Supporting Information

# Structure and Valency of a Cobalt-Phosphate Water Oxidation Catalyst Determined by *in situ* X-ray Spectroscopy

Matthew W. Kanan,[‡,§] Junko Yano,[†] Yogesh Surendranath,[‡] Mircea Dincă,[‡] Vittal K. Yachandra,[†,*] and Daniel G. Nocera[‡,*]

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139,*

*Physical Bioscience Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*

Email: vkyachandra@lbl.gov (V.K.Y.), nocera@mit.edu (D.G.N.)

*Index* *Page*



[§] Current Address: Department of Chemistry, Stanford University, Stanford, CA 94305-5080

## EXAFS Curve Fitting

The goodness of the fit was evaluated by the EXAFS R-factor ($R_f$) that represents the absolute difference (least-square fit) between theory and data. For evaluation among different models, the reduced $\chi^2$ ($\chi_\nu^2$) was used:[2,3]

$$\chi_\nu^{\ 2} = \chi^2 / (N_{\mathrm{idp}} - N_{\mathrm{var}})$$

where $N_{\mathrm{idp}}$ is the number of independent points in the measurement, and $N_{\mathrm{var}}$ is the number of variable parameters in the fit. $\chi^2$ is defined by the following equation:

$$\chi^2 = \frac{N_{idp}}{N_{pts}\varepsilon_k^{\ 2}} \sum_i^{Npts} \left[ \chi_i^{data} - \chi_i^{calc} \right]^2$$

where $\varepsilon_k$ is the measurement uncertainty in *k*-space, and $N_{\mathrm{pts}}$ is the number of points in the fitting range of the data. The measurement uncertainty was estimated by the root-mean-square (rms) average of $\chi(R)$ between 15 and 25 Å as described in the literature.[3]

## Estimation of Uncertainty in the Parameters

The uncertainty in the variables, scaled by the square root of $\chi_\nu^2$, are estimated by fitting parameters using a Fourier-filtered spectrum of a relevant R´ range of absorber-backscatter distances. This method avoids creating unrealistically large errors, particularly for the higher R´ values due to the relatively small contribution of such components in the goodness of the fits. For peaks I to III region, $1 \leq R´ (Å) \leq 4$ was used for Fourier-filtering to estimate errors for Co–O (~1.8 Å), Co–Co (~2.8 Å), and Co–O (~3.8 Å) interactions. For the peak IV region, $4.0 \leq R´ (Å) \leq 6.0$ was used for Co-Co (~4.8 Å) and Co-Co (~5.7 Å) interactions.


1. Newville, M. *J. Synchrotron Rad*. **2001**, *8*, 322-324.
2. Ravel, B.; Newville, M. *J. Synchrotron Rad*. **2005**, *12*, 537-541.
3. Newville, M.; Boyanov, B. I.; Sayers, D. E. *J. Synchrotron Rad.* **1999**, 6, 264-265.

**Table S1**. Co EXAFS curve fitting results of CoO(OH) in detail. Four paths shown in Fit #2 are the predominant components in the CoO(OH) EXAFS spectrum. Peak III region can be improved by considering CoO ~ 3.8Å interaction that arises from the interlayer interaction between Co and O. Contributions of the longer Co–O interaction (~4.5 Å) or interlayer Co–Co interaction (~5.2 Å) seem to be negligible, yielding a marginal improvement observed in $R_f$ (Fit #4-6). Therefore, only Fit #3 is shown in the main text (Table 1 and Figure 3(b)).

| Fit # | Path | R (Å) | | N | $\sigma^2$ (Å$^{-2}$) | $\Delta E_0$ (eV) | $\chi_\nu^2$ | $R_f$ (%) |
|---|---|---|---|---|---|---|---|---|
| | | XRD | EXAFS | | | | | |
| 1 | CoO | | 1.90 (0.012) | **6.0** | 0.004 (0.001) | 1.8 (1.3) | 15.2 | 8.3 |
| | CoCo | | 2.85 (0.009) | **6.0** | 0.005 (0.001) | | | |
| 2 | CoO | | 1.90 (0.012) | **6.0** | 0.004 (0.001) | 1.6 (1.0) | 9.4 | 4.1 |
| | CoCo | | 2.85 (0.009) | **6.0** | 0.005 (0.001) | | | |
| | CoCo | | 4.98 (0.030) | **6.0** | 0.009 (0.003) | | | |
| | CoCo** | | 5.76 (0.021) | **6.0** | 0.004 (0.001) | | | |
| 3 | CoO | | 1.90 (0.010) | **6.0** | 0.004 (0.001) | 1.2 (1.1) | 9.1 | 3.4 |
| | CoCo | | 2.85 (0.008) | **6.0** | 0.005 (0.001) | | | |
| | CoO* | | 3.78 (0.025) | **6.0** | 0.006 (0.003) | | | |
| | CoCo | | 4.98 (0.030) | **6.0** | 0.009 (0.003) | | | |
| | CoCo** | | 5.76 (0.021) | **6.0** | 0.004 (0.001) | | | |
| 4 | CoO | | 1.90 (0.010) | **6.0** | 0.004 (0.001) | 1.0 (1.2) | 10.5 | 3.0 |
| | CoCo | | 2.85 (0.008) | **6.0** | 0.005 (0.001) | | | |
| | CoO* | | 3.77 (0.025) | **6.0** | 0.005 (0.003) | | | |
| | CoO | | 4.72 (0.093) | **12.0** | 0.013 (0.013) | | | |
| | CoCo | | 4.98 (0.034) | **6.0** | 0.006 (0.003) | | | |
| | CoCo* | | 5.19 (0.021) | **12.0** | 0.019 (0.003) | | | |
| | CoCo** | | 5.75 (0.021) | **6.0** | 0.004 (0.001) | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 5 | CoO | | 1.90 (0.010) | **6.0** | 0.004 (0.001) | 0.6 (1.7) | 11.1 | 3.2 |
| | CoCo | | 2.84 (0.008) | **6.0** | 0.005 (0.001) | | | |
| | CoO | | 3.25 (0.032) | **6.0** | 0.013 (0.005) | | | |
| | CoO* | | 3.76 (0.025) | **6.0** | 0.005 (0.003) | | | |
| | CoCo | | 4.98 (0.034) | **6.0** | 0.008 (0.003) | | | |
| | CoCo* | | 5.26 (0.021) | **12.0** | 0.023 (0.003) | | | |
| | CoCo** | | 5.75 (0.021) | **6.0** | 0.004 (0.001) | | | |
| 6 | CoO | 1.90 | 1.90 (0.009) | **6.0** | 0.004 (0.001) | 2.0 (1.3) | 11.6 | 2.8 |
| | CoCo | 2.85 | 2.85 (0.007) | **6.0** | 0.005 (0.001) | | | |
| | CoO | 3.44 | 3.46 (0.032) | **6.0** | 0.014 (0.005) | | | |
| | CoO* | 3.83 | 3.76 (0.020) | **6.0** | 0.003 (0.002) | | | |
| | CoO | 4.46 | 4.70 (0.09) | **12.0** | 0.011 (0.013) | | | |
| | CoCo | 4.94 | 4.97 (0.029) | **6.0** | 0.006 (0.003) | | | |
| | CoCo* | 5.25 | 5.16 (0.021) | **12.0** | 0.019 (0.003) | | | |
| | CoCo** | 5.71 | 5.76 (0.021) | **6.0** | 0.004 (0.001) | | | |

Fitting region: $1 \leq R(Å) \leq 6$, $2.88 \leq k(Å^{-1}) \leq 11.73$
Bold numbers indicate fixed values
Parenthesis shows uncertainty
* interlayer interactions
** multiple scattering path, Co–Co–Co

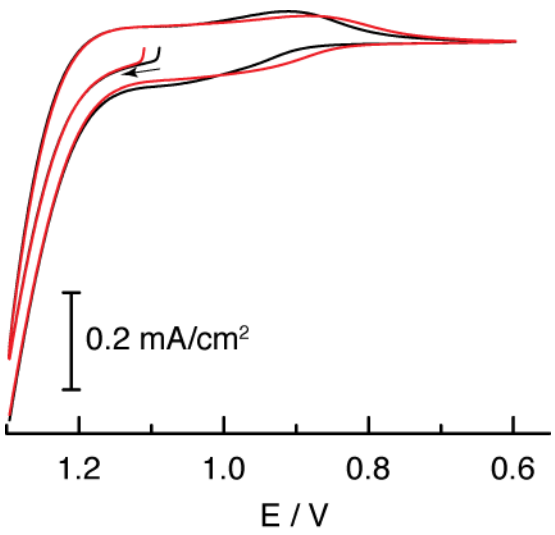



**Figure S1.** Cyclic voltammogram of a freshly-prepared Co-Pi film deposited at 1.25 V until 60 mC/cm$^2$ charge was passed (black) or at 1.05 V until 4.6 mC/cm$^2$ charge was passed (red). E is vs. NHE.

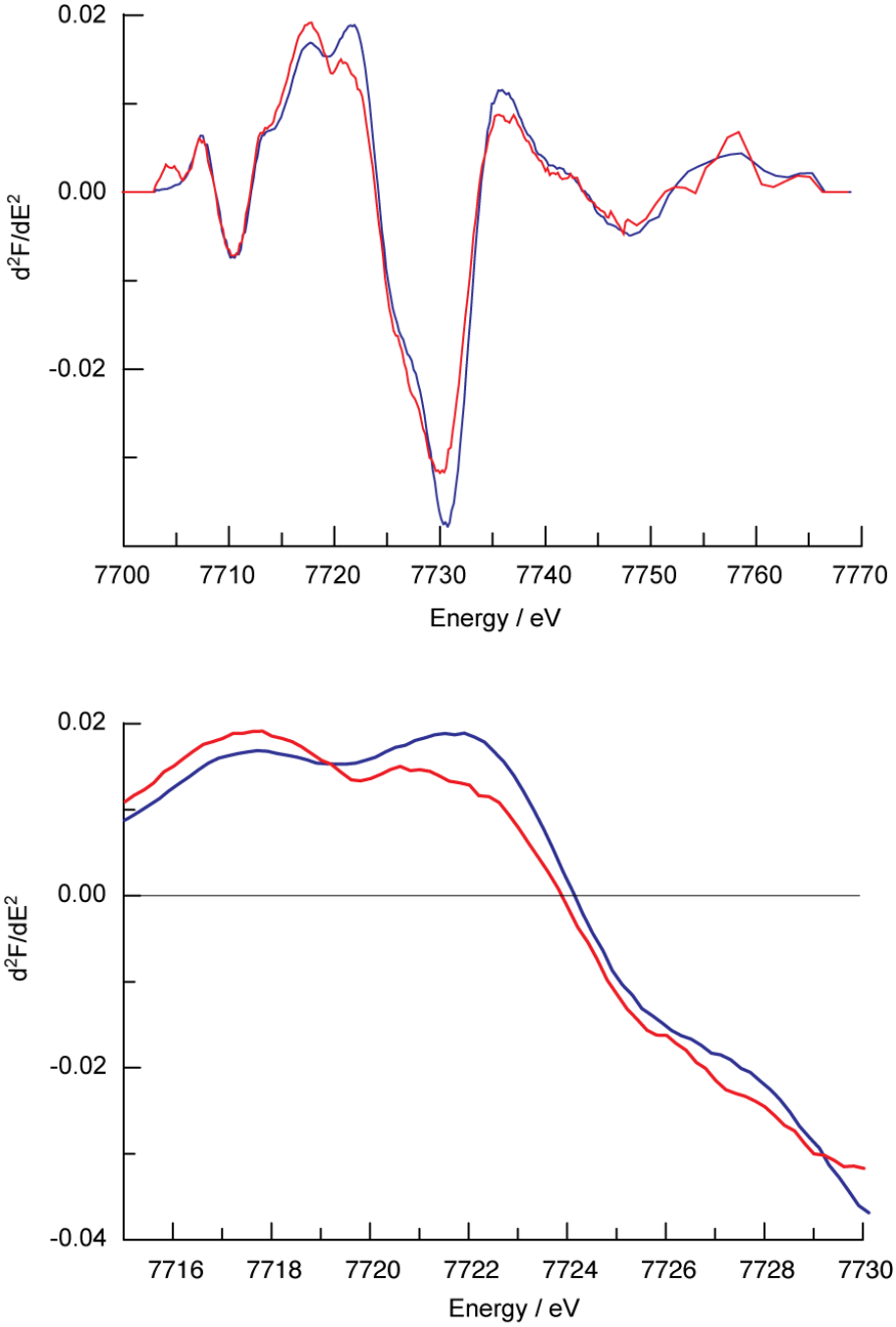



**Figure S2.** Second-derivatives of the full X-ray absorption spectrum (top) and near-edge region (bottom) for surface Co-Pi (red) and bulk Co-Pi (blue) at 1.25 V.

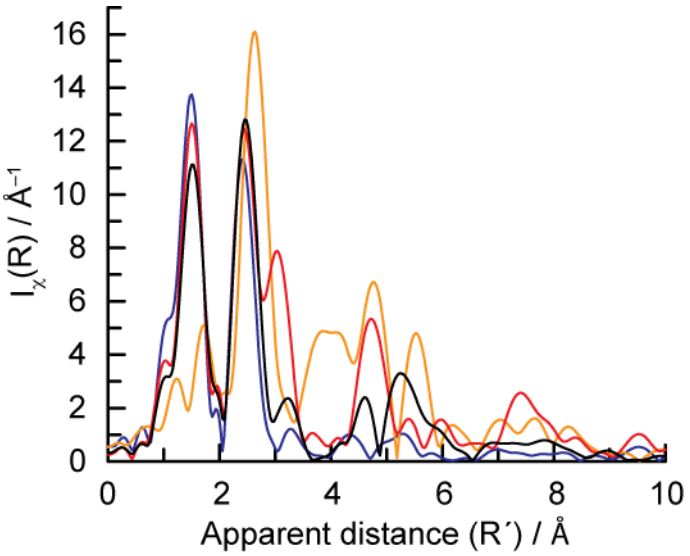
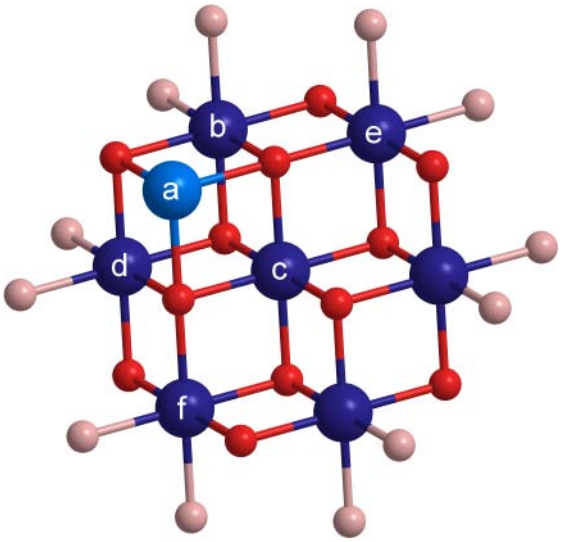



**Figure S3.** Fourier transforms of the EXAFS spectra for CoO(OH) (black), bulk Co-Pi (blue), $Co_3O_4$ (red) and CoO (orange).




a–b = a–c = a–d = 2.52 Å
a–e = a–f = 3.78 Å

**Figure S4**. Structural consequences of forming a cubane on an MCC. The added Co ion (a) is depicted in light blue. Shorter nearest-neighbor Co–Co vectors (a–b, a–c, a–d) and linear Co–O–Co vectors (a–e, a–f) are introduced whose distances are inconsistent with the EXAFS data.

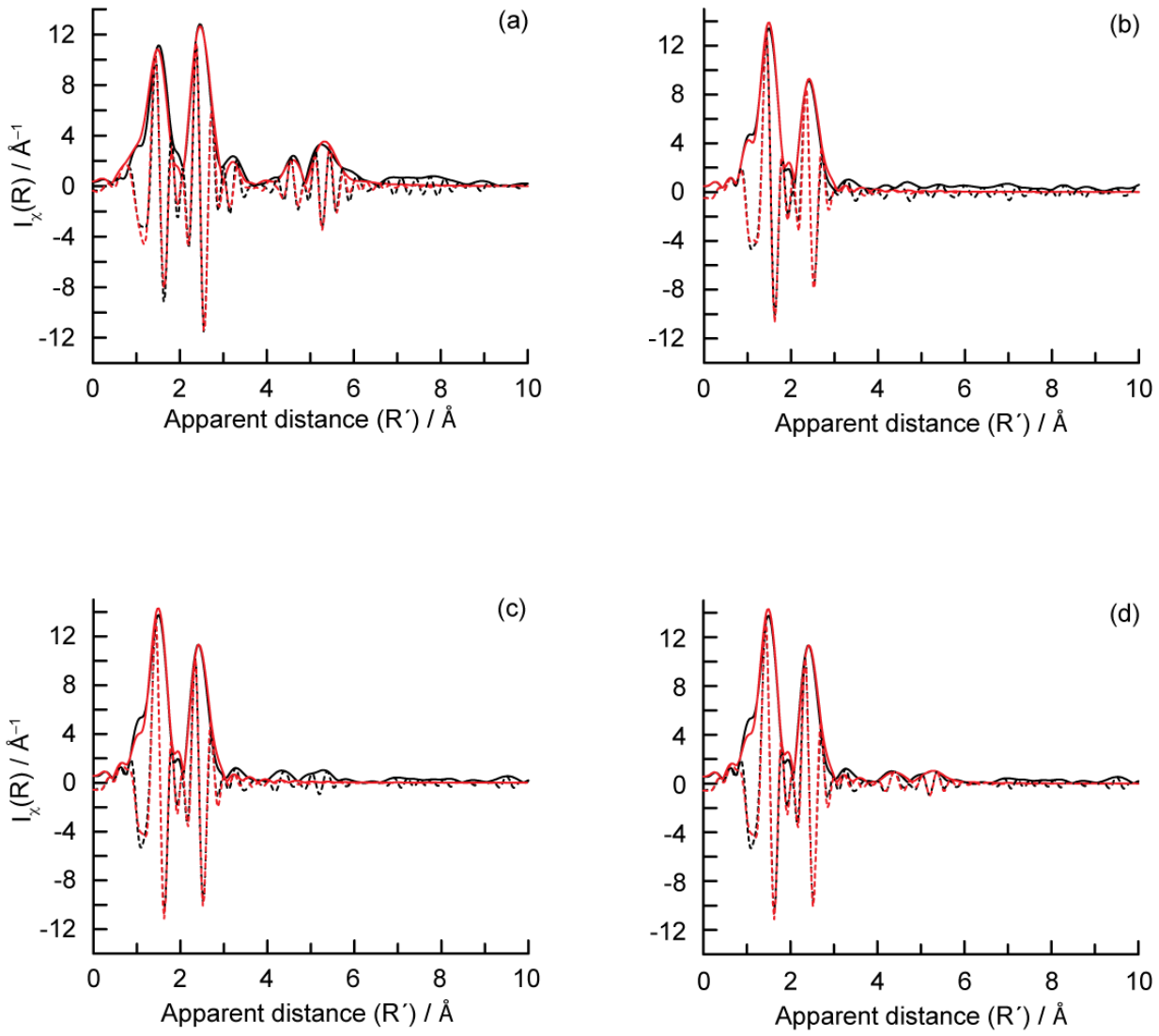



**Figure S5**. FT EXAFS spectra of CoO(OH) and surface and bulk Co-Pi. Black and red lines show the data and the fits. The solid lines are the magnitude and the dotted lines are the real part of the spectra. (a) CoO(OH); (b) surface Co-Pi; (c) bulk Co-Pi fit #1; (d) bulk Co-Pi fit #2.