

# Cobalt Polyoxometalates as Heterogeneous Water Oxidation Catalysts

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## Supporting Information

**ABSTRACT:** An insoluble salt of the water oxidation catalyst  $[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$  ( $\text{Co}_9$ ) has been used to modify amorphous carbon paste electrodes. The catalytic activity of this polyoxometalate is maintained in the solid state. Good catalytic rates are reached at reasonable overpotentials. As a heterogeneous catalyst,  $\text{Co}_9$  shows a remarkable long-term stability in turnover conditions. The oxygen evolution rate remains constant for hours without the appearance of any sign of fatigue or decomposition in a large pH range, including acidic conditions, where metal oxides are unstable.

In natural photosynthesis, a sequence of complex reactions transforms solar energy, carbon dioxide, and water into sugars and oxygen. In artificial photosynthesis, the objective is to mimic this process to obtain fuels and oxygen.<sup>1,2</sup> One of the bottlenecks in the design of a working artificial photosynthesis device is the lack of a good enough catalyst for the production of oxygen. The search for a robust, fast, and inexpensive water oxidation catalyst (WOC) is currently a hot topic.<sup>3</sup> The state-of-the-art in terms of feasible industrial applications is lead by heterogeneous transition metal oxides.<sup>4–14</sup>

Homogeneous catalysts have shown superior performance in terms of rates and efficiency.<sup>15–18</sup> They are also easier to optimize and process. However, long-term stability is an important issue. Most of them are transition-metal complexes with organic ligands, unstable toward oxidative deactivation. Because of this, polyoxometalates (POMs)<sup>19</sup> are attracting much attention in the field. POMs are all-inorganic species and possess very high stability toward oxidative degradation.

A ruthenium-based POM was the first to show WOC activity.<sup>20–22</sup> Since then, over 20 POMs have been described as WOCs.<sup>23,24</sup> Without a doubt, the most remarkable examples are the cobalt-containing POMs obtained from Earth-abundant materials, as discovered by Hill and collaborators.<sup>25</sup> Several structural types have shown to be active as homogeneous catalysts for chemical and electrochemical water oxidation.<sup>26–31</sup>

The activity of cobalt-containing POMs as homogeneous WOCs has been put into question. The formation of active  $\text{CoO}_x$  films competes with the genuine POM activity in certain conditions.<sup>32,33</sup> This is a common problem for all homogeneous catalysts because oxidative decomposition of the organic ligands

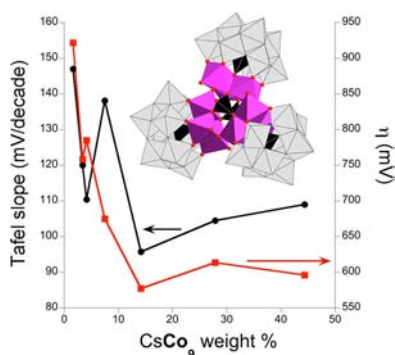
also yields metal oxides.<sup>34–37</sup> Still, there is an important difference in the case of POMs. The origin of the  $\text{CoO}_x$  species is not decomposition of the supporting ligand but the solution equilibria that liberate traces of free  $\text{Co}^{2+}$  ions as precursors for the oxide. Indeed, the use of chelating agents able to trap free  $\text{Co}^{2+}$  ions precludes the formation of any oxide.<sup>25,29,30</sup> Here we report the incorporation of insoluble  $\text{Co}_9$  salts into modified amorphous carbon paste electrodes because this POM is an active WOC in heterogeneous conditions.

$\text{Cs}_{15}\text{K}[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3] \cdot 41\text{H}_2\text{O}$  ( $\text{CsCo}_9$ , see SI) was obtained by the addition of  $\text{CsCl}$  to a  $\text{Co}_9$ <sup>38</sup> water solution. This salt is insoluble in water or any other solvent. As prepared, it contains a homogeneous particle size distribution in the 5–10- $\mu\text{m}$ -diameter range (Figure S1 in the SI). Without further treatment, this polycrystalline solid was blended with carbon paste to prepare POM-modified amorphous carbon (POM-C) electrodes with a POM content between 1 and 60% in weight. Blends above 60% catalyst became too brittle. Cyclic voltammetry with a POM-C working electrode showed a strong water oxidation wave, indicating participation of a catalytic process (Figure S2 in the SI). During successive cycles, gas bubbles formed on the electrode, and the typical oxygen reduction wave below  $-0.3$  V appeared at negative potentials, confirming oxygen evolution.

Controlled potential water electrolysis with these POM-C electrodes was carried out in a two-compartment cell with a pH 7 sodium phosphate buffer ( $\text{NaPi}$ , 50 mM)/water solution with  $\text{NaNO}_3$  (1 M) as electrolyte. Steady-state currents were reached after a few minutes. The current density ( $j$ ) follows a Tafel law (Figure S3 in the SI). The slope of the Tafel plot decreases very rapidly for a very small catalyst content, indicating faster kinetics (Figure 1) and the appearance of a catalytic process. The 1.5% blend already shows 148 mV/decade, from the 178 mV/decade found for a carbon paste electrode. Above 3% catalyst content, the slope remains essentially constant in the 90–110 mV/decade range. These values suggest an electron-transfer rate-limiting process. Our hypothesis is that this behavior arises from the competition between the catalytic oxidation that increases with the POM content and from the electrical conductivity of the blend that decreases because  $\text{CsCo}_9$  is an insulating component. The kinetics of the different blends can also be compared by the

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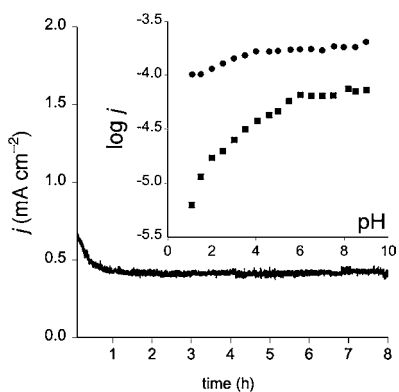
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**Figure 1.** Tafel slope (black) and overpotential needed to reach  $1 \text{ mA/cm}^2$  (red) for catalytic water electrolysis with a POM-C working electrode as a function of the  $\text{Co}_9$  content. Inset: Structure of the  $\text{Co}_9$  polyanion.

overpotential ( $\eta$ ) needed to reach  $j = 1 \text{ mA/cm}^2$ . The result is analogous to that observed for the Tafel slope, reaching a minimum value above 14% (540 mV).

Bulk water electrolysis with a POM-C electrode shows remarkable stability. After a short induction period of  $\approx 30$  min, where the intensity decreases, the current remains constant for the rest of the experiment for over 8 h (Figure 2). This



**Figure 2.** Current density at +1.3 V (vs NHE) with a 44% POM-C modified electrode. Inset: Dependence on pH at +1.5 V for a carbon paste (squares) and a 14% POM-C electrode (circles).

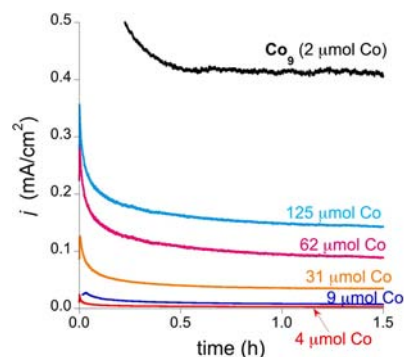
demonstrates the long-term stability of  $\text{Co}_9$  in heterogeneous conditions. During this experiment, we monitored oxygen evolution with a fluorescence probe (Figure S4 in the SI). The final yield reaches over 90% compared with the theoretical amount of oxygen expected for a stoichiometric reaction ( $4e^-$  per oxygen molecule). In any case, the reaction should be quantitative because no other component can be oxidized at these potentials (up to +1.5 V vs NHE). No traces of  $\text{CO}_2$  or of any other small molecule besides  $\text{O}_2$  were found in the analysis of the headspace.

Catalytic water electrolysis with a POM-C blend electrode shows very small variations with pH (Figure 2, inset).  $j$  increases up to pH 4 and then remains essentially constant. The catalytic current is over 1 order of magnitude higher than for a carbon paste electrode, and the pH dependence shows a different trend. In the absence of catalyst, it reaches a maximum above pH 6, and the variation at low pH is much more pronounced.

It has been shown that WOCs can suffer important changes in turnover conditions to yield highly active WOCs as cobalt oxide.<sup>32,39</sup> However, our experiments suggest that cobalt oxide is

not being formed in situ. During bulk water electrolysis at POM-C electrodes, the current decreases with time. However, oxide formation should increase the catalytic activity because cobalt oxide is a better catalyst than  $\text{Co}_9$ .<sup>32</sup>

We performed analogous experiments with  $\text{Co}_3\text{O}_4$  carbon paste blends (CoX-C).<sup>40–43</sup> POM-C electrodes yield 2 orders of magnitude larger current densities than the corresponding CoX-C blends for equimolar amounts of cobalt content (Figure 3). A



**Figure 3.** Current density at +1.3 V (vs NHE) with a 44% POM-C electrode (black) and with CoX-C working electrodes at different  $\text{Co}_3\text{O}_4$  contents (color lines). Labels indicate the total amount of Co in the blends.

huge excess of cobalt oxide is needed to reach similar activity. For example, we obtained a much larger current density with just 2  $\mu\text{mol}$  of total cobalt as  $\text{Co}_9$  (20 mg,  $0.22 \mu\text{mol}$ ) than with 125  $\mu\text{mol}$  of total cobalt as  $\text{Co}_3\text{O}_4$  (20 mg,  $41.7 \mu\text{mol}$  of oxide). Although direct correlations are difficult to draw because the formation of cobalt oxide nanoparticles could yield higher activity than the fine cobalt oxide powder that we used for the blend preparation, our experiments suggest that most of the POM had to be converted into oxide to reach such a high catalytic activity. The POM-C blends after 8 h of water oxidation showed features identical with those of the freshly prepared  $\text{CsCo}_9$  (Table S1 and Figures S5–S7 in the SI). This confirms that the catalyst remains essentially intact in turnover conditions for very long periods of time. If very small, undetected amounts of  $\text{Co}_9$  decompose into cobalt oxide during water oxidation, such small traces cannot justify the high activity exhibited by the POM-C blends.

The difference in the catalytic activity between POM-C and CoX-C blends is even more remarkable when bulk electrolysis is performed at pH 1, where cobalt oxide is unstable (Figure S8 in the SI). Indeed, the CoX-C blend shows no significant effect on the current density, yielding  $j$  values identical with those of the pure carbon paste electrodes. In the case of the POM-C electrodes, catalytic water oxidation proceeds with current densities 100 times higher for just a total cobalt content of 2  $\mu\text{mol}$ . This high activity of the POM-C blends in acidic media is a unique feature for a metal-based catalyst and additional evidence that no adventitious cobalt oxide is significantly participating in the catalytic process. Because  $\text{Co}^{2+}$  can engage in water oxidation in acidic media via ephemerally adsorbed species, we also studied water electrolysis at pH 1 with the addition of  $\text{Co}(\text{NO}_3)_2$  to the electrolyte. In this case,  $j$  increases up to a maximum value for a total cobalt content of  $\approx 18 \mu\text{mol}$ , roughly twice the carbon paste activity and far from the rates found for the POM-C blends. After this maximum,  $j$  decreases upon further addition of the cobalt salt. This also demonstrates that adventitious aqueous  $\text{Co}^+$  ions

cannot be responsible for the high activity of the POM-C electrodes in acidic media.

The cyclic voltammograms of the POM-C blends as a function of the pH (Figure S9 in the SI) show remarkable differences from the pH dependence reported for the CoO<sub>x</sub> catalysts. Cobalt oxide is inactive at low pH, and the water oxidation wave increases until pH >8.<sup>44</sup> The POM-C catalytic water oxidation wave shows no significant changes in intensity or position.

In conclusion, we have shown how homogeneous molecular WOCs from POM chemistry are also active catalysts in the solid state. As insoluble salts, they can be incorporated into a solid-state matrix to promote heterogeneous catalytic water electrolysis. For example, the Co<sub>9</sub> WOC, unstable under certain homogeneous turnover conditions, can be blended into a carbon paste electrode as an insoluble Cs<sup>+</sup> salt to yield a robust catalytic process. Water oxidation occurs at these modified electrodes, maintaining constant rates for hours without apparition of any sign of fatigue or decomposition. This catalytic process is robust also in a large pH range. High activity was found in acidic media (pH ≤ 1) where metal oxides are unstable.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Additional experimental data including electrochemical and structural characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare the following competing financial interest(s): J.S.-L., S.G.-F., L.V., and J.R.G.-M. are co-inventors of a patent application (EP11382322).

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