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Intercalation of Cobalt into the Interlayer of Birnessite Improves Oxygen Evolution Catalysis

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ABSTRACT We show that the activity of cobalt for the oxygen evolution reaction (OER) can be enhanced by confining it in the interlayer region of birnessite (layered manganese oxide). The cobalt intercalation was verified by employing state-of-the-art characterization techniques such as XRD, Raman and electron microscopy. It is demonstrated that the Co²⁺/birnessite electrocatalyst can reach 10 mA cm⁻² at an overpotential of 360 mV with near unity Faradaic efficiency. This overpotential is lower than that which can be achieved by using a pure cobalt hydroxide electrocatalyst for the OER. Furthermore, the Co²⁺/birnessite catalyst shows no degradation after 1000 electrochemical cycles.

Implementation of sustainable and affordable clean energy technologies requires cheap and highly active (electro)catalysts.¹ Among all renewable energy research, electrochemical and photoelectrochemical water splitting has been identified as promising fuel producing reactions, although the reaction is hindered by sluggish kinetics.^{2, 3} Recent developments in renewable energy research have led to the discovery of highly active hydrogen evolution reaction (HER) catalysts with earth abundant materials such as MoS₂, WS₂, CoP, Ni₃Se₂ with overpotentials (η) less than 100 mV.⁴⁻⁷ Even the best precious metal based oxygen evolution reaction (OER) catalysts such as IrO₂ and RuO₂, however, suffer from high overpotentials (>300 mV) and stability issues in alkaline media.^{8, 9} Recent research, however, in the context of lowering η for the OER, has shown that a ternary catalyst (FeCoW oxyhydroxide) exhibits a η of ~200 mV for OER.¹⁰

Apart from heterogeneous water oxidation catalysts (WOC), molecular based WOC have been extensively studied mainly due to the ease of designing well-defined catalytically active centers, which is convenient in elucidating reaction mechanisms.^{11, 12} Developments in molecular based WOC research has been able to discover extremely active catalysts where the reported turn over frequency (> 300 s⁻¹) is

comparable with nature's WOC, photosystem II (PS II).¹³ However successful integration of these molecular based catalysts into commercial water splitting devices is yet to be reported.

Numerous studies have investigated manganese based materials for OER.¹⁴⁻¹⁷ The motivation for these studies have in part been due to nature's use of manganese as an active component in the PS II cluster, which is known to perform water oxidation. As part of this prior research, birnessite, a material composed of two dimensional layers of edge sharing manganese octahedra (MnO₆), has been investigated. It has been shown that this layered material is a moderately active electrocatalyst for the OER.¹⁶⁻²¹ Compared to other manganese oxide phases, however, birnessite is one of the least active materials, exhibiting a η of ~750mV (at 10 mA cm⁻²) in alkaline media.^{16, 17, 20, 22} Despite being a moderately active electrocatalyst, birnessite can be an active water oxidation catalyst when ceric ammonium nitrate (CAN) is used as a sacrificial oxidizing agent.^{14, 15} The reason for this discrepancy between electrochemical water oxidation and chemical water oxidation using CAN is still under debate.^{22, 23}

A prime motivation for the current study is to investigate whether the activity of cobalt for the OER can be further enhanced by intercalating the catalyst in the interlayer region of birnessite. A prior study from our laboratory showed that birnessite intercalated with nickel (Ni²⁺/birnessite) was more active than either a nickel hydroxide or birnessite catalyst alone.²⁴ In particular the Ni²⁺/birnessite and nickel hydroxide catalysts exhibited a η of 420 and 550 mV (at 10 mA cm⁻¹), respectively, for the OER. Rationale for this experimental observation was based on a recent molecular dynamics (MD) simulation study.²⁵ This study suggested that the interaction between interlayer water molecules and intercalated metal cations in birnessite leads to a unique water structuring (i.e., frustrated water), which enhances electron transfer reactions in the interlayer. The current study aims to determine whether this strategy to increase the OER activity of a catalyst by confining it in a

unique spatially confined region continues to hold true. Relative to manganese oxide, cobalt based materials show superior activity towards OER catalysis.⁸ This superior catalytic activity of cobalt based OER catalysts is presumably due to optimal binding (i.e. not too strong and not too weak) of reaction intermediates (*OOH and *OH) on the catalytic sites that facilitate the OER.²⁶ Thus cobalt was chosen as an intercalant in this study. We believe that enhancing this activity still further would be noteworthy.

Figure 1. Powder X-ray diffraction pattern of birnessite and Co^{2+} /birnessite. The inset is the enlarged (001) reflection which indicates that interlayer spacing changes with cobalt confinement within the interlayer.

Cobalt was intercalated into the interlayer of birnessite using a simple ion exchange reaction using a cobalt hydrazine complex $[\text{Co}(\text{N}_2\text{H}_4)_x(\text{H}_2\text{O})_y]^{2+}$ (see SI for details) at room temperature. We refer to this material as Co^{2+} /birnessite. Generally, the interlayer spacing of a layered material is sensitive to the presence of guest molecules or atoms in the interlayer region.^{27, 28} X-ray diffraction (XRD) data presented in Figure 1 show that the (001) Bragg reflection for Co^{2+} /birnessite is shifted towards a higher two theta value relative to birnessite, indicating that the interlayer spacing of birnessite is decreased when birnessite is exposed to the cobalt hydrazine complex. The XRD data show that the interlayer spacing decreases from a value of 7.51 Å for pristine birnessite to 7.30 Å at a Co concentration of 8.4 at. % and to 7.22 Å at a Co concentration of 12.2 at. % (determined by inductively coupled plasma optical emission spectroscopy). Both scanning and transmission electron microscopy (SEM and TEM) show similar nano-flower morphologies for pristine birnessite and Co^{2+} /birnessite (Figure S1). However, a closer look at electron microscopy images reveals that there are changes in particles size before and after intercalation. We carried out Brunauer-Emmett-Teller (BET) specific surface area analysis to obtain further information. The resulting BET surface areas were 33 and 95 m^2/g for birnessite and Co^{2+} /birnessite respectively. To confirm the spatial distribution of the intercalated Co, we performed electron energy loss spectroscopy (EELS) across a cross section of the Co^{2+} /birnessite. Figure 2 (a) is an annular dark field (ADF) scanning transmission electron microscopy (STEM) image

taken of a cross section of Co^{2+} /birnessite, where the lattice fringes of (001) plane are visible. Quantitative analysis of the relative composition of O, Mn and Co is shown in Figure 2(b). The atomic composition of each element is 59.8 % $\pm$ 4.0 % for O, 28.4 % $\pm$ 3.3 % for Mn, and 11.8 % $\pm$ 3.9 % for Co. The EEL spectrum collected from a line scan for quantitative analysis is displayed in Figure 2(c). This particular data gives direct evidence of interlayer Co, consistent with the conclusions drawn from the XRD data. We mention that while atomic resolution STEM imaging found no evidence for structural defects in Co-free birnessite (Figure S2), it did show the presence of defects such as edge dislocations and grain boundaries after cobalt intercalation (Figure S3). As a control experiment birnessite was exposed to hydrazine (without complexing with cobalt) and as expected it led to significant structural changes (Mn_3O_4 formation was observed, Figure S4). XRD of this material (Figure S5) showed that the 001 reflection was at the same two-theta position as pristine birnessite. This experimental observation supports our contention that the shift of the 001 reflection associated with birnessite after exposure to cobalt/hydrazine is due to Co intercalation and a change in the interlayer spacing of birnessite. Additionally, BET specific surface area analysis on birnessite exposed to hydrazine (108 m^2/g) yielded a significant surface area enhancement. Based on this experimental result, we believe that the enhancement in surface area for Co^{2+} /birnessite was due to the presence of hydrazine during the intercalation process.

The oxidation state as well as chemical nature of intercalated cobalt was investigated using X-ray photoelectron spectroscopy (XPS). Figure 3(a) shows the Co 2p region of Co^{2+} /birnessite along with cobalt hydroxide standards. The similarity of the spectra suggests that the interlayer Co is in a +2 oxidation state. Based on the presence of an O 1s feature (Figure 3(b)) at 531.3 eV for both Co^{2+} /birnessite and $\text{Co}(\text{OH})_2$ (absent for pristine birnessite), we propose that the intercalated Co exists at least in part as a hydroxide. Additional insight into the structure of Co^{2+} /birnessite was obtained with Raman spectroscopy. A typical Raman spectrum

Figure 2. EELS line scan across the cross-section of the Co^{2+} /birnessite. (a) STEM ADF image of the cross section of the birnessite; (b) relative composition of O, Mn and Co, scattered dots are original data, mean value and standard deviation of each element are shown by solid line and dashed area; (c) EEL spectrum showing O K-edge, Mn $L_{3,2}$ -edge, and Co $L_{3,2}$ -edge that are used for quantitative composition analysis.

of birnessite exhibits two main modes at 575 cm^{-1} (in plane Mn-O vibration) and $\sim 646\text{ cm}^{-1}$ (out of plane Mn-O stretching).²⁹ Broadening of these modes can be attributed to a disorder of the structure induced by intercalation of guest molecule or atoms in the interlayer space.^{17, 29} We experimentally observed such a broadening in our Raman spectra for Co^{2+} /birnessite compared to birnessite (Figure S7). We take this result as further evidence to support the notion that cobalt resides in the interlayer region of birnessite, causing structural disorder in the layered birnessite, as observed by STEM (Figures S2 and S3). Finally, XPS as well as energy dispersive spectroscopy (Figure S8) shows that Co^{2+} /birnessite does not contain K^+ , suggesting that Co^{2+} intercalation leads to the displacement of K^+ from the interlayer to maintain charge neutrality.

The electrocatalytic activity of Co^{2+} /birnessite toward OER in alkaline media (pH ~ 14) was evaluated using a typical three-electrode configuration. A catalyst ink was prepared by mixing catalyst with conductive carbon and nafion (binder). The ink was drop-cast onto a glassy carbon electrode, which was used as the working electrode (see SI for details). For comparison, the catalytic activities of α -cobalt hydroxide, β -cobalt hydroxide, cobalt oxide (Co_3O_4), cobalt substituted birnessite, and Ir/C (20 wt. %) were also examined (Figure 4(a)). The cobalt substituted birnessite sample was prepared by synthesizing birnessite in the presence of CoCl_2 (see SI for details). This preparation method led to a birnessite with 12 at. % cobalt. In contrast to Co^{2+} /birnessite,

Figure 3. XPS spectra of birnessite, Co^{2+} /birnessite, $\alpha\text{-Co(OH)}_2$ and $\beta\text{-Co(OH)}_2$. a) Co 2p region and b) O 1s region.

XRD (Figure S9) of this material did not show a shift of the (001) reflection relative to pristine birnessite and K^+ was not displaced during the synthesis of cobalt substituted birnessite. These experimental observations suggested that Co^{2+} did not reside in the interlayer of this material and instead, Co^{2+} replaced manganese ions in the 2D sheets.

Based on the polarization curves presented in Figure 4, the Co-intercalated Co^{2+} /birnessite electrocatalyst exhibits a remarkable OER activity compared to all the other catalytic materials that were tested. Co^{2+} /birnessite exhibits a η of 360 mV at a current density of 10 mA cm^{-2} with a Tafel slope of $\sim 46\text{ mV dec}^{-1}$ whereas cobalt substituted birnessite shows a η of $\sim 490\text{ mV}$ (with a Tafel slope of 82 mV dec^{-1}). This particular comparison is direct evidence to support the contention that a significant portion of OER catalysis occurs in the interlayer region.²⁴ Furthermore, assessment of the OER activity for 8.4 and 12.2 % Co^{2+} /birnessite (Figure S10) showed that η decreased as the concentration of cobalt was increased within the interlayer region. This observation further supports the claim of interlayer cobalt being the active

Figure 4. a) Linear sweep voltammograms and b) chronoamperometry of various catalysts tested. Inset shows the chronoamperometry curve for birnessite (at $\eta=800\text{ mV}$) in comparison with Co^{2+} /birnessite (at $\eta=360\text{ mV}$).

site for these cobalt modified materials. Evaluation of the data compiled in Table 1 also shows that the η associated with Co^{2+} /birnessite is lower than $\alpha\text{-Co}(\text{OH})_2$ (380 mV), $\beta\text{-Co}(\text{OH})_2$ (420 mV), and Co_3O_4 (500 mV). This additional comparison leads to the conclusion that incorporation of an active catalyst into the interlayer region of birnessite leads to an even more active catalyst, consistent with the conclusion from our prior study of Ni^{2+} /birnessite.²⁴

We also conducted electrocatalytic studies at pH 7 solution conditions (using 0.5 M phosphate buffer as the electrolyte) in an effort to observe the possibility of similar enhancement due to metal intercalation (see Table S1) when H_2O was being directly oxidized (in contrast to OH^- at pH 14). Data in Figure S11 shows that at pH 7, as expected, the OER activity for the different electrocatalysts are suppressed relative to their performance in an alkaline medium, consistent with prior studies^{30, 31} with transition metal oxide OER catalysts. More important to the focus of this contribution is that the trend in OER activity for different electrocatalysts is similar to the trend obtained in an alkaline medium (η for OER for Co^{2+} /Birnessite < cobalt hydroxides < birnessite). These results taken together with the pH 14 results suggest that the superior activity of Co^{2+} /birnessite (relative to pure $\text{Co}(\text{OH})_2$ phases) is maintained whether H_2O or OH^- is the dominant molecular species.

To further support the validity of our conclusions we determined the electrochemically active surface area (ECSA) of the electrocatalysts. Since the double layer capacitance (C_{dl}) of an electrocatalyst is proportional to ECSA, one can investigate C_{dl} to estimate the ECSA. Figure S12 depicts C_{dl} values for the different catalysts tested. The absence of a significant enhancement in C_{dl} for Co^{2+} /birnessite suggests that the improved OER activity is not primarily due to a surface area related phenomena (Figure S12), but instead is due to favorable interactions of interlayer water with intercalated cobalt towards OER. Moreover, electrochemical investigation of birnessite exposed to hydrazine (Figure S13), revealed that there is no enhancement in OER activity even with the significant enhancement in surface area. Thus we believe that the increased activity of Co^{2+} /birnessite for the OER is not attributable to an increased surface area, but rather due to cobalt active sites in the interlayer. Furthermore, inspection of polarization curves for Co^{2+} /birnessite and cobalt hydroxides reveal that the oxidation of Co^{2+} to Co^{3+} occurs at a lower potential (1.07 V vs RHE) for Co^{2+} /birnessite relative to cobalt hydroxide (1.13 V vs RHE). Consistent with this experimental observation are previously mentioned MD simulations^{24, 25} for Ni^{2+} /birnessite that suggested that there is a lowering of the barrier for electron transfer for a metal cation (e.g., Ni^{2+}) coordinated by interlayer water compared to the same metal cation coordinated by bulk water. In analogy with the current results for the $\text{Co}^{2+}/\text{Co}^{3+}$ couple, it was shown in the earlier work that Ni^{2+} oxidized to Ni^{3+} at a lower potential when it was intercalated in birnessite than when it was present in bulk $\text{Ni}(\text{OH})_2$. This phenomenon²⁴ was proposed to be due to frustrated water in the interlayer of birnessite. In essence, if interlayer cations are abundant, coordination of water to the cation to form a complete solvation shell is hindered resulting in enhanced solvent fluctuations (i.e., frustrated) as individual water molecules seek to align their dipoles with inter-layer cations. These enhanced fluctu-

ations of interlayer water lower the reorganization energy for electron transfer reactions.^{19, 20}

As illustrated by Table 1, the improved OER activity of Co^{2+} /birnessite is further emphasized by turnover frequencies (TOF) and mass activities. Specifically, Co^{2+} /birnessite (TOF $\sim 0.02 \text{ s}^{-1}$) shows an order of magnitude improvement in TOF relative to cobalt substituted birnessite (TOF $\sim 0.002 \text{ s}^{-1}$). Furthermore, the Faradaic efficiency was determined by performing electrolysis at a constant current using an airtight H-type cell and evolved oxygen was analyzed using gas chromatography (SI Figure S14). In order to evaluate the stability of the catalyst, chronopotentiometry (at constant current of 20 mA cm^{-2}) and chronoamperometry (at 360 mV overpotential) were performed and the Co^{2+} /birnessite catalyst was stable for more than 24 hours (Figure 4(b) and S15). Additionally, electrochemical redox cycling was performed on this cobalt confined birnessite and even after 1000 cycles no degradation of catalytic activity was experimentally observed (Figure S16).

Table 1. Summary of OER activities in 1 M KOH and atomic ratios from ICP-OES and EDS

Catalyst	Confined or substituted atomic Co %	η (mV) at 10 mA cm^{-2}	TOF (s^{-1}) at $\eta=0.40 \text{ V}$	mass activity (A g^{-1}) at $\eta=0.40 \text{ V}$	Tafel slope (mV dec^{-1})
Birnessite	-	770	0.0004	2.0	243 $\pm$ 7
Co^{2+} /Birnessite	12.2	360	0.023	92	46 $\pm$ 3
Co^{2+} /Birnessite	8.4	392	0.011	45	66 $\pm$ 4
Co-substituted Birnessite	12.4	490	0.0023	3.0	82 $\pm$ 3
$\beta\text{-Co}(\text{OH})_2$	-	420	0.0051	30	52 $\pm$ 3
$\alpha\text{-Co}(\text{OH})_2$	-	380	0.013	54	51 $\pm$ 4
Co_3O_4	-	500	0.0008	4.5	76 $\pm$ 4
20% Ir/C	-	350	0.018	72	72 $\pm$ 4

In closing, we mention that the results presented in this contribution for Co^{2+} /birnessite taken together with those published elsewhere for Ni^{2+} /birnessite further emphasize the unique interlayer environment of birnessite. In short, both Co^{2+} and Ni^{2+} , when intercalated in birnessite, exhibit a lowering of their respective oxidation potentials and an enhancement in their activity toward the OER. In stark contrast, the simple substitution of Co^{2+} into the octahedrally coordinated sheets of birnessite or adsorption of Ni^{2+} on the octahedral sheets of birnessite²⁴ does not lead to the enhancements in OER activity that are observed when the metal cations are intercalated. Ongoing research in our laboratory is further investigating the unique chemical environment of the interlayer with experiment, MD simulations, and theory.

ASSOCIATED CONTENT

Supporting Information

Experimental details, XPS, Raman spectra, LSV polarization curves, Electron microscopy. This material is available free of charge via the Internet at <http://pubs.acs.org>.

KEYWORDS

Oxygen evolution reaction, Cobalt intercalation, Birnessite, Electrocatalyst, Water splitting,

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REFERENCES

- (1) Gray, H. B. *Nat. Chem.* **2009**, 1, 7-7.
- (2) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci.* **2006**, 103, 15729-15735.
- (3) Nocera, D. G. *Acc. Chem. Res.* **2012**, 45, 767-776.
- (4) Caban-Acevedo, M.; Stone, M. L.; Schmidt, J. R.; Thomas, J. G.; Ding, Q.; Chang, H.-C.; Tsai, M.-L.; He, J.-H.; Jin, S. *Nat. Mater.* **2015**, 14, 1245-1251.
- (5) Callejas, J. F.; Read, C. G.; Popczun, E. J.; McEnaney, J. M.; Schaak, R. E. *Chem. Mater.* **2015**, 27, 3769-3774.
- (6) Cheng, L.; Huang, W.; Gong, Q.; Liu, C.; Liu, Z.; Li, Y.; Dai, H. *Angew. Chem. Int. Ed.* **2014**, 53, 7860-7863.
- (7) Shi, J.; Hu, J.; Luo, Y.; Sun, X.; Asiri, A. M. *Catal. Sci. Tech.* **2015**, 5, 4954-4958.
- (8) Jung, S.; McCrory, C. C. L.; Ferrer, I. M.; Peters, J. C.; Jaramillo, T. F. *J. Mater. Chem. A* **2016**, 4, 3068-3076.
- (9) Lee, Y.; Suntivich, J.; May, K. J.; Perry, E. E.; Shao-Horn, Y. *J. Phys. Chem. Lett.* **2012**, 3, 399-404.
- (10) Zhang, B.; Zheng, X.; Voznyy, O.; Comin, R.; Bajdich, M.; García-Melchor, M.; Han, L.; Xu, J.; Liu, M.; Zheng, L.; García de Arquer, F. P.; Dinh, C. T.; Fan, F.; Yuan, M.; Yassitepe, E.; Chen, N.; Regier, T.; Liu, P.; Li, Y.; De Luna, P.; Janmohamed, A.; Xin, H. L.; Yang, H.; Vojvodic, A.; Sargent, E. H. *Science* **2016**, 352, 333-337.
- (11) Li, W.; He, D.; Sheehan, S. W.; He, Y.; Thorne, J. E.; Yao, X.; Brudvig, G. W.; Wang, D. *Energ. Environ. Sci.* **2016**, 9, 1794-1802.
- (12) Sala, X.; Romero, I.; Rodríguez, M.; Escriche, L.; Llobet, A. *Angew. Chem. Int. Ed.* **2009**, 48, 2842-2852.
- (13) Duan, L.; Bozoglian, F.; Mandal, S.; Stewart, B.; Privalov, T.; Llobet, A.; Sun, L. *Nat. Chem.* **2012**, 4, 418-423.
- (14) Boppana, V. B. R.; Yusuf, S.; Hutchings, G. S.; Jiao, F. *Adv. Funct. Mater.* **2013**, 23, 878-884.
- (15) McKendry, I. G.; Kondaveeti, S. K.; Shumlas, S. L.; Strongin, D. R.; Zdilla, M. J. *Dalton Trans.* **2015**, 44, 12981-12984.
- (16) Meng, Y.; Song, W.; Huang, H.; Ren, Z.; Chen, S.Y.; Suib, S. L. *J. Am. Chem. Soc.* **2014**, 136, 11452-11464.
- (17) Thenuwara, A. C.; Shumlas, S. L.; Attanayake, N. H.; Cerkez, E. B.; McKendry, I. G.; Frazer, L.; Borguet, E.; Kang, Q.; Zdilla, M. J.; Sun, J.; Strongin, D. R. *Langmuir* **2015**, 31, 12807-12813.
- (18) Baricuatro, J. H.; Saadi, F. H.; Carim, A. I.; Velazquez, J. M.; Kim, Y.-G.; Soriaga, M. P. *J. Phys. Chem. C* **2016**, 120, 15618-15631.
- (19) Lee, S. Y.; González-Flores, D.; Ohms, J.; Trost, T.; Dau, H.; Zaharieva, I.; Kurz, P. *ChemSusChem* **2014**, 7, 3442-3451.
- (20) Nakayama, M.; Fujii, Y.; Fujimoto, K.; Yoshimoto, M.; Kaide, A.; Saeki, T.; Asada, H. *RSC Advances* **2016**, 6, 23377-23382.
- (21) Huynh, M.; Shi, C.; Billinge, S. J. L.; Nocera, D. G. *J. Am. Chem. Soc.* **2015**, 137, 14887-14904.
- (22) Pokhrel, R.; Goetz, M. K.; Shaner, S. E.; Wu, X.; Stahl, S. S. *J. Am. Chem. Soc.* **2015**, 137, 8384-8387.
- (23) Wiechen, M.; Najafpour, M. M.; Allakhverdiev, S. I.; Spiccia, L. *Energ. Environ. Sci.* **2014**, 7, 2203-2212.
- (24) Thenuwara, A. C.; Cerkez, E. B.; Shumlas, S. L.; Attanayake, N. H.; McKendry, I. G.; Frazer, L.; Borguet, E.; Kang, Q.; Remsing, R. C.; Klein, M. L.; Zdilla, M. J.; Strongin, D. R. *Angew. Chem. Int. Ed.* **2016**, 55, 10381-10385.
- (25) Remsing, R. C.; McKendry, I. G.; Strongin, D. R.; Klein, M. L.; Zdilla, M. J. *J. Phys. Chem. Lett.* **2015**, 6, 4804-4808.
- (26) Man, I. C.; Su, H.Y.; Calle-Vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. *ChemCatChem* **2011**, 3, 1159-1165.
- (27) Lu, Z.; Wang, H.; Kong, D.; Yan, K.; Hsu, P.-C.; Zheng, G.; Yao, H.; Liang, Z.; Sun, X.; Cui, Y. *Nat. Commun.* **2014**, 5, doi:10.1038/ncomms5345.
- (28) Motter, J. P.; Koski, K. J.; Cui, Y. *Chem. Mater.* **2014**, 26, 2313-2317.
- (29) Julien, C.; Massot, M.; Baddour-Hadjean, R.; Franger, S.; Bach, S.; Pereira-Ramos, J. P. *Solid State Ionics* **2003**, 159, 345-356.
- (30) Gardner, G.; Al-Sharab, J.; Danilovic, N.; Go, Y. B.; Ayers, K.; Greenblatt, M.; Charles Dismukes, G. *Energ. Environ. Sci.* **2016**, 9, 184-192.
- (31) Kim, H.; Park, J.; Park, I.; Jin, K.; Jerng, S. E.; Kim, S. H.; Nam, K. T.; Kang, K. *Nat. Commun.* **2015**, 6, doi:10.1038/ncomms9253.

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Supporting Information

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Experimental

Materials and Methods

All the chemicals used here were purchased from commercial vendors and used without any further purification. X-ray diffraction (XRD) data were acquired on a Bruker Kappa APEX II DUO diffractometer using Mo K α radiation from a sealed molybdenum tube with a TRIUMPH monochromator. X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo Scientific K-alpha+ at the University of Delaware. A JEOL JEM-1400 microscope operating at 120 kV was used to obtain transmission electron microscopy (TEM) images. SAED patterns, STEM images and EEL spectra were taken using an aberration corrected JEOL JEM-ARM200CF scanning transmission electron microscope operated at 200 kV. Atomic resolution STEM images were taken with an annular bright-field detector. The image contrast was inverted so that the atoms appear to be bright, and the inverted ABF images were processed with a low-pass filter to remove high frequency noise. The STEM image for the EELS line scan was taken with an annular dark-field detector. Scanning electron microscopy (SEM) images were obtained using a FEI Quanta 450 FEG-SEM microscope operating at 30 kV. Energy dispersive spectroscopy (EDS) analysis was performed with an Oxford systems nano-analysis EDS system, using Aztec 2.1 as the analyzing software. Elemental analysis was performed using a Thermo Scientific iCAP 7000 Series Inductively Coupled Plasma with an Optical Emission Spectrometer (ICP-OES). Raman measurements were performed using a Horiba Labram HR800 Evolution

confocal Raman spectrometer with 532 nm excitation and a 100X objective. All samples were pressed into pellets by applying pressure to obtain a smooth surface for Raman analysis. The Brunauer-Emmett-Teller (BET) specific surface area measurements were performed by single-point BET N₂ adsorption using an ASAP 2020 surface area analyzer (Micromeritics).

Synthesis of potassium birnessite. Hydrochloric acid (4 M, 50.0 mL) was added drop wise via a syringe pump at 1 mL/min to a heated and stirred (80 °C, 360 rpm) solution of potassium permanganate (KMnO₄, 0.200 M, 250 mL) in a 400 mL beaker. Heating continued at 80 °C for an additional 0.5 h after addition was completed. The resulting 300 mL solution was then covered to prevent excessive evaporation overnight and aged for 15 h at 50 °C. Finally, the resulting suspension was washed several times with distilled water and dried at room temperature.

α -cobalt hydroxide synthesis. A colorless solution was formed by dissolving cobalt chloride hexahydrate (CoCl₂•6H₂O) and NH₄F in distilled water ([Co²⁺] = 0.6 mol dm⁻³) while keeping the molar ratio of NH₄F to Co²⁺ equal to 0.25. Propylene oxide was used as the precipitation agent and the molar ratio of propylene oxide and metal ions were kept at 10. A precipitate formed within 0.5–2 h under vigorous stirring. After reaction for 24 h, green colored cobalt hydroxide nanosheets were obtained by vacuum filtration, water-washed, and dried at 80°C.

β -cobalt hydroxide synthesis. β -Co(OH)₂ nanostructures were synthesized by a hydrothermal synthesis method. First, CoCl₂•6H₂O (2 mmol) was dissolved in 40 mL of distilled water and 1.0 mL of N(CH₂CH₃)₃ was added to the Co-containing solution while being constantly stirred.

Next, the resultant slurry was transferred to a 50 mL autoclave and heated at 180 °C for 24 h in a furnace. The autoclave was then left to cool to room temperature. Finally, the solid product was recovered, washed with water several times, and air-dried.

Co₃O₄ synthesis. Cobalt oxide was formed by dissolving CoCl₂•6H₂O and NH₄F, in distilled water ($[\text{Co}^{2+}] = 0.6 \text{ mol dm}^{-3}$) while keeping the molar ratio of NH₄F to Co²⁺ equal to 2. Propylene oxide was used as the precipitation agent and the molar ratio of propylene oxide to metal ions was kept at 10. A precipitate was then produced within 0.5–2 h under vigorous stirring. After reaction for 24 h, the resulting pink precipitate was obtained by vacuum filtration. The precipitate was then water-washed and air-dried. Co₃O₄ was produced by annealing the pink powder in air at 400 °C for 4 h.

Synthesis of cobalt substituted birnessite. Hydrochloric acid (2 M, 50.0 mL) and cobalt(II) chloride hexahydrate (47 mmol, 50.0 mL) were added simultaneously via a syringe pump operating at 1 mL/min to a heated and stirred solution (80°C, 360 rpm) of KMnO₄ (0.200 M, 250 mL). After the addition was completed, heating at 80°C was continued for 30 min at which point the temperature was reduced to 40° C and material was aged overnight. The resulting blue-black precipitate was then washed several times with distilled water via centrifugation and dried in air at room temperature.

Synthesis of birnessite intercalated with cobalt. Co-intercalated birnessite (referred to as Co²⁺/birnessite hereafter) was prepared via a wet chemical ion exchange reaction. The cobalt precursor solution was prepared by adding 0.100 g (0.422 mmol) of CoCl₂•6H₂O to 20 mL of

deionized water (18.3 MΩ cm). A stoichiometric amount (19 μL, 0.204 mmol) of hydrazine solution (35 wt. % in H₂O) was added to the cobalt precursor solution. A noticeable color change from pink to pale green was observed after the addition of hydrazine, which is an indication of the formation of the cobalt-hydrazine complex (Equation S1). After stirring for 5 min, 0.100 g of synthetic birnessite was added to the green colored cobalt-hydrazine complex containing solution and the suspension was stirred vigorously for 30 min. Finally, the solution was vacuum filtered and the residue washed with deionized water. In order to examine the effect of reaction time, a series of Co²⁺/birnessite samples were synthesized by changing the exposure time of birnessite to the cobalt-hydrazine complex from 30 to 60 min.

Electron microscopy Characterization

TEM selected area electron diffraction (SAED) patterns were taken from both pristine and Co²⁺/birnessite, as shown in Figure S16. Comparing to the SAED pattern from Co²⁺/birnessite, the one from pristine birnessite show more and sharper diffraction rings, suggesting better crystallinity, in accordance with the XRD results. Atomic resolution STEM images further confirm the crystal quality down to atomic level. Figure S2 (a) shows the atomic structure of the pristine birnessite from its [010] direction that matches the atomic model given in Figure S2 (b), while a lower magnification image of the layered structure is shown in Figure S2 (c). Despite slight bending, the pristine birnessite manifests good crystallinity with virtually no defects. As opposed to pristine birnessite, Co²⁺/birnessite is found to be defect-rich. As shown in Figures S3 (a-c), edge dislocations and grain boundaries are clearly visible from the cross sectional images.

Electrochemical Characterization

The electrocatalytic studies were conducted in 1 M KOH (pH ~14) or 0.5 M phosphate buffer (pH~7) using a CHI 660E potentiostat operating in a standard three-electrode configuration at ambient temperature (22 ± 2 °C). Glassy carbon (GC) electrodes (3 mm diameter from CH instruments) were used as working electrodes. Before electrochemical experiments the GC electrodes were polished using 1, 0.3, and 0.05 μm alumina powder, respectively, and sonicated in DI water to clean the electrode surfaces. All the potentials were measured with respect to a calomel reference electrode (CH instruments) and Pt wire was used as the counter electrode. The working electrode was prepared by drop casting 5 μL of catalyst ink suspension on the glassy carbon electrode (loading 0.28 mg/cm^2). Ink solutions were prepared as follows: 4 mg of catalyst and 4 mg of carbon (VulcanXC-72) were added to 1 mL isopropanol and 35 μL of Nafion solution (5% in alcohol, Ion Power Inc.) and the resulting mixture was sonicated for at least 30 min to form the catalyst ink. All polarization curves were recorded at a scan rate of 10 mV/s. For all the catalysts tested, polarization curves were replicated at least 5 times. The overpotential (at a current density of 10 mA/cm^2) and Tafel slopes reported are based on an analysis of these data. Estimation of the electrochemically active surface area (ECSA) of the catalysts was carried out by plotting charging current density differences ($\Delta j = j_a - j_c$) as a function of scan rate. The charging current density differences can be obtained by performing cyclic voltammetry (CV) at different scan rates in a potential window of 100 mV, where the open circuit potential (OCP) falls in the middle. The double layer capacitance was estimated

from the slope of the charging current density differences at OCP vs scan rate plot. The slope is twice the double layer capacitance. Since double layer capacitance is proportional to the ECSA of the catalyst, the ratio of double layer capacitance can be considered as the ratio of ECSA. For stability testing, carbon fiber paper (CFP) was also used as electrodes. For the CFP electrodes, the catalyst loading was 1 mg/cm². For Faradaic efficiency determination an H-type cell was used. Electrolysis was performed at a constant current of 7 mA and the electrochemically-generated headspace gas was analyzed using a gas chromatograph (HP 5890 series II) equipped with a molecular sieve column and thermal conductivity detector.

Catalytic parameter calculations

The turnover frequency (TOF) value is calculated from the equation:

$$TOF = \frac{JA}{4Fn}$$

Where, J is the measured current density (mA cm⁻²) at $\eta = 0.40$ V, A is the geometric area of the electrode, n is the number of moles of catalyst, and F is the Faraday constant (96500 C mol⁻¹).

The mass activity was calculated from following equation:

$$mass\ activity = \frac{J}{m}$$

The mass activity (A g⁻¹) was calculated on the basis of the catalyst loading $m = 0.28$ mg cm⁻² and the measured current density j (mA cm⁻²) at $\eta = 0.40$ V.

Figure S1. Electron micrographs of Co^{2+} /birnessite: (a) TEM and (b) SEM. Micrographs of birnessite: (c) TEM and (d) SEM. Co-intercalation did not significantly alter the morphology of birnessite.

Figure S2. Inverted ABF image of pristine birnessite. (a) atomic resolution image of pristine birnessite, view from [010] direction; (b) atomic model of birnessite from its [010] direction, the black parallelogram indicates the primitive unit cell; (c) lower magnification image showing layered structure with good crystallinity, virtually with no defects.

Figure S3. Inverted ABF image of Co²⁺/birnessite. (a-c) High resolution images of the cross section of Co²⁺/birnessite, yellow circles indicate defects such as edge dislocations and grain boundaries.

Figure S4. Experimental XRD pattern for birnessite exposed to hydrazine (without Co^{2+} ions) shown together with the diffraction peak positions associated with tetragonal Mn_3O_4 (JCPDS no. 24-0734). A comparison suggests that birnessite transforms into Mn_3O_4 when exposed to hydrazine.

Figure S5. XRD spectra of birnessite and birnessite exposed to hydrazine. Inset is the enlarged (001) region that corresponds to the interlayer spacing. The spectra suggest that hydrazine does not alter interlayer spacing of birnessite (i.e., octahedral sheet) does not alter the interlayer spacing.

Figure S6. Top left panel is a STEM micrograph for Co^{2+} / Birnessite. Also included in the figure are energy dispersive spectroscopy (EDS) elemental maps for Mn, O and Co.

Figure S7. Raman spectra of birnessite and Co²⁺/birnessite. We attribute the broadening of the Raman peaks to the disorder in the birnessite lattice induced by the presence of cobalt in the interlayer region.

Figure S8. K $2p$ XPS of birnessite and Co^{2+} /birnessite. An evaluation of the spectra shows the loss of potassium ions from the birnessite interlayer as a consequence of the intercalation reaction.

Figure S9. XRD diffractograms of birnessite and Co substituted birnessite. Inset is the enlarged (001) region that corresponds to the interlayer spacing. The spectra suggest that substitution of cobalt into the birnessite structure (i.e., octahedral sheet) does not alter the interlayer spacing.

Figure S10. Polarizations curves for 12.2 atm. % Co²⁺/birnessite and 8.4 atm. % Co²⁺/birnessite in 1 M KOH.

Figure S11. Polarizations curves for Ir/C, Co^{2+} /birnessite, Co-substituted birnessite, birnessite, and cobalt hydroxides collected in phosphate buffer (pH 7).

Figure S12. The difference in current density ($(\Delta j = j_a - j_c)$) at open circuit potential (OCP) plotted against scan rate fitted to a linear regression to estimate the ECSA of birnessite, Co^{2+} /Birnessite, $\alpha\text{-Co(OH)}_2$ and $\beta\text{-Co(OH)}_2$.

Figure S13. Polarization curves for birnessite and birnessite exposed to hydrazine in 1 M KOH. The results suggest that reaction with hydrazine does not improve the catalytic performance of birnessite.

Figure S14. O₂ evolution from Co²⁺/birnessite as a function of electrolysis time at a constant current of 7 mA. Inset shows an example of the detector response (from GC) for evolved oxygen.

Figure S15. Chronopotentiometry curves for Co²⁺/birnessite at a current density of 20 mA cm⁻² using CFP as the working electrode. Inset is the chronopotentiometry of birnessite performed at 10 mA cm⁻².

Figure S16. Polarization curves for Co^{2+} /birnessite with increasing electrochemical cycles.

Figure S17. Polarizations curves for Ir/C, Co^{2+} /birnessite, Co-substituted birnessite, birnessite, and cobalt hydroxides collected in 1 M KOH.

Figure S18. Mn $2p_{3/2}$ core level spectra of birnessite and Co²⁺/birnessite. Mn(IV) fits are shown in green, Mn(III) fits are shown in blue and Mn(II) fits are shown in orange. The spectral fitting suggests that average oxidation state of Mn has decreased in from 3.74 to 3.57 after cobalt becomes intercalated in birnessite.

Figure S19. SAED patterns taken from Co-birnessite (left half) and pristine birnessite (right half) showing significant difference in crystallinity. Sharper rings and diffraction from more planes suggest better crystallinity in pristine birnessite.

Figure S20. Electron micrographs of α -Co(OH)₂: (a) SEM and (b)TEM. Micrographs of Co₃O₄: (c) SEM and (d) TEM.

Figure S21. TEM micrograph of β -Co(OH)₂.

Figure S22. XRD spectra of α -Co(OH)₂, β -Co(OH)₂, Co₃O₄, birnessite, and Co²⁺/birnessite.

Figure S23. XRD diffractograms of birnessite and birnessite exposed to 1 M Co^{2+} . Inset is the enlarged (001) region that corresponds to the interlayer spacing. The inset suggest surface adsorbed cobalt does not alter the interlayer spacing.

Figure S24. FTIR spectra of birnessite.

Table S1. Summary of OER activities in phosphate buffer.

Catalyst	η (mV) at 10 mA cm ⁻²	TOF (s ⁻¹) at $\eta=0.50$ V	mass activity (A g ⁻¹) at $\eta=0.50$ V	Tafel slope(mV dec ⁻¹)
birnessite	920	0.0012	7	238±6
Co ²⁺ /birnessite	618	0.0064	25	98±3
Co-substituted birnessite	725	0.0031	14	168±7
β-Co(OH) ₂	725	0.0022	8.9	124±3
α-Co(OH) ₂	632	0.0051	21	92±2
Co ₃ O ₄	740	0.0057	8.9	173±4
20% Ir/C	480	0.23	100	60±3

Table S2. Experimental data for birnessite.

Sample	K:Mn	Co:Mn	Mn(IV)	Mn(III)	Mn(II)	AOS^a	formula
Birnessite	0.31	-	75.8	22.3	1.9	3.74	$\text{K}_{0.31}\text{MnO}_{2.02}\cdot 0.54 \text{H}_2\text{O}$
Co^{2+} /Birnessite	-	0.12	67.2	22.7	10.1	3.57	$\text{Co}_{0.12}\text{MnO}_{1.97}\cdot 1.56\text{H}_2\text{O}$
Co-substituted Birnessite	0.12	0.12	65.12	3.65	-	3.65	$\text{K}_{0.12}\text{Co}_{0.108}\text{Mn}_{0.9}\text{O}_{2.048}\text{H}_2\text{O}$

^a AOS, average oxidation state of manganese were determined via XPS (Figure S15).

The K:Mn ratios determined by ICP-OES and EDS.

Formula was determined using the XPS,ICP-OES and EDS.