Intermediate-Range Structure of Self-Assembled Cobalt-Based Oxygen-Evolving Catalyst

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**Supporting Information

ABSTRACT: Continual improvements in solar-to-fuels catalysis require a genuine understanding of catalyst structure–function relationships, not only with respect to local order, but also intermediate-range structure. We report the X-ray pair distribution function analysis of the nanoscale order of an oxidic cobalt-based water-splitting catalyst and uncover an electrolyte dependence in the intermediate-range structure of catalyst films. Whereas catalyst films formed in borate electrolyte (CoBi) exhibit coherent domains consisting of 3–4 nm cobaltate clusters with up to three layers, films deposited in phosphate electrolyte (CoPi) comprise significantly smaller clusters that are not coherently stacked. These structural insights are correlated with marked differences in activity between CoPi and CoBi films.

Hydrogen and oxygen generation by solar-driven water splitting provides a means to store sunlight in a renewable manner.1–3 However, the kinetic complexity of water splitting,4 particularly for the oxygen evolution reaction (OER), mandates the use of catalysts to store and discharge the redox equivalents productively by performing the 4e−−4H+ proton-coupled electron transfer (PCET) of the OER at low overpotential.5–11 Electrodeposited thin-film OER catalysts, which self-assemble from solutions of Co3+(aq)12–14 and Ni2+(aq)15,16 in the presence of a buffering electrolyte, such as phosphate (P_i), methyolphosphonate (MeP_i), or borate (B_i), perform the OER remarkably well.17 Extended X-ray absorption fine structure (EXAFS) investigations18–20 of these catalyst films establish that they are composed of edge-sharing MO_6 clusters of molecular dimensions. A recent X-ray scattering and PDF analysis study21 has extended the initial EXAFS studies and demonstrated that the domains of CoP_i films consisted of clusters comprising on the order of 14 Co ions.

Whereas EXAFS provides key insight into the local order in these films, atomic pair distribution function (PDF) has the added benefit that it allows a direct probe that is also sensitive to intermediate-range structure on the nanoscale.22–24 Nanoscale structure is a crucial determinant of the electronic structure of a variety of functional materials. In the case of the self-assembled OER catalysts, intermediate-range order in these porous thin films is also anticipated to be critical to charge/mass transport between active sites and hence overall catalytic activity. Indeed, changes in microstructure of thin films and electronic structure would be expected to impact the activity and performance of any OER anode. The kinetics of CoPi nucleation and film deposition indicates that the electrolyte plays a pivotal role in modulating catalyst self-assembly.25 We surmise that the identity of the electrolyte could impact the structure of Co-O-EC, and in the future permit the tuning of catalytic activity. To this end, the self-assembled Co-P_i/B_i films offer a unique platform to explore nanoscale structure–activity relationships of OER catalysts at length scales beyond the molecular dimension. We now show by X-ray PDF analysis of CoPi and CoBi films that the B_i templates a unique intermediate layered microstructure, thus establishing the importance of film microstructure in overall catalytic activity.

Catalyst films were electrodeposited onto FTO plates (Hartford Glass) by controlled-potential electrolysis of Co^{2+}(aq) solutions containing P_i or B_i at pH 7.0 or 9.2, respectively. Following electrodeposition, films were rinsed and dried in air, and catalyst material was removed from the substrate surface. Nanoparticulate (50 nm) CoO_OH was used as received (Sigma-Aldrich), and CoO(OH) was prepared according to an established procedure.26 Samples were packed into polyimide capillary tubes for X-ray analysis. X-ray analysis was performed at the X7B beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Diffraction data were collected using the rapid acquisition pair distribution function (RaPDF) technique,27 utilizing a 2D X-ray detector. Full experimental details pertaining to sample preparation and X-ray analysis are provided in the Supporting Information (SI).

All raw 2D data images were azimuthally integrated and converted to intensity versus θ using the software Fit2D,28 where θ is the angle between the incident and scattered X-rays. The data were corrected using PDFgetX3,29 a home-written data analysis program, to obtain the total scattering structure function, S(Q), where Q is the magnitude of the scattering vector (as defined in the SI) and the PDF, G(r). Plots of Q(S(Q) − 1) for all samples are shown in Figure 1a, and G(r) plots for CoPi and CoBi are shown in Figure 1b. PDFs of all samples are presented in Figure S1. Unlike the crystalline analogues which exhibit sharp

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It is also evident from Figure 1b that CoBi possesses more structural coherence than CoPi, since there is a wider range of q for the former over which structural correlations persist. Whereas Du and co-workers have observed extra features in their PDF data that were attributed to CoO cube defects and distortions to the terminal Co−O positions,21 we do not observe any evidence for such features. The fact that our samples are catalytically active without the presence of the defect features suggests that they are not essential for the activity, though additional studies are required to resolve this issue.

Figure 1. (a) Structure functions for (from top to bottom) crystalline Co₃O₄ (green line), CoO(OH) (grey line), and nanocrystalline samples of CoBi (blue line) and CoPi (red line). (b) Comparison of PDFs of CoBi (blue line) and CoPi (red line). PDFs have been truncated at r = 20 Å to highlight the differences. The difference is shown by the lower trace (purple line), which is offset for clarity.

Bragg peaks in the diffraction pattern (Figure 1a) and possess PDFs that extend to high r (Figure S1), the catalyst samples exhibit only diffuse scattering due to finite size effects (Figure 1a). However, PDFs of CoPi and CoBi display sharp peaks in real space (Figure 1b), indicating a well-defined local order (i.e., they are not glassy). The peaks diminish with increasing r, signifying that the samples are nanocrystalline with domain sizes between 15 and 30 Å. It is also evident from Figure 1b that CoBi possesses more structural coherence than CoPi, since there is a wider range of r for the former over which structural correlations persist. Whereas Du and co-workers have observed extra features in their PDF data that were attributed to CoO cube defects and distortions to the terminal Co−O positions,21 we do not observe any evidence for such features. The fact that our samples are catalytically active without the presence of the defect features suggests that they are not essential for the activity, though additional studies are required to resolve this issue.

Two crystalline structural analogues, Co₃O₄ and CoO(OH), were also measured for structural comparison to the CoPi/Bi samples. Their PDFs were truncated to simulate nanoparticle effects and compared to CoPi and CoBi (Figures S2–S5). In general, there is poorer agreement of CoP/Bi to CoO(OH) (Figures S2 and S3) as compared to CoO(OH) (Figures S4 and S5), indicating that the CoP/Bi samples are of the cobaltate structure, in agreement with previous EXAFS and PDF structural studies.18−21 However, there is significantly poorer agreement between CoO(OH) and the CoP/Bi at high r compared to low r, representing some difference in intermediate-range structure. For example, a significant discrepancy in peak position between CoO(OH) and either CoPi and CoBi is found in the doublet between 4 and 5 Å. The CoO(OH) structure consists of aligned layers of edge-shared Co₆ octahedra with hydrogen atoms in the interlayer region.30 The first peak in the doublet arises from the nearest-neighbor intralayer Co−Co distance in the CoO(OH) structure, and the second peak is from the second nearest-neighbor interlayer Co−Co distance. Since the largest discrepancy is in the position of the first peak of the doublet, this indicates that CoPi, and CoBi, have the CoO(OH) structure, but with diminished coherence in the stacking direction due to turbostratic disorder between stacked layers, or because the clusters are not coherently stacked at all.

Preliminary modeling was performed using the PDFgui software,31 with the model PDFs attenuated by the characteristic function for a sphere. Modeling was performed according to standard procedures,22,23 using the maximum number of parameters allowed by the space groups of the model structures. In agreement with our initial observations, the CoO(OH) model performed better by a considerable margin than Co₃O₄ (Figures S6 and S7), as evidenced by the greatly improved goodness-of-fit parameter, R_w. Both models refined with large cobalt atomic displacement parameters along the c-axis of the cell, providing evidence for turbostratic disorder among the stacked layers.32,33

More advanced modeling was performed using atomistic nanoparticle models created from the CoO(OH) structure. These models were fit using our recently developed SRREAL and SRFTIT programs.34 Models were created for refinement using a nanoparticle template approach; a geometric shape is used to excise a nanoparticulate model from a crystal structure. This allows us to vary not only the crystal structure, but also the dimensions of the nanoparticle by varying the template. It also allows us to decorate the model with additional scatterers and to distort the model. This was not done here, but will be explored in future modeling efforts. The nanoparticle models for CoBi and CoPi, were created using a cylindrical template. The template was allowed variable dimensions and location, with the axis of the cylinder aligned with the c-axis of the CoO(OH) structure. For simplicity, hydrogen atoms were excluded from the models. Since circular cuts were made in the hexagonal layers, the resulting structures that were used for modeling did not necessarily have fully coordinated Co ions at the perimeter. The resulting finite-sized nanoparticle models are then used to calculate the PDF using the Debye equation. Unlike the PDFgui approach, this method does not use periodic boundary conditions.

The refined PDF fits and models for CoBi and CoPi, catalysts are shown in Figures 2 and 3, and some structural parameters are tabulated in Table S1. The CoBi model has three layers on average, and the diameter of the layers is approximately 35 Å. We
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The performance of the anode can be improved by depositing thicker films. However, the behavior for CoBi and CoPi differs. Whereas the CoBi films display a monotonic increase in activity with film thickness, the activity of CoPi attains a limiting activity at catalyst loadings in excess of 1 µmol Co/cm². At loadings greater than 0.25 µmol Co/cm², CoBi activity is significantly superior to that of CoPi. These results suggest that the effective surface area of the CoBi catalyst increases with increasing film thickness while preserving the intrinsic transport properties within the film. The PDF results now offer a concrete difference in CoPi and CoBi, thus allowing the first insight into a tangible structure-function correlation. The mesoscale ordering of the CoBi film suggests enhanced catalytic activity. Electrochemical and stopped-flow spectroscopic studies using molecular model compounds establish that the mechanism for charge transport in these films is best thought of as involving a series of PCET self-exchange reactions between CoIII and CoIV centers of different cluster subunits.38 Along these lines, the larger domain size of CoBi, relative to CoPi, provides a mechanism to delocalize the mobile holes over a larger region, which can be manifest in more efficient charge transport owing to (1) fewer discrete hole hops needed in a given distance for charge transport among clusters and (2) a reduced reorganizational energy for electron transfer since charge is delocalized over a larger cluster area. Indeed, charge delocalization has been observed to enhance apparent self-exchange rates and attendant hole mobility on polymer36,37 and nanoparticulate38 films. In addition, interlayer hopping of holes may be facilitated by less disorder in a film comprising a multilayer CoBi structure as compared to more disorder in the single-layer structure of CoPi films. Together, these factors will contribute to an enhanced hole hopping rate, and hence a greater charge transport mobility in CoBi films, accounting for the ability of these films to sustain higher net activity than CoPi. In addition, we hypothesize that such nanoscale differences may impact a long-range morphology of these materials, such as their porosity and, by extension, their capacity for mass transport. Detailed transport and surface-area measurements will shed more light on these questions.

The electrolyte in OER self-assembly of Co and Ni/Pi and Bi films has several important roles. First, the anionic electrolyte is a mechanistic element of film nucleation and film growth. Second, the electrolyte is a proton acceptor in the PCET reaction of OER. Third, the electrolyte is the critical determinant of the self-healing nature of these films. The structural insights uncovered here by PDF analysis now indicate yet another important role of the electrolyte as an element that directs the intermediate-range structural order of the oxidic cobalt clusters within the films. Previous kinetic studies have provided a mechanistic framework for understanding the conflicting interactions between the buffering electrolyte as both proton acceptor and adsorbing anion.25 Whereas the latter role inhibits catalyst assembly, the former serves to assist formation and growth of clusters by facilitating the PCET oxidation of CoII precursors.25 Thus, it is reasonable to expect that the size of the domains formed would depend critically on the balance between these factors; a high binding constant between buffering anion and cobalt centers—most likely at the edges of nascent clusters—would favor the formation of new domains versus the growth of existing ones, whereas a weaker adsorption isotherm would promote larger domain sizes. The intercalation of anions between clusters, as observed in solid-state 31P NMR studies of CoPi,39 may serve as a mechanism by which the electrolyte defines the degree of coherence in stacking of cobaltate clusters. The fundamental
Communication especially important to OER activity in CoPi and CoBi. In this regard, CoBi provides a link between molecular and extended solid-state materials. Thus the CoBi OER catalyst offers a molecular-like understanding of the structure–function relationships of OER oxide catalysts. The edges of the clusters are known to be especially important to OER activity in CoPi and CoBi films. Hence, the results described herein suggest that traditional metal oxides may restructure to give metallate cluster active sites of the type observed in this study. Insights such as these, which provide a bridge between molecular and extended solids, should be useful to accelerating the discovery of both homogeneous and heterogeneous catalysts systems.

ASSOCIATED CONTENT

* Supporting Information

Full experimental details, additional PDF data, and fitting plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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