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## A CoV<sub>2</sub>O<sub>4</sub> precatalyst for the oxygen evolution reaction: highlighting the importance of postmortem electrocatalyst characterization†

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**Vanadium-doped cobalt oxide materials have emerged as a promising class of catalysts for the oxygen evolution reaction. Previous studies suggest vanadium doping in crystalline Co spinel materials tunes the electronic structure and stabilizes surface intermediates. We report a CoV<sub>2</sub>O<sub>4</sub> material that shows good activity for the oxygen evolution reaction. However, postmortem characterization of the catalyst material shows dissolution of vanadium resulting in an amorphous CoO<sub>x</sub> material, suggesting that this vanadium-free material, and not CoV<sub>2</sub>O<sub>4</sub>, is the active catalyst. This study highlights the importance of postmortem characterization prior to mechanistic and computational analysis for this class of materials.**

The sluggish kinetics of the oxygen evolution reaction (OER) hinders the development of practical water-splitting technologies, and has driven the search for efficient OER electrocatalysts comprised of earth-abundant materials that operate with high current densities at low overpotential with long-term operational stability.<sup>1–4</sup> V-Doped Co oxide materials have recently emerged as a promising class of alkaline OER catalysts. Previous studies of V-doped Co oxide materials show increased activity for the OER at low overpotentials,<sup>5–14</sup> and typically suggest that this increased activity is a result of changes to the catalyst's electronic structure and/or in increased stabilization of adsorbed OER intermediates.<sup>5–8</sup>

In this study, we report a CoV<sub>2</sub>O<sub>4</sub> material that shows exceptional specific activity per BET surface area for the OER based on as-synthesized characterization data. However, materials characterization conducted after OER electrolysis shows the CoV<sub>2</sub>O<sub>4</sub> precatalyst transforms into a V-free amorphous Co-based material during the OER. This suggests that V ions are not present in the active catalyst material, and rather, CoV<sub>2</sub>O<sub>4</sub> serves as a template for the generation of an active amorphous CoO<sub>x</sub> species. Our study highlights the need for careful postmortem characterization of electrocatalytic materials to ensure continued catalyst integrity prior to conducting detailed mechanistic interpretations.

CoV<sub>2</sub>O<sub>4</sub> was prepared by solid state synthesis from CoO and V<sub>2</sub>O<sub>3</sub> metal precursors. A 1 : 1 molar ratio of CoO and V<sub>2</sub>O<sub>3</sub> was ground and mixed, compressed into a pellet, and heated at 800 °C for 20 h under Ar. Selected characterization parameters of the as-synthesized materials are summarized in Table S2 (ESI†). The powder X-ray diffraction (PXRD) pattern of the as-synthesized CoV<sub>2</sub>O<sub>4</sub> matches that of the CoV<sub>2</sub>O<sub>4</sub> reference with minor contributions from V<sub>2</sub>O<sub>3</sub> impurities as shown in Fig. 1a. Note that V<sub>2</sub>O<sub>3</sub> is not OER active (see Fig. S1, ESI†), so we do not expect trace V<sub>2</sub>O<sub>3</sub> impurities to affect our OER measurements. The sharp diffraction peaks suggest a highly crystalline specimen with a large domain size which might be the product of particle agglomeration due to the high temperatures and long times in the solid-state synthesis preparation. The large grain size is supported both by transmission electron microscopy (TEM) analysis which show particles > 100 nm in size (Fig. 1b) and the catalyst's small surface area of only 0.80 m<sup>2</sup> g<sup>-1</sup> as determined by BET gas adsorption analysis – two orders of magnitude smaller than that of Co<sub>3</sub>O<sub>4</sub> (Table S2, ESI†). Elemental mapping experiments with TEM-energy dispersive X-ray analysis (TEM-EDX) show relatively uniform distribution of Co, V, and O in the as-synthesized material (Fig. 1b).

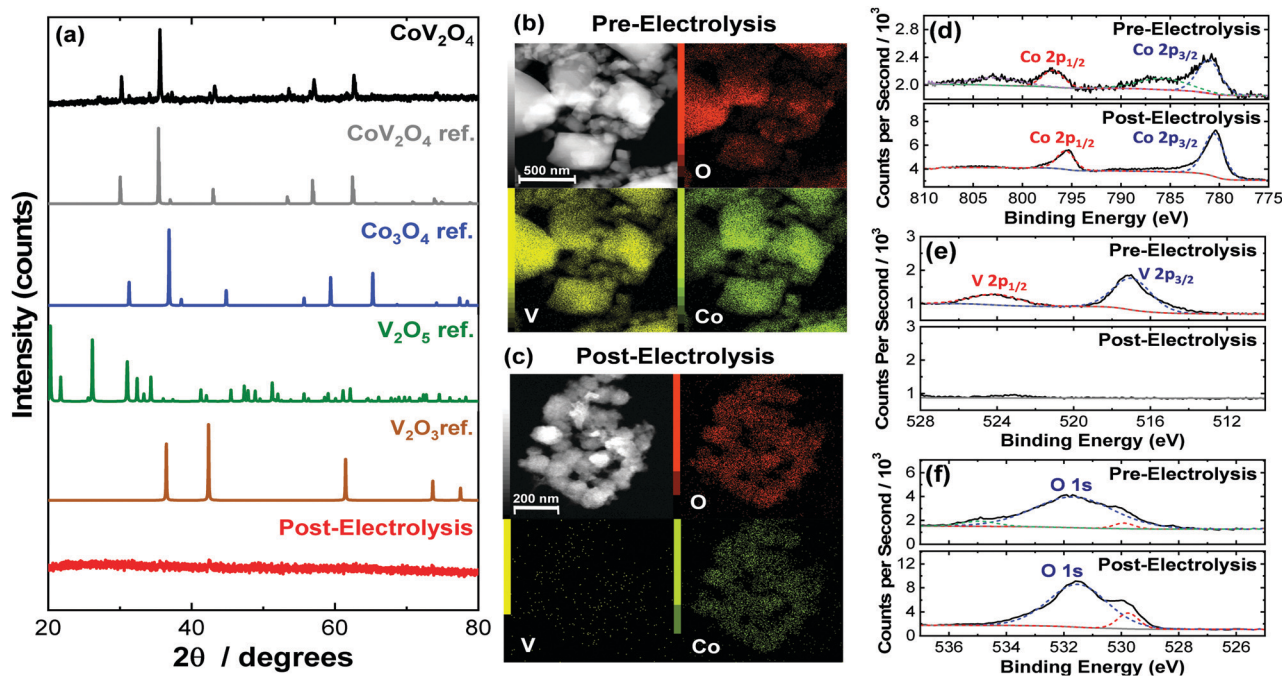
The as-synthesized CoV<sub>2</sub>O<sub>4</sub> material was further characterized with X-ray photoelectron spectroscopy (XPS). XPS core scans of the as-synthesized CoV<sub>2</sub>O<sub>4</sub> material in the Co 2p, V 2p, and O 1s

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† Electronic supplementary information (ESI) available: Experimental methods and details, additional characterization data for the as-synthesized and post-OER materials, cyclic voltammograms of V<sub>2</sub>O<sub>3</sub> in alkaline conditions, measured O<sub>2</sub> production using an *in situ* O<sub>2</sub> probe, and comparative table of the OER activities of other nanoparticulate catalysts based on as-synthesized activity metrics. See DOI: 10.1039/d0cc06513g



**Fig. 1** (a) PXRD patterns for as-synthesized  $\text{CoV}_2\text{O}_4$  along with reference patterns for comparison. The PXRD for  $\text{CoV}_2\text{O}_4$  after 28-h CCE under OER conditions is also included. (b) Representative TEM images and TEM-EDX maps of as-synthesized  $\text{CoV}_2\text{O}_4$ . (c) Representative TEM images and TEM-EDX maps of  $\text{CoV}_2\text{O}_4$  after 28 h CCE under OER conditions. (d–f) High resolution XPS spectra of  $\text{CoV}_2\text{O}_4$  both as-synthesized and after 28 h CCE in the (d) Co 2p region, (e) V 2p region, and (f) O 1s region.

regions are shown in Fig. 1d–f, and in the C 1s region in Fig. S2 (ESI<sup>†</sup>). In the Co 2p spectra of the as-synthesized material (Fig. 1d), two peaks centered at 780.8 and 796.6 eV are assigned to Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub> respectively, and the two shoulder peaks at 785.3 and 802.5 eV suggest the Co is in a CoO-like (Co<sup>2+</sup>) environment.<sup>15</sup> In the V 2p spectra (Fig. 1e), there is a peak at 516.5 eV assigned to V 2p<sub>3/2</sub>, which resembles that of reported V<sub>2</sub>O<sub>3</sub> samples and suggests V is in a 3+ oxidation state.<sup>16,17</sup> There is a complicated O 1s peak at ~531.5 eV (Fig. 1f) consistent with a mixed species of O on the surface (metal oxide/hydroxide/adsorbed water), but due to the convoluted nature, the peak cannot be used in V or Co oxidation state estimations.<sup>18</sup> The Co/V ratio based on XPS analysis was 0.58. This XPS characterization is consistent with other synthesized  $\text{CoV}_2\text{O}_4$  materials.<sup>5,19</sup>

OER activity measurements were performed using previously reported protocols.<sup>20,21</sup> Catalyst inks were prepared by mixing the as-synthesized catalyst particles and Nafion in a water–isopropanol solution, and the resulting inks were dropcast onto polished glassy carbon electrode surfaces (0.196 cm<sup>2</sup>) resulting in films with mass loadings of 0.84 mg cm<sup>-2</sup>. The putative  $\text{CoV}_2\text{O}_4$  catalyst shows promising activity for the OER, operating with increased activity per geometric area compared to the parent  $\text{Co}_3\text{O}_4$  as shown in Fig. 2a, and dramatically increased specific activity per BET surface area compared to  $\text{Co}_3\text{O}_4$  as shown in Fig. 2b. Activity descriptors for the putative  $\text{CoV}_2\text{O}_4$  catalyst compared to other representative OER catalysts are shown in Table S3 (ESI<sup>†</sup>). The long-term performance stability of the putative  $\text{CoV}_2\text{O}_4$  system was confirmed by rapid potential cycling measurements and long-term controlled-current electrolysis experiments (CCE) which showed minimal change in

activity over 10 000 cycles and 28 h controlled current measurements (Fig. 2c). The faradaic efficiency for the OER was measured as 90 ± 5% using an *in situ* O<sub>2</sub> probe (Fig. S4, ESI<sup>†</sup>).

The activity measurements for the putative  $\text{CoV}_2\text{O}_4$  catalyst suggest it shows remarkable stability and activity, particularly specific activity per BET surface area, for the OER. Sequential cycles of RDEVs at 1600 rpm of the putative  $\text{CoV}_2\text{O}_4$  catalyst in 1 M NaOH are shown in Fig. 2d. In the first cycle, there is a large oxidative feature negative of the OER electrocatalytic onset, and this oxidative feature decreases with subsequent scans before approaching a steady-state peak current after six cycles. RDEVs conducted under identical conditions for V<sub>2</sub>O<sub>3</sub> show a similar oxidative feature in the first cycle that disappears in subsequent cycles (Fig. S5, ESI<sup>†</sup>), which is consistent with previous studies that show V<sub>2</sub>O<sub>3</sub> dissolves under oxidation when exposed to alkaline conditions.<sup>22</sup> Our RDEV studies suggest that the large oxidative feature observed for  $\text{CoV}_2\text{O}_4$  is likely due to oxidative dissolution of V, and the steady-state redox feature after six cycles is assigned to the Co<sup>2+/3+</sup> redox couple of the resulting CoO<sub>x</sub> material.<sup>23</sup> The stability of the catalytic performance of the putative  $\text{CoV}_2\text{O}_4$  suggests that dissolution of V has a minimal effect on the OER activity.

To confirm the postulated V dissolution during our experiments, we conducted a series of postmortem characterization studies on the putative  $\text{CoV}_2\text{O}_4$  catalyst. TEM-EDX conducted on a sample after the CCE measurements show a dramatic loss of V consistent with oxidative V dissolution during electrocatalytic studies. Similarly, ICP-MS measurements taken after



**Fig. 2** Cyclic RDEVs of the as-synthesized  $\text{CoV}_2\text{O}_4$  catalyst compared to previously reported  $\text{Co}_3\text{O}_4$  in  $\text{O}_2$ -saturated 1 M NaOH showing (a) the current density per geometric area and (b) the specific current density per the BET surface area of the as-synthesized materials at  $0.01 \text{ V s}^{-1}$  scan rate and 1600 rpm rotation rate. The RDEVs shown are the 2nd cycle for each sample. The  $\text{Co}_3\text{O}_4$  data is taken from ref. 20. (c) Stability studies for the putative  $\text{CoV}_2\text{O}_4$  during OER. The green circles are measured overpotentials at  $10 \text{ mA cm}^{-2}$  geometric ( $\eta_j = 10 \text{ mA cm}^{-2}$ ) during 28 h CCE measurements plotted vs. the polarization time on the bottom axis. The blue squares are the  $\eta_j = 10 \text{ mA cm}^{-2}$  values during 10000 cycle experiments plotted vs. the number of cycles on the top x-axis, and the bottom axis also reflects the time points in the cycling measurements. The  $\eta_j = 10 \text{ mA cm}^{-2}$  values were average measurements from at least three independently-prepared samples, and the error bars represent the standard deviations. (d) The first six RDEVs measured for the as-synthesized  $\text{CoV}_2\text{O}_4$ . There is a large pre-catalytic peak at  $\eta \approx 0.05 \text{ V}$  that shifts negative and decreases in intensity in subsequent scans.

the CCE stability measurements show almost complete disappearance of V (Table S2, ESI<sup>†</sup>). XPS measurements taken after the CCE measurements show a dramatic decrease of the V 2p peaks consistent with a loss of V from the material (Fig. 1c), and in the Co 2p region the disappearance of the shoulder peaks and the decreased FWHM of the two Co 2p peaks suggest a shift towards a  $\text{Co}_3\text{O}_4$  like surrounding (Fig. 1d).<sup>24</sup> The reduced shoulder peak of O 1s (531.5 eV), which is attributed to oxide defect sites or hydroxyl groups,<sup>25</sup> in the post-CCE XPS suggests the loss of defect sites and surface oxyhydroxyl (M-OOH) groups while the loss of the peak at 535 eV represents the loss of  $\text{H}_2\text{O}$  species. Note that the XPS measured on the post-cycling samples were analogous to the post-CCE samples (Fig. S6, ESI<sup>†</sup>).

PXRD measurements of the post-CCE catalyst material are consistent with an amorphous structure (Fig. 1), and high-resolution TEM measurements of the post-CCE material also show a broadly amorphous structure with a random dispersion of small nanocrystalline domains with  $d = 0.24 \text{ nm}$  lattice spacing consistent with the (311) plane of V-free  $\text{Co}_3\text{O}_4$  (Fig. S7, inset, ESI<sup>†</sup>). Selected area diffraction (SAED) measurements also show a decrease in catalyst crystallinity post-electrolysis compared to the as-synthesized material (Fig. S8, ESI<sup>†</sup>).

All electrochemical and post-CCE characterization data suggest that the active OER catalyst is not  $\text{CoV}_2\text{O}_4$ , but instead

an amorphous, V-free  $\text{CoO}_x$  material. We postulate that the  $\text{CoV}_2\text{O}_4$  material undergoes a structural rearrangement under electrocatalytic conditions forming a soluble  $\text{VO}_x$  phase, possibly  $\text{V}_2\text{O}_5$ , consistent with the Pourbaix diagram for V.<sup>26,27</sup> Upon dissolution of  $\text{VO}_x$ , the  $\text{CoV}_2\text{O}_4$  lattice collapses resulting in an amorphous  $\text{CoO}_x$  material that is presumed to be the active species for the OER. This process is qualitatively similar to electrochemical dealloying previously used to make porous battery materials and catalysts.<sup>28–33</sup> We postulate that the increased observed activity for our catalyst compared to  $\text{Co}_3\text{O}_4$  may be due in part to an increased surface area after V-dissolution. Unfortunately, we were not able to harvest sufficient amounts of material post-CCE for BET gas adsorption measurements. Moreover, we do not use electrochemical double-layer capacitance measurements to estimate surface area for OER materials – we believe such measurements are of questionable utility due to the well-documented fallibility of that approach applied to metal oxide catalysts.<sup>21,34–37</sup> We did estimate average particle sizes based on the TEM images in Fig. 1, and we observe a decrease in the average (and median) particle size post-CCE that is qualitatively consistent with our postulated increase in surface area assuming no loss of material (Table S1, ESI<sup>†</sup>). However, the measured decrease in average particle size does not account for any changes in porosity or mass-loss from V dissolution that would also influence the overall surface area, and so it is reported here only as a qualitative metric.

Previous studies have reported that V-doped Co oxide materials show higher activity for the OER than their parent oxide materials.<sup>5–13</sup> In many cases, this observed higher OER activity compared to the V-free parent materials is attributed to specific changes in the physical and/or electronic structure upon V incorporation resulting in changes to material conductivity, adsorption energy of OER intermediates, and/or the rate determining step in the catalytic mechanism. In the case of V-doped amorphous  $\text{CoO}_x$  films,<sup>7,9</sup> crystalline V-doped  $\text{CoOOH}$ <sup>8</sup> and CoFe-based<sup>12</sup> nanoparticles, and Co-V hydroxide nanostructures,<sup>13</sup> postmortem characterization shows these materials retain significant concentrations of V after OER stability measurements, consistent with the assertion that the continued presence of V is an important component of the OER mechanism for these materials.<sup>7,8,12,13</sup>

However, in previous studies of crystalline V-doped  $\text{Co}_3\text{O}_4$ -based spinel materials, a lack of postmortem characterization introduces ambiguity as to the role of V in the catalytic mechanism. For example, in previous studies of OER by  $\text{CoV}_{2-x}\text{Fe}_x\text{O}_4$  and  $\text{Co}_{3-x}\text{V}_x\text{O}_4$  nanoparticles, comprehensive mechanistic and computational analysis was conducted with the assumption that V was an important component in the active catalyst species.<sup>5,6</sup> However, in these studies, either postmortem analysis was not reported to confirm the presence of V in the material after the OER,<sup>6</sup> or reported postmortem characterization showing the loss of V during the OER was not considered in the mechanistic analysis.<sup>5</sup> Similarly, studies of V-doped CoP materials and Co-Mo-V catalysts both attribute increased catalytic activity to the presence of V in the materials, but did not include postmortem characterization

showing the continued presence of V after the OER.<sup>10,14</sup> This is not to say that the mechanistic arguments in these previous studies are incorrect, but rather suggests that the composition of the post-OER catalyst should be reported and discussed when considering possible catalytic mechanisms.

V-Doped Co oxide materials are an emerging class of promising electrocatalysts for the OER. In our work, we show that a putative CoV<sub>2</sub>O<sub>4</sub> spinel catalyst shows remarkable specific activity based on as-synthesized catalyst characterization when compared to Co<sub>3</sub>O<sub>4</sub> and other reported OER catalysts. However, postmortem characterization shows dissolution of V from the material resulting in the formation of amorphous CoO<sub>x</sub> particles, the presumed true active catalysts for the OER. Our findings introduce uncertainty into the mechanistic arguments made in previous studies of V-doped Co<sub>3</sub>O<sub>4</sub>-based spinel materials for the OER that suggest V plays an important role in catalytic mechanism without considering post-mortem materials characterization to confirm the continued presence of V during the OER. Conducting compositional and structural characterization of OER materials after electrocatalytic stability studies is recommended as a minimum requirement in assigning plausible catalytic active species according to recent reviews of best practices for OER measurements.<sup>36–39</sup> We believe our work serves as a case study highlighting the importance of postmortem characterization in determining possible catalytic species prior to in-depth mechanistic analysis.

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## Conflicts of interest

There are no conflicts to declare.

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