily for comparison to the TOF for  $\text{CoO}_x$ , vide infra.

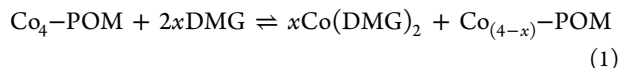
Additionally, the calculated TOF for the putative  $\text{Co}_4$ -POM based catalyst is underestimated since the current densities decayed to 15–25% of their initial values during the 60 s electrolysis, as shown in Figure 3B. Decomposition of activity for glassy carbon is not unexpected at these large, 1.4 V positive potentials. Decay in oxidation current likely corresponds primarily to electrode surface changes and not significant decomposition in the  $\text{Co}_4$ -POM solution since oxidation activity of the system is restored upon polishing/cleaning the glassy carbon electrode (Supporting Information, Figure S6).

Despite the oxidative fouling of the glassy carbon electrode, the faradaic efficiency (i.e., the current to  $\text{O}_2$  efficiency) of the  $\text{Co}_4$ -POM solution was found to be  $75.0 \pm 2.2\%$  and  $88.8 \pm 1.4\%$  at pH 5.8 and 8.0. This efficiency is important since it indicates most of the current corresponds to the catalyzed  $\text{O}_2$  producing reaction and not to oxidative catalyst decomposition pathways. In comparison the control bulk electrolysis experiments, where no  $\text{Co}_4$ -POM is present in solution, no  $\text{O}_2$

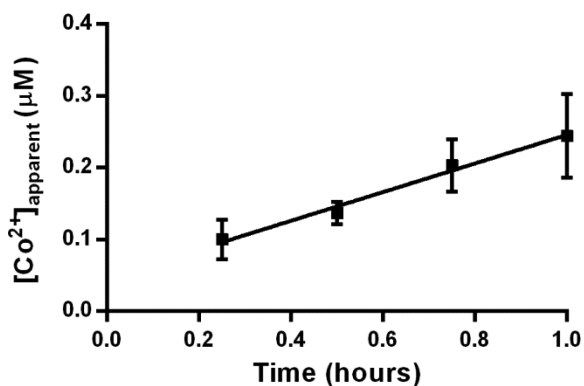
increase is seen at pH 5.8 and only 2.0 nmol of O<sub>2</sub> are produced at pH 8.0.

In short, these electrochemical studies show that (i) significant water oxidation activity is present in Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub><sup>10-</sup> solutions at applied potentials greater than 1.25 V vs Ag/AgCl, (ii) this activity saturates at low (~5 μM) Co<sub>4</sub>-POM concentrations, and (iii) this activity occurs at approximately 200 mV more overpotential than heterogeneous CoO<sub>x</sub> catalysts—three lines of evidence which demonstrates that CoO<sub>x</sub> formed from dissociated Co<sup>2+</sup> is *not* the active catalyst under the specific conditions of 2.5 μM Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub><sup>10-</sup> at ≥1.3 V vs Ag/AgCl.

**Determination of [Co<sup>2+</sup>] in Co<sub>4</sub>-POM Solutions.** To investigate the hydrolytic stability under nonoxidizing conditions, the aqueous [Co<sup>2+</sup>]<sub>apparent</sub> was determined by cathodic stripping voltammetry at pH 8.<sup>57,63</sup> This electrochemical method was used by us previously<sup>47</sup> to determine the [Co<sup>2+</sup>]<sub>apparent</sub> in 500 μM Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub><sup>10-</sup> solution and found to accurately report the apparent aqueous cobalt(II) concentration determined by an alternative, independent electrochemical method. (Specifically, the [Co<sup>2+</sup>]<sub>apparent</sub> was determined to be 56 ± 2 μM using the cathodic stripping technique and 58 ± 2 μM using the alternative method which relies on the measurement of an anodic current-[Co<sup>2+</sup>] relationship.)<sup>47</sup> However, it should be noted that the observed [Co<sup>2+</sup>] is likely an upper limit to the true aqueous [Co<sup>2+</sup>] since complexation of cobalt(II) by the additive dimethylglyoxime (DMG) can shift the equilibrium in eq 1 to the right. To minimize this effect, the dimethylglyoxime was added only 5 min before the measurement was taken as detailed in the Experimental Section.



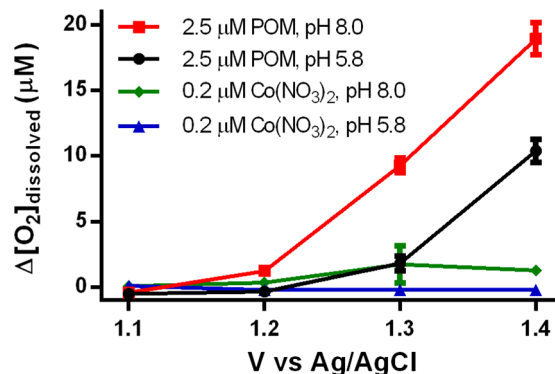
As shown in Figure 4, about 100 nM Co<sup>2+</sup> is present in the 2.5 μM Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub><sup>10-</sup> solution after 15 min of aging which increases to 250 nM (0.25 ± 0.06 μM) Co<sup>2+</sup> after 1 h. That is, 10% of the Co<sub>4</sub>-POM has released a cobalt atom from their core or, alternatively, 2.5% of the Co<sub>4</sub>-POM has released all four core cobalts after 1 h in 0.1 M phosphate buffer solution. This result confirms our prior observation that, in



**Figure 4.** Apparent Co<sup>2+</sup> concentration, determined using cathodic stripping voltammetry in 2.5 μM Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub><sup>10-</sup> plus 20 μM dimethylglyoxime in 0.1 M, pH 8.0 sodium phosphate buffer, taken at 15 min aging intervals. The concentrations were calculated using a standard curve generated from Co(NO<sub>3</sub>)<sub>2</sub> solutions (Supporting Information, Figure S7). Error bars indicate the standard deviation of three experiments.

general, Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub><sup>10-</sup> is not 100% stable in aqueous pH 8.0, 0.1 M sodium phosphate buffer.

**Controls with Co(NO<sub>3</sub>)<sub>2</sub>.** With the degree of Co<sup>2+</sup> dissociated from the parent Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub><sup>10-</sup> established, it is then possible to conduct the proper control experiments comparing the activity observed in Co<sub>4</sub>-POM solutions to the above measured amount of [Co<sup>2+</sup>]<sub>apparent</sub>. In Figure 5 the O<sub>2</sub> yields for both 2.5 μM Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub><sup>10-</sup>

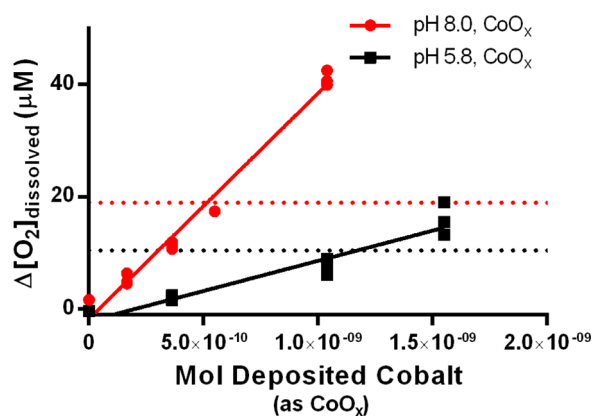


**Figure 5.** Dissolved oxygen production (μM) during catalytic water oxidation at a glassy carbon electrode and the given Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub><sup>10-</sup> (POM) or Co(NO<sub>3</sub>)<sub>2</sub> concentrations, pH, and potential during a 60 s bulk electrolysis. Oxygen was measured using a FOXY-R O<sub>2</sub> detection probe. The plotted lines are meant solely to guide the eye. Error bars indicate the standard deviation of three experiments.

0.2 μM Co(NO<sub>3</sub>)<sub>2</sub> are shown. Interestingly, these 0.2 μM Co(NO<sub>3</sub>)<sub>2</sub> controls *do not* account for the observed O<sub>2</sub> generating catalysis. This result contrasts starkly with our prior results at higher polyoxometalate concentrations and lower electrochemical potentials (i.e., at 500 μM Co<sub>4</sub>-POM and 1.1 V vs Ag/AgCl) where the 58 ± 2 μM Co<sup>2+</sup> dissociated from the parent POM accounted quantitatively (101 ± 12%) for the observed O<sub>2</sub> production.<sup>47</sup>

Although the above evidence indicates a Co<sup>2+</sup> to CoO<sub>x</sub> catalyst formation mechanism is *not* a dominant O<sub>2</sub> production pathway under the specific conditions investigated herein (i.e., when using the [Co<sup>2+</sup>] present after approximately 1 h of aging), it does not rule out the possibility that a small portion of the current could correspond to direct transformation of the electrode-adsorbed Co<sub>4</sub>-POM into highly active CoO<sub>x</sub> (Scheme 1, *vide supra*). Therefore it is crucial (i) to determine how much authentic CoO<sub>x</sub> is needed to carry the water oxidation activity observed in the Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub><sup>10-</sup> solution, and then (ii) determine whether this amount of Co<sub>4</sub>-POM decomposition can be observed.

**Controls with Authentic CoO<sub>x</sub>.** To address the question whether direct oxidative decomposition of the cobalt POM into CoO<sub>x</sub> could account for the catalytic water oxidation activity observed in Co<sub>4</sub>-POM solutions, a series of CoO<sub>x</sub> coated electrodes were prepared by electro-deposition of the CoO<sub>x</sub> material from cobalt(II) nitrate solutions at pH 8.0, and then tested in pure sodium phosphate electrolyte for their ability to generate O<sub>2</sub> at 1.4 V vs Ag/AgCl (Figure 6). By dividing the slopes of these curves by the reaction time (i.e., 60 s), an approximate, average turnover frequency for the CoO<sub>x</sub> catalyst is found to be TOF = 1.0 and 0.27 mol O<sub>2</sub>·s<sup>-1</sup>·mol cobalt<sup>-1</sup> at pH 8.0 and 5.8, respectively. Additional details of this calculation can be found in the Supporting Information. This

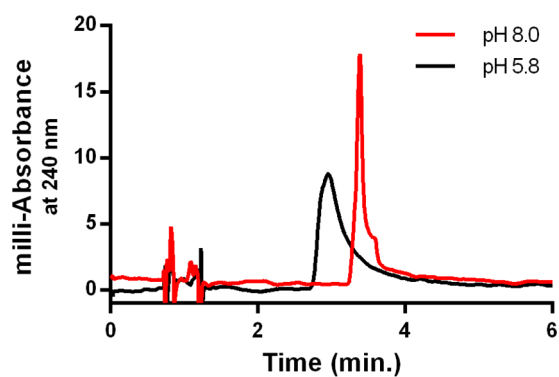


**Figure 6.** Calibration curve of oxygen yielded during a 60 s, 1.4 V electrolysis of predeposited  $\text{CoO}_x$  catalysts containing the approximate mols of cobalt indicated. The  $\text{CoO}_x$  catalysts were prepared in 0.1 mM  $\text{Co}(\text{NO}_3)_2$  plus pH 8.0, 0.1 M sodium phosphate at 0.79 V for predetermined amounts of time (as described in the main text). The dashed lines indicate the observed  $\text{O}_2$  yield in a  $2.5 \mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  bulk electrolysis at 1.4 V for 60 s at pH 5.8 (black) and 8.0 (red) (i.e., the same conditions as in Figure 3); that is, the amounts of deposited  $\text{CoO}_x$  at (or above) the dashed lines are equivalent to (or more active than) the  $2.5 \mu\text{M}$   $\text{Co}_4$ -POM solutions under identical reaction conditions.

estimate is likely an underestimate of the true activity since the deposited  $\text{CoO}_x$ -glassy carbon catalyst is not stable under the reaction conditions (vide infra). In comparison, Surendranath et al. reported a  $\text{CoO}_x$  TOF =  $0.0026 \text{ mol O}_2 \cdot \text{s}^{-1} \cdot \text{mol cobalt}^{-1}$  in pH 7.0 potassium phosphate and at 410 mV of overpotential. That is, they observed TOF values which would be  $1.2 \times 10^5$  and  $9.0 \times 10^3 \text{ mol O}_2 \cdot \text{s}^{-1} \cdot \text{mol cobalt}^{-1}$  if their observed current-overpotential relationship of 61 mV/decade is extrapolated to our working overpotentials of 878 mV and 748 mV at pH 8.0 or 5.8 and at 1.4 V vs Ag/AgCl. Again, these TOF estimates and ranges are, admittedly, crude, but are provided herein as initial estimates from which to base the needed future studies. Once one has the true, per-active-site, TOFs for  $\text{CoO}_x$ ,  $\text{Co}_4$ -POM, and other POMs, metal oxides, and WOCs of interest, then the problem of determining the true catalyst, as well as which type of WOC merits future emphasis, will become much easier and clearer.

When the  $\text{O}_2$  yields of these  $\text{CoO}_x$  coated electrodes were compared to the yields observed for  $\text{Co}_4$ -POM solutions, it was found that  $0.45$ – $0.58 \text{ nmols}$  (at pH 8.0) and  $1.0$ – $1.5 \text{ nmols}$  (at pH 5.8) of cobalt in the form of deposited  $\text{CoO}_x$  can account for the total amount of oxygen generated at 1.4 V during a 60 s bulk electrolysis experiment. Restated, as little as 4 to 8% transformation of the starting POM into  $\text{CoO}_x$  could carry the observed  $\text{O}_2$  production of the  $\text{Co}_4$ -POM solutions at pH 8 or 5.8, assuming all four cobalts from  $\text{Co}_4$ -POM are converted into  $\text{CoO}_x$ . Therefore, it is necessary to determine the oxidative stability of the initially  $2.5 \mu\text{M}$   $\text{Co}_4$ -POM under the oxidizing reaction conditions (i.e., the postreaction level of decomposition of  $\text{Co}_4$ -POM).

**Polyoxometalate Stability Measured by HPLC.** Stability of  $\text{Co}_4$ -POM under the highly oxidizing reaction conditions was quantified by HPLC with absorbance detection. The HPLC separation used herein is based upon an ion-pair chromatography method developed previously by our group (Figure 7).<sup>58</sup> In these experiments, the  $2.5 \mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  pre- and post-bulk electrolysis



**Figure 7.** HPLC traces of  $\text{Co}_4$ -POM solutions with  $2.5 \mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  in 0.1 M sodium phosphate buffer at the indicated pH; the chromatograms are corrected by subtracting a blank HPLC trace which contained only 0.1 M sodium phosphate at the same pH as the sample. Chromatograms were monitored using the 240 nm absorbance of the sample. HPLC conditions are 80% water, 20% acetonitrile, 30 mM butylammonium chloride, 10 mM sodium citrate, pH 6.5, 1.25 mL flow rate, and room temperature.

solutions were compared to determine whether any loss of  $\text{Co}_4$ -POM could be detected (Supporting Information, Figure S8). Evidence that the HPLC measurement is faithfully reporting the  $[\text{Co}_4\text{-POM}]$  includes: (i) the background subtracted chromatograms show a single peak at pH 5.8, which (ii) increases in area linearly with  $\text{Co}_4$ -POM concentration (Supporting Information, Figure S9), and (iii) collection of the eluent from  $t = 2.5$ – $3.0$  min with subsequent visible spectroscopy shows that the eluted sample has the expected visible absorption spectrum when compared to a nonchromatographed  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  sample (Supporting Information, Figure S10). When the  $\text{Co}_4$ -POM sample in pH 8.0 sodium phosphate buffer is tested by HPLC, a shoulder is observed immediately next to the primary peak; this may be due to partial conversion of the  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  to one of the related POMs where one or two of the cobalt atoms have dissociated from the core and have been replaced by sodium (e.g.,  $\text{NaCo}_3(\text{H}_2\text{O})(\text{PW}_9\text{O}_{34})_2^{11-}$  or  $\text{Na}_2\text{Co}_2(\text{PW}_9\text{O}_{34})_2^{12-}$ ).<sup>64</sup> Note that the dissociation of cobalt from  $\text{Co}_4$ -POM is supported by the independent determination of  $[\text{Co}^{2+}]_{\text{apparent}}$  above (Figure 4).

At pH 5.8 or 8.0 and electrochemical potentials ranging from 1.1 to 1.4 V vs Ag/AgCl the relative stability of  $\text{Co}_4$ -POM is listed in Table 1, data which indicate that the starting polyoxometalate is somewhat, but not absolutely, stable under the oxidizing environment encountered in this study. HPLC measured  $\text{Co}_4$ -POM stability at lower electrochemical potentials is consistent with  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  being hydrolytically stable over the approximately 15 min duration of the experiment, plus or minus the 2–12% error of the method. Significantly, at pH 5.8 and pH 8.0 the change in  $[\text{Co}_4\text{-POM}]$  after a 1.4 V electrolysis (Table 1) corresponds to the loss of  $1.41 \pm 0.76$  and  $0.4 \pm 1.1 \text{ nmols}$  of cobalt during electrolysis while the  $\text{CoO}_x$  electrolysis controls (Figure 6) indicate that  $1.2 \pm 0.3$  and  $0.51 \pm 0.07 \text{ nmols}$  of  $\text{CoO}_x$  are capable of carrying the observed WOC activity under these conditions. These closely matched values indicate that deposited and/or soluble, colloidal  $\text{CoO}_x$  cannot be ruled out as a WOC when beginning with  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  under the specific conditions of this study.

**Table 1. Stability of 2.5  $\mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  Solutions during Bulk Electrolysis Determined by HPLC<sup>a</sup>**

pH	potential vs Ag/AgCl	electrolysis time (s)	$\text{Co}_4$ -POM stability <sup>b,c</sup>
5.8	1.1	60	97.4% $\pm$ 6.4
5.8	1.2	60	99.0% $\pm$ 2.1
5.8	1.3	60	90.1% $\pm$ 8.9
5.8	1.4	60	90.6% $\pm$ 5.1
8	1.1	60	93.7% $\pm$ 2.5
8	1.2	60	100.8% $\pm$ 5.5
8	1.3	60	100.8% $\pm$ 12.3
8	1.4	60	97.3% $\pm$ 7.6

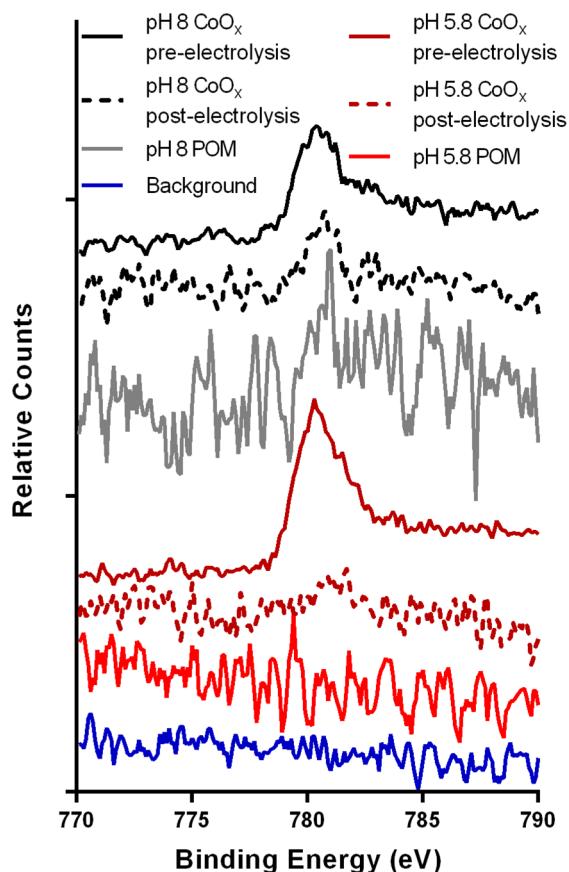
<sup>a</sup>Electrolysis conditions are the same as described in Figure 3.

<sup>b</sup>Stability is calculated by dividing the area of the electrolyzed  $\text{Co}_4$ -POM HPLC peak (at  $t = 3$ – $4$  min in Figure 7) by the unelectrolyzed  $\text{Co}_4$ -POM HPLC peak:  $\text{Co}_4$ -POM Stability =  $\text{Area}_{\text{electrolyzed}} / \text{Area}_{\text{unelectrolyzed}} \cdot 100\%$ . <sup>c</sup>Error bars are the standard deviation of three experiments.

**Determination of  $[\text{Co}^{2+}]$  in Post-Catalysis  $\text{Co}_4$ -POM Solutions.** To further support the hypothesis of  $\text{Co}_4$ -POM instability under the oxidizing reaction conditions, the post-electrolysis cobalt(II) concentrations were determined via cathodic stripping voltammetry. In these experiments, a standard solution of 2.5  $\mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  plus pH 8.0, 0.1 M sodium phosphate was subjected to a 60 s bulk electrolysis at 1.4 V vs Ag/AgCl. Then, using cathodic stripping voltammetry, the  $[\text{Co}^{2+}]$  in the  $\text{Co}_4$ -POM solution was found to be  $250 \pm 27$  nM. In comparison, a  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  solution which was not subjected to bulk electrolysis had  $[\text{Co}^{2+}] = 200 \pm 22$  nM, even though this solution was aged an additional 9 min compared to the electrolyzed sample. That is, bulk electrolysis of the  $\text{Co}_4$ -POM results in  $50 (\pm 34)$  nM higher aqueous cobalt(II) concentrations—evidence which is consistent with the oxidative instability of the starting polyoxometalate.

Additionally, if a 2.5  $\mu\text{M}$   $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  plus pH 8.0, 0.1 M sodium phosphate solution is subjected to *three consecutive 1.4 V vs Ag/AgCl bulk electrolysis experiments* for 60 s each, the resultant  $[\text{Co}^{2+}]$  is significantly higher,  $[\text{Co}^{2+}] = 825$  nM. The corresponding unelectrolyzed  $\text{Co}_4$ -POM solution, examined as a control, contained only  $[\text{Co}^{2+}] = 273$  nM. This substantial increase in  $[\text{Co}^{2+}]$  during only 3 min of electrolysis is consistent with at least 5.5% of the starting polyoxometalate being transformed into aqueous  $\text{Co}^{2+}$  during the electrolysis (in addition to the 2.7% which appears to be hydrolytically unstable), assuming all four of the core cobalt atoms are removed from the parent  $\text{Co}_4$ -POM. This calculation is only a lower limit on the stability since we do not know the amounts of other possible  $\text{Co}_4$ -POM decomposition products including both colloidal and deposited  $\text{CoO}_x$ . In summary of the  $\text{Co}^{2+}$  determinations post water oxidation reactions, the data corroborate the HPLC results by showing increasing  $\text{Co}_4$ -POM decomposition with increasing electrolysis time. This, in turn, provides a very important insight: *even if  $\text{Co}_4$ -POM is initially a WOC, it is not stable in a thermodynamic sense under at least the reaction conditions employed herein.*

**Surface Characterization of the Glassy Carbon Electrode.** Additional evidence concerning the identity of any deposited catalyst was collected via XPS of the post-electrolysis glassy carbon electrode. Figure 8 shows the cobalt  $2p_{3/2}$  portion of the spectrum for glassy carbon electrodes treated with either the  $\text{Co}_4$ -POM solutions or a  $\text{CoO}_x$  control



**Figure 8.** XPS data for the Co  $2p_{3/2}$  region using 2.5  $\mu\text{M}$   $\text{Co}_4$ -POM treated electrodes after bulk electrolysis and  $\text{CoO}_x$  coated electrodes both before and after electrolysis. Conditions for the electrolysis were 1.4 V vs Ag/AgCl for 60 s in 0.1 M sodium phosphate buffer at the pH given in the legend. Also shown is a blank glassy carbon electrode. The  $\text{CoO}_x$  covered electrodes were prepared by controlled potential electrolysis of 0.1 mM  $\text{Co}(\text{NO}_3)_2$  plus pH 8.0, 0.1 M sodium phosphate at 0.79 V for 15 and 42 s for the pH 8.0 and pH 5.8 experiments, respectively.

which showed the same  $\text{O}_2$  producing activity within experimental error as the  $\text{Co}_4$ -POM. At pH 8, it was found that trace cobalt was observable in the film for both the  $\text{Co}_4$ -POM and the  $\text{CoO}_x$  control, while at pH 5.8 only the  $\text{CoO}_x$  control showed detectable amounts of cobalt. The low surface cobalt coverage was also consistent with SEM/EDX imaging and spectroscopy which showed no discernible difference between blank glassy carbon and the samples (Supporting Information, Figure S11); the lack of cobalt detection by EDX is somewhat expected in this case since this method is much less sensitive to surface composition.<sup>65</sup>

In contrast to the low cobalt coverages observed in postcatalysis electrodes, the pre-electrolysis  $\text{CoO}_x$  controls showed significantly higher amounts of surface cobalt (Figure 8). This indicates that even the deposited heterogeneous  $\text{CoO}_x$  is not stable at the oxidizing 1.4 V conditions herein. That is, care must be taken when attempting to distinguish homogeneous and heterogeneous electrocatalysis based solely on the presence or absence of an ex-situ catalytic film on the electrode at the end of the electrolysis. Multiple, complementary methods should always be used to confirm or refute initial observations when attempting to answer the question of whether a catalyst is homogeneous or heterogeneous.<sup>66,67</sup>



In the present case, surface characterization of the glassy carbon electrodes is ultimately inconclusive since minimal (if any)  $\text{CoO}_x$  is deposited during electrolysis of  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  and since controls with authentic deposited  $\text{CoO}_x$  show dissolution of the heterogeneous catalyst during electrolysis at 1.4 V vs Ag/AgCl. *In operando* nanobalance experiments<sup>68</sup> may be useful for this system, but even there the oxidative instability of the  $\text{CoO}_x$  films and the large positive potential of the electrode promise to prove problematic.

## CONCLUSIONS

In summary, one conclusion from this study is that heterogeneous, deposited  $\text{CoO}_x$  is not formed in catalytically significant amounts from aqueous  $\text{Co}^{2+}$  dissociated from the parent  $2.5 \mu\text{M Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  when using a glassy carbon working electrode, at applied potentials  $\geq 1.3$  V vs Ag/AgCl, and pH 5.8 or 8.0 sodium phosphate buffer. The specific results which lead directly to this conclusion are as follows: (1) The apparent concentration of aqueous  $\text{Co}^{2+}$  in the  $\text{Co}_4$ -POM solution prior to the reaction is found to be  $0.17 \mu\text{M}$  (average during a 1 h aging period at pH 8.0), and (2) testing an equivalent amount of  $\text{Co}(\text{NO}_3)_2$  (i.e.,  $0.2 \mu\text{M}$ ) in bulk electrolysis experiments at 1.4 V demonstrates that the 2.0 nmols of  $\text{O}_2$  produced in these controls is significantly lower relative to the 28.4 nmols  $\text{O}_2$  produced under equivalent conditions using  $2.5 \mu\text{M Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$ . Additional electrochemical evidence which is inconsistent with a  $\text{Co}^{2+}$ -to- $\text{CoO}_x$  WOC formation mechanism includes (3) cyclic voltammetry of the  $\text{Co}_4$ -POM solutions show an oxidative wave onset of 1.25 V (compared to 1.10 V for a  $\text{CoO}_x$  catalyst); (4) repeated CV scans show no evidence of a  $\text{CoO}_x$  type catalyst growing in (i.e., negative evidence for  $\text{CoO}_x$ ); (5) rinsing of the glassy carbon electrode used in  $\text{Co}_4$ -POM bulk electrolysis followed by electro-catalytic testing in pure sodium phosphate electrolyte (i.e., no added  $\text{Co}_4$ -POM) shows currents comparable to background levels (additional negative evidence for a deposited catalyst); and (6) the pH dependence of  $-36$  mV/pH unit for  $\text{Co}_4$ -POM solutions versus  $-64$  mV/pH unit for  $\text{CoO}_x$  is considerably different (i.e., consistent with a substoichiometric proton transfer versus a single proton transfer involved in, or prior to, the rate determining step starting from  $\text{Co}_4$ -POM vs  $\text{CoO}_x$ ). This finding, that a  $\text{Co}^{2+}$  to electrodeposited  $\text{CoO}_x$  catalyst is not the kinetically dominant catalyst when starting in  $2.5 \mu\text{M Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  and at  $\geq 1.3$  V vs Ag/AgCl, contrasts with our prior investigation at higher  $\text{Co}_4$ -POM concentrations and lower potentials (i.e.,  $500 \mu\text{M Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  and 1.1 V vs Ag/AgCl) where heterogeneous  $\text{CoO}_x$  deposited from aqueous  $\text{Co}^{2+}$  is clearly the dominant catalyst.<sup>47</sup> That is, the precise conditions can have a profound effect on the dominant, observed water oxidation reaction pathway and catalyst.<sup>69</sup>

A second primary conclusion—backed by the electrochemical, HPLC, and surface characterization methods applied herein—is that we are unable to definitively distinguish between homogeneous polyoxometalate and heterogeneous  $\text{CoO}_x$  (either electrode-bound or soluble, colloidal) formed *via direct oxidation of Co<sub>4</sub>-POM*. This conclusion is supported by the following observations: (7) bulk electrocatalytic testing of  $\text{Co}_4$ -POM gives  $28.4 \pm 1.8$  and  $15.6 \pm 1.2$  nmol  $\text{O}_2$  at 2.5  $\mu\text{M}$  (3.8 nmol of catalyst) at 1.4 V and pH 8.0 and 5.8, respectively; and, (8) controls using predeposited  $\text{CoO}_x$  indicate that transformation of only  $3.9\% \pm 0.4$  and  $8.2\% \pm 1.1$  of  $\text{Co}_4$ -

POM into a  $\text{CoO}_x$  type catalyst would account for the observed amount of  $\text{O}_2$  generation during a 60 s electrolysis under the same 1.4 V potential and at pH 8.0 or 5.8 conditions. In addition, (9) comparison of the electrolyzed and unelectrolyzed  $\text{Co}_4$ -POM solutions by HPLC indicate the loss of  $2.7\% \pm 7.6$  (at pH 8.0) to  $9.5\% \pm 5.1$  (at pH 5.8) of  $\text{Co}_4$ -POM during electrolysis described in point (8) above; that is, if the lost  $[\text{Co}_4\text{-POM}]$  is transformed completely into a  $\text{CoO}_x$  type catalyst, then all of the  $\text{O}_2$  generating activity of the  $\text{Co}_4$ -POM solution could be accounted for by  $\text{CoO}_x$ . (10) Furthermore, determination of the  $[\text{Co}^{2+}]$  in the postbulk electrolysis  $\text{Co}_4$ -POM solutions is consistent with the instability of the starting polyoxometalate under the oxidizing reaction conditions. But, even with all of the quantitative evidence and controls, often at the nmol level, we are unable to definitively distinguish a  $\text{CoO}_x$  catalyst from a  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  based catalyst (or from a combination of the two).<sup>70</sup>

A third, major—and perhaps most important—conclusion of these studies is that increasing amounts of  $\text{Co}_4$ -POM decomposition, as detected by  $[\text{Co}_4\text{-POM}]$  decreases in HPLC and increasing  $[\text{Co}^{2+}]$  in post catalysis reactions, is seen with increasing reaction times. From this it seems inescapable that  $\text{Co}_4$ -POM is not stable in a thermodynamic sense to the conditions examined herein.

Overall, our studies highlight the challenges of distinguishing homogeneous and heterogeneous water oxidation catalysis when beginning with micromolar molecular cobalt precursors (other than aqueous cobalt(II) salts) and where nanomolar heterogeneous metal-oxide will account for the observed  $\text{O}_2$  generation—a finding consistent with the efforts of other researchers in the area.<sup>71–74</sup> Ultimately, a successful approach to answering the “who is the true WOC?” question in a given system will rely on identifying and characterizing all hypothesized forms of the catalyst, determining the possible (or actual) amounts of those materials formed during the reaction, and then conducting control experiments comparing the catalytic activity of each species present en route to determining the true catalyst. Our own efforts in the area of “who is the true WOC?” are continuing.

## ASSOCIATED CONTENT

### Supporting Information

Additional cyclic voltammetry, Tafel plots, bulk electrolysis, HPLC, SEM, and EDX data and TOF calculations are provided for the interested reader. 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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(69) We have noted this point previously in our prior study (ref 47). Specifically, we “emphasize that the present studies [ref 47 herein] have not examined either the system or the precise conditions utilized in the 2010 *Science* paper [and ...] further study of the (slightly) different conditions in the present [ref 47 herein] and prior [ref 46 herein] study is needed before one could have any firm basis for believing [...] the central claim made in ref 6” is incorrect. Although ref 12 agrees that conditions can be significant in determining the true catalyst, and good evidence for that conclusion is an important part of the valuable review in ref 12, the review’s authors do misinterpret our conclusions in ref 47 by stating incorrectly that “a report by Finke following Hill’s papers [...] suggested that the catalysis [in ref 46 herein] is in fact heterogeneous”. As our conclusion quoted above clearly states, one cannot directly extrapolate our results to those of Hill and co-workers because of the different conditions involved.

(70) Other electrochemical evidence—described in points (3) to (6) in the conclusion, especially the different current-pH relationship and potential of catalytic  $\text{O}_2$  production onset when beginning with the  $\text{Co}_4$ -POM versus  $\text{CoO}_x$ —is consistent with the possibility of a polyoxometalate (or polyoxometalate derived) WOC. Additionally, (11) the absence of significant amounts of cobalt observed in XPS, SEM, and EDX electrode characterization, is also consistent with  $\text{Co}_4$ -POM being a true WOC. However, and despite the negative evidence for deposited  $\text{CoO}_x$  given in experiments (3)–(5) in the conclusion and (11) above, care must be taken in interpreting these results since (12) control cyclic voltammetry and XPS experiments indicate that *predeposited  $\text{CoO}_x$  is unstable at 1.4 V*. Restated, the absence of a catalytic film on the electrode at the end of the electrolysis does not in itself rule out heterogeneous catalysis. Needed at this point are authentic examples of  $\text{CoO}_x$  colloids (i.e., stabilized by whatever ligands and other stabilization mechanisms are present under the reaction conditions) and *in operando* methods capable of detecting nanomolar amounts of  $\text{CoO}_x$ .

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