

## A Self-Healing Oxygen-Evolving Catalyst

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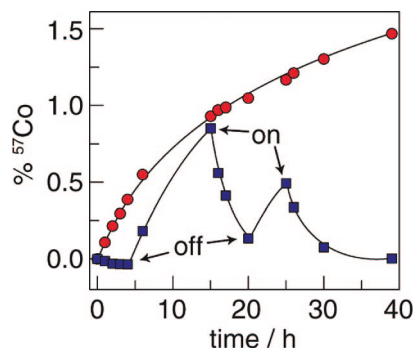
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Metal centers of catalysts activate many small molecules, especially those pertaining to renewable energy, by mediating multielectron transformations of the substrate. To accommodate these reactions without imposing prohibitively high energy barriers, the primary coordination environment of the metal center is typically reorganized and ligand exchange is common. Accordingly, catalysts that effect multielectron transformations are prone to structural rearrangement, and hence instability, during turnover. For this reason, the design of catalysts that repair themselves has been identified as a primary challenge for energy science.<sup>1,2</sup> The need for repair is particularly germane to water oxidation catalysts, which must mediate a four-electron, four-proton exchange under highly oxidizing conditions.<sup>3</sup> Recently, we reported the electrodeposition of a cobalt-based oxygen evolving catalyst from phosphate electrolyte and other proton-accepting electrolytes.<sup>4,5</sup> Molecular mechanisms involving  $O_2/H_2O$  cycles at cobalt centers suggest the involvement of  $Co^{2+}$ ,  $Co^{3+}$ , and likely  $Co^{4+}$  oxidation states during catalysis.<sup>6,7</sup>  $Co^{2+}$  is a high spin ion and is substitutionally labile, whereas  $Co^{3+}$  and higher oxidation states are low spin and substitutionally inert in an oxygen-atom ligand field.<sup>8</sup> As the propensity of metal ion dissolution from solid oxides has been shown to correlate with ligand substitution rates,<sup>9</sup> the cobalt oxygen-evolving catalyst is expected to be structurally unstable during turnover. To probe the dynamics of the catalyst during water-splitting, we now report the electrosynthesis of the catalyst using radioactive  $^{57}Co$  and  $^{32}P$  isotopes. By monitoring these radioactive isotopes during water-splitting catalysis, we show that the catalyst is self-healing and that phosphate is responsible for repair.

The cobalt–phosphate water oxidation catalyst (Co–Pi) forms *in situ* upon the application of a potential of 1.3 V vs NHE to an ITO or FTO electrode immersed in 0.1 M phosphate (pH = 7.0) electrolyte (Pi) containing 0.5 mM  $Co^{2+}$ .<sup>4</sup> At this potential,  $Co^{2+}$  is oxidized to  $Co^{3+}$  and an amorphous catalyst deposits on the electrode that incorporates phosphate as a major constituent. The characteristics of the deposition and the properties of the catalyst prepared in this manner have been described previously.<sup>4,5</sup>

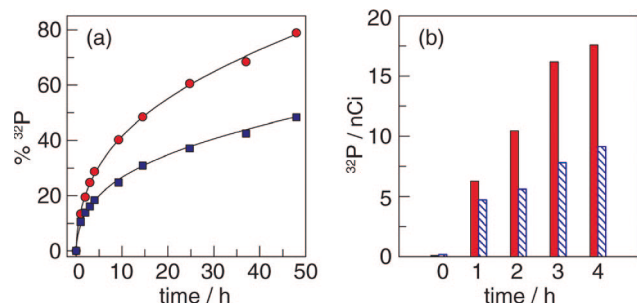
For the studies described here, a Pi solution containing 0.5 mM  $Co(NO_3)_2$  was enriched with 10 mCi of  $^{57}Co(NO_3)_2$ . Details of the sample preparation and handling are provided in the Supporting Information. After deposition, catalyst films were washed with Pi to remove adventitious  $^{57}Co^{2+}$  ions (see Supporting Information). Two separate electrodes coated with the catalyst were placed in the working compartment of two different electrochemical H-cells containing Co-free Pi electrolyte. A potential of 1.3 V was applied to one electrode, and the other was held at open circuit potential; the catalyst is active on the former electrode, and water-oxidation catalysis proceeds as previously described.<sup>4,5</sup> Aliquots of the electrolyte were removed from the H-cell at different time points, and the radioactivity was quantified for each aliquot at the conclusion of the experiment. The total available  $^{57}Co$  was determined by acidifying the electrolyte with concentrated HCl to dissolve the catalyst completely and accounting for the



**Figure 1.** Percentage of  $^{57}Co$  leached from films of the Co–Pi catalyst on an electrode: with a potential bias of 1.3 V (NHE) (blue squares) turned on and off at the times designated and held at open circuit potential (red circles). Lines added to figure simply as a guide to the eye.

radioactivity of the removed aliquots (see Supporting Information). Figure 1 plots the amount of  $^{57}Co$  that leached from the catalyst film as a percentage of the total available  $^{57}Co$ . Cobalt was continually released from the catalyst film on the electrode held at open circuit potential; after 39 h, ~1.5% of the cobalt ion is detected in solution. Conversely, no cobalt is observed in the electrolyte solution when the electrode is held at 1.3 V. After the potential bias is removed from the electrode at 4 h, cobalt promptly dissolves from the catalyst. Reabsorption of the cobalt is observed upon reapplication of the potential to the electrode at 15 and 25 h at which time the cobalt ion concentration in solution is 1.8 and 1.0  $\mu M$ , respectively. Cobalt uptake is complete with continuous application of a potential bias; after 14 h, only 0.002% cobalt remains in solution. The results of Figure 1 are consistent with (i) the slow liberation of  $Co^{2+}$  from the catalyst in the absence of an applied potential and (ii) reoxidation of the liberated  $Co^{2+}$  to reform the catalyst when the 1.3 V potential is reapplied.

Given the dynamic behavior of cobalt in the catalyst, the other major constituent of the catalyst, phosphate, was monitored by means of a  $^{32}P$ -phosphate label. The catalyst was simultaneously electrodeposited on two electrodes immersed in a Pi solution of 0.5 mM  $Co(NO_3)_2$  that was enriched with 1.5 mCi of  $^{32}P$ -orthophosphoric acid. Catalyst films were washed and then placed in two different electrochemical H-cells containing Pi. Figure 2a shows that  $^{32}P$ -phosphate leaches from a catalyst film held at open circuit potential at double the rate for a film held at 1.3 V. The same trend is observed for phosphate incorporation into the catalyst film. Eight ITO electrodes were arranged in a concentric array within the working electrode compartment of an H-cell (see Figure S1), and the catalyst was electrodeposited from a nonisotopically enriched Pi solution. After deposition, the electrodes were separated into two groups of four and arranged in concentric arrays. The two sets of electrodes were immersed in H-cells containing Pi electrolyte that was enriched with ~1.5 mCi of  $^{32}P$ -phosphate. One group of electrodes was held at a potential of 1.3 V, and the other was held at open circuit potential. An electrode was removed every hour from each H-cell and washed, and the catalyst was dissolved



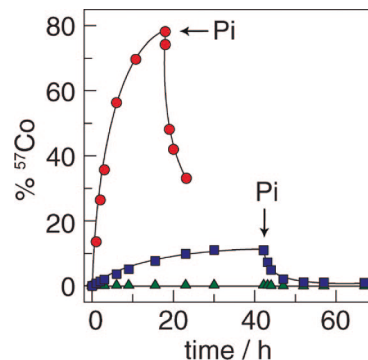
**Figure 2.** Plots monitoring: (a)  $^{32}\text{P}$  leaching from Co-Pi catalyst and (b)  $^{32}\text{P}$  uptake by the Co-Pi catalyst on an electrode with an applied potential of 1.3 V (NHE) (blue squares and bars with blue hash marks) and held at open circuit potential (red circles and red bars).

with concentrated HCl. Figure 2b plots the total  $^{32}\text{P}$  activity obtained at each time point. As in Figure 2a, more phosphate exchange is observed for the electrodes under no applied potential. Elemental analysis of catalyst films establishes that the phosphate anion composition is balanced by an alkali cation ( $\text{Na}^+$  or  $\text{K}^+$ ).<sup>5</sup> In contrast to the slow exchange of phosphate, >90% exchange of  $\text{Na}^+$  for  $\text{K}^+$  (or  $\text{K}^+$  for  $\text{Na}^+$ ) is observed after 10 min of catalyst operation in the alternate electrolyte medium (Table S2). These data together suggest that the phosphate is coordinated to cobalt since a slower ligand exchange would be expected for  $\text{Co}^{3+}$ , which predominates on the electrode held against a potential bias. In addition, the much higher exchange of phosphate as compared to cobalt suggests that the metal ion is a constituent of a more robust metal-oxygen framework.

In the absence of proton accepting electrolytes, catalyst dissolution is rapid and irreversible. Co-based films ( $\text{Co-X}$ ,  $\text{X} = \text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ) electrodeposit from unbuffered electrolyte solutions containing high concentrations of  $\text{Co}^{2+}$  ion.<sup>10</sup> A film was electrodeposited onto an ITO electrode from a solution of 25 mM  $\text{Co}(\text{NO}_3)_2$  containing 2 mCi of  $^{57}\text{Co}(\text{NO}_3)_2$  in 0.1 M  $\text{K}_2\text{SO}_4$  ( $\text{pH} = 7.0$ ) at 1.65 V.  $^{57}\text{Co}$  dissolution measurements and assays were performed with a procedure analogous to that employed for Figure 1 (see Supporting Information). At 1.3 V, the initial sustained current densities were  $<0.1 \text{ mA/cm}^2$ . A potential of 1.5 V was applied to Co-X films to achieve current densities ( $\sim 1 \text{ mA/cm}^2$ ) comparable to those of Co-Pi operated at 1.3 V. The trends in Figure 3 deviate significantly from those in Figure 1. Whereas an applied potential led to cobalt uptake for Co-Pi, the same potential applied to the Co-X system leads to enhanced cobalt release relative to an electrode held at open circuit potential. Moreover, cobalt dissolution increases with increased applied potential. These results are consistent with corrosion of the Co-X system. In the absence of a proton accepting electrolyte, the best proton acceptor is the electrodeposited Co-X film itself. With increased potential, increased production of protons engenders hastened corrosion of these films.

A repair mechanism is not established in the absence of phosphate or other suitable electrolytes (e.g., borate, methylphosphonate).<sup>5</sup> This contention is demonstrated by adding phosphate to the corroding films of Figure 3. Addition of KPi electrolyte (1 M,  $\text{pH} = 7.0$ ) to attain a final concentration of 0.1 M Pi leads to a rapid redeposition of cobalt onto the catalyst film (no precipitation of cobalt is observed; see Supporting Information).

The results reported here establish that phosphate is the crucial component in the self-healing of the Co-Pi catalyst. As originally surmised,<sup>4</sup> in situ formation of the catalyst implies a pathway for catalyst self-repair. Any  $\text{Co}^{2+}$  formed and released into solution during water-splitting catalysis will be redeposited upon oxidation to  $\text{Co}^{3+}$  in the presence of phosphate. Moreover, catalyst degradation, in the



**Figure 3.** Percentage of  $^{57}\text{Co}$  leached from Co-X films on an electrode under a potential bias of 1.3 V (red circles) and 1.5 V (blue squares) (NHE) and held at open circuit potential (green triangles). Pi was added at the time points indicated by the arrows.

absence of an applied potential, is repaired when the potential is reapplied and phosphate is present in solution. Thus phosphate ensures the long-term stability of the catalyst system. More generally, redox reactions of small molecules such as  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  entail that the metal centers of catalysts occupy multiple oxidation states. Because the most stable ground state of a metal in widely varying oxidation states often possesses very different coordination environments, the same ligand field cannot stabilize the system across the entire multielectron transformation. If a ligand field is imposed about the metal, then excess overpotential will be introduced into the redox cycle. By introducing a repair mechanism, the constraint of a structurally stable catalytic center may be relaxed while retaining functional stability at a lower overpotential.

**Acknowledgment.** We thank Matt Kanan and Mircea Dincă for helpful discussions and Bill McCarthy for assistance in radiolabeling experiments. This research was supported by a Center for Chemical Innovation grant from the NSF (Grant CHE-0533150) and a grant from the Chesonis Family Foundation. D.A.L. thankfully acknowledges the Jane Coffin Childs Memorial Fund for Medicinal Research for a postdoctoral fellowship. Y.S. gratefully acknowledges the Department of Defense for a predoctoral fellowship (NDSEG).

**Supporting Information Available:** Full experimental details, photographs of electrode arrays, and elemental composition data for Na/K exchange experiments. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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JA900023K