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Enhancing Electrocatalytic Performance of Bifunctional Cobalt Manganese Oxynitride Nanocatalysts on Graphene

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We report the synthesis and characterization of graphene-supported cobalt manganese oxynitride nanocatalysts (CoMnON/G) as bifunctional electrocatalysts for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). A nitriding treatment of spinel compound CoMnO increases the ORR activity considerably, and the most active material catalyzes the ORR with only a 30 mV half-wave potential difference from the commercial carbon-supported platinum (Pt/C) in alkaline media. In addition to high activity, the catalyst also exhibits an intrinsic stability that outperforms Pt/C. An appropriately designed nitridation thus facilitates new directions for developing active and durable non-precious-metal oxynitride electrocatalysts.

The need for high energy production with low environmental impact has led to a tremendous amount of research dedicated to the development of anion-exchange membrane fuel cells (AMFCs)^[1] and electrolyzers.^[2] Oxygen reduction/evolution reactions (ORR/OER) are key reactions in these energy conversion devices. The ORR, the cathode reaction in fuel cells, and the OER, the anodic reaction in water electrolyzers, are both sluggish with high overpotentials, and better electrocatalysts are required to overcome these impediments.^[3] Carbon-supported platinum catalysts are typical catalysts for the ORR,^[4] while RuO₂ and IrO₂ are known to be active catalysts for the OER.^[5] The major drawbacks of these noble metal and metal oxide electrocatalysts are their prohibitive cost and limited availability. In particular, platinum prices are volatile and would be expected to increase with a further demand for fuel cell power systems. Therefore, it would greatly facilitate the commercialization of fuel cell technology if non-precious metal catalysts could replace Pt and Pt-based catalysts.

Different categories of non-precious metal catalysts have been widely investigated,^[6] including transition-metal oxides,^[7] nitride/carbide materials,^[8] transition-metal macrocycles,^[9] and transition metal oxynitrides.^[10] Among these materials, spinel compounds of AB₂O₄ (A, B are Co, Mn) composition exhibit some promising performance for both the ORR/OER,^[11] and possess the advantages of bifunctional oxygen electrochemical properties, low cost and low environmental impact. However, they still need to be further improved in terms of both activity and stability to replace noble-metal catalysts. Recently transition-metal oxynitrides synthesized by doping nitrogen into metal oxides have shown reasonably good ORR electrocatalytic performance and corrosion resistance.^[8b, 12] It is believed that nitrogen doping modifies the catalysts' electronic structure by lowering the *d*-band gap of metal oxides, resulting in higher ability of electron donation to oxygen.^[12a] Therefore, it is worthwhile to explore new transition-metal oxynitrides by nitriding spinel compounds such as Mn-based oxides to improve their electrochemical ORR/OER activity and stability. Herein, we report the synthesis, structural characterization, and

electrocatalytic performance of graphene(G)-supported cobalt manganese oxynitrides (CoMnON/G), which present unique morphology, high ORR activity and stability, as well as improved OER activity in comparison to a spinel compound of cobalt manganese oxide (CoMnO/G) in basic media.

CoMnON/G was prepared in two steps, including the synthesis of the spinel compounds of CoMnO and then followed by annealing them in ammonia.^[11c] Detailed synthesis methods are presented in the Supporting Information (SI). CoMnO was synthesized by chemical reduction of a mixture of MnO₂ and CoCl₂·6H₂O in water (the molar ratio of the Co:Mn precursor was 1:2). As shown in Figure 1, the XRD pattern after the chemical reduction exhibited a spinel structure having peaks between cubic Co₂MnO₄ and Co₂MnO_{4.5} spinel compounds (PDF#23-1237); the resulting atomic ratio of Co:Mn:O (2:1:4~4.5) is in good agreement with that from the energy-dispersive X-ray spectroscopy spectrum (EDS) (Co:Mn:O =2.0:1.0:4.5 in Figure S1a). CoMnON/G was then synthesized by nitriding a mixture of CoMnO and graphene at different temperatures (300-700 °C) under flowing ammonia. The XRD (Figure S2) revealed that the phase at 300 °C remained similar to CoMnO but prominent changes in structure were observed above 400 °C.

Figure 1 shows that the XRD patterns of CoMnON/G obtained at 400 °C and 550 °C exhibit broad peaks lying between references of cubic CoO (PDF#65-2902) and cubic MnO (PDF#07-0230), which have the same NaCl-type structure. The marked feature here is that the XRD peaks of the CoMnON/G 550 °C sample showed a shift to lower angles compared with the CoMnON/G 400 °C sample. This demonstrates the formation

Figure 1. Synchrotron XRD of CoMnO/G by chemical reduction and CoMnON/G by subsequent nitriding at 400 °C and 550 °C in ammonia. The assignments of the diffraction peaks are included (● Mn₂CoO_{4.5}; ○ Mn₂CoO₄; □ MnO; ▲ CoO; ▲ CoN). Wavelength: 0.77936 Å. The inset shows a schematic of the proposed structure of CoMnON/G 550 °C.

of an oxynitride structure; we consider that the basic structure is a mixture of NaCl-type CoO and MnO, and some oxygen atoms in the oxide (approximately 12 % of oxygen, derived from the EDS) have been substituted by nitrogen atoms. Since nitrogen has a larger ionic radius than oxygen, the introduction of nitrogen into the oxide causes an increase in bonding distance. This can be understood by the fact that reflection peaks of CoN (PDF#11-0116) are located at lower angles compared with CoO (PDF#48-1719). The incorporation of nitrogen into the catalyst was also confirmed by the EDS (Figure S1b), which showed 6.2 atom-% nitrogen and the molar ratio of Co:Mn:O:N of 2.1:1:3:0.4

Figure 2. (a, b) Typical TEM bright field images of a CoMnON sample annealed at 550 °C in ammonia.

for the CoMnON/G 550 °C sample. The mole ratio of (Co+Mn):(O+N) is ca. 1:1. The proposed crystal structure of this catalyst is illustrated in the inset of Figure 1. As discussed below, the CoMnON/G 550 °C sample exhibited the highest ORR activity among the catalysts examined, and the electrochemical performance is thus related to the oxynitride structure induced by the annealing and nitrogen doping.

We performed transmission electron microscopy (TEM) observations of the oxynitride catalysts to investigate their morphology. As shown in Figures 2b and 2c, the bright field TEM images showed that the CoMnON catalyst annealed at 550 °C consists of two distinct shapes; one with nanoparticles and the other with nanorods. The nanoparticles, the more abundant of the two types, have an average size of 5 nm, while the nanorods have an average width of 5 nm with length varying from 20 nm to 100 nm. More pictures are shown in Figure S3 in the SI, together with a plausible mechanism of the nanorod formation.

The ORR polarization curves of CoMnO/G, CoMnON/G annealed at 550 °C,

and Pt/C were compared in an O₂-saturated 0.1 M KOH solution at a sweep rate of 50 mV/s (Figure 3a). Remarkably, the CoMnON/G catalyst exhibited a much more positive ORR onset potential, E_{onset} (0.920 V vs. RHE), and a higher half-wave potential, $E_{1/2}$ (0.807 V), compared with CoMnO/G (E_{onset} of 0.880 V and $E_{1/2}$ of 0.716 V). The nitriding treatment indeed enhanced considerably the ORR performance (e.g., 91 mV increase in $E_{1/2}$). We emphasize that the $E_{1/2}$ of CoMnON/G was only 30 mV lower than the commercial state-of-the-art Pt/C sample (Pt loading 6 $\mu\text{g}/\text{cm}^2$) and 46 mV lower than Pt/C at a “standard” loading of 20 $\mu\text{g}/\text{cm}^2$ reported elsewhere,^[9a] along with similar diffusion-limit current density. The Koutecky-Levich plots derived from the ORR curves at various rpm (Figure S4b) showed the linearity and parallelism of the fitting lines indicative of first-order reaction kinetics with respect to the concentration of dissolved oxygen. Rotating ring-disk electrode (RRDE) measurements were performed to detect the formation of peroxide species (H₂O₂) during the ORR process (Figures 3b and 3c). The measured H₂O₂ yields for CoMnON/G ranged from 5% to 10% in the potential range of 0.10-0.80 V, giving an electron transfer number $n=3.8$ (see Equations (1) and (2) in the SI). This indicates that a catalytic pathway of complete 4-electron reduction of O₂ to H₂O is the primary mechanism. The avoidance of a less efficient 2-electron reduction path is essential for non-precious metal catalysts to replace Pt/C as a fuel cell cathode material. Kinetic currents derived from the mass transport correction of the ORR RRDE currents show a Tafel slope of -79 mV per decade, close to the -81 mV per decade for the Pt/C catalyst (Figure S4c).

The stability of non-precious metal catalysts is another crucial factor for practical application in fuel cell systems. The ORR activities of CoMnO/G, CoMnON/G and Pt/C after 10,000 potential cycles between 0.6 V and 1.0 V are also presented in Figure 3a. The decrease in $E_{1/2}$ after 10,000 cycles for CoMnON/G was only 7 mV, showing the excellent stability performance compared with CoMnO/G (14 mV loss in $E_{1/2}$) and Pt/C (36 mV loss in $E_{1/2}$). We should emphasize that the activity and stability for the ORR observed on the CoMnON/G catalyst are the highest among nitrogen-doped oxynitride catalysts in alkaline media; moreover, the activity is the second highest next to the Co_xN/NHCS (nitrogen-rich hollow carbon spheres) catalyst^[8e] among nitrogen-doped nitride catalysts in alkaline media, as listed in Table S1.

Figure 3. (a) ORR polarization curves for CoMnON/G (red, 69 $\mu\text{g}_{\text{CoMn}}/\text{cm}^2$), CoMnO/G (blue, 69 $\mu\text{g}_{\text{CoMn}}/\text{cm}^2$) and Pt/C (black, 6 $\mu\text{g}_{\text{Pt}}/\text{cm}^2$) catalysts before and after 10,000 potential cycling between 0.6 V and 1.0 V at a sweep rate of 50 mV/s. (b) RRDE peroxide yield for ORR along with (c) number of electron transferred during ORR. All curves were measured in O₂-purged 0.1 M KOH at a sweep rate of 10 mV/s at a rotation rate of 1600 rpm.

Figure 4. *In situ* XANES of (a) the Co K edge and (b) the Mn K edge of CoMnON/G in 0.1 M KOH at different potentials. Also shown are *ex situ* XANES spectra of (a) CoO, Co₃O₄, and LiCoO₂, and (b) MnO, Mn₃O₄, and MnO₂ for references. Fitted linear relationships between the oxidation states (ψ) and the half step energy values ($U_{1/2}$) of (c) Co K edge of various cobalt species and (d) Mn K edge of various manganese species. The insets show the Fourier-transformed EXAFS spectra at low R regions of (c) Co K edge from CoMnON/G and CoO and (d) Mn K edge of CoMnON/G and MnO.

Figures 4a and 4b show *in situ* X-ray absorption near-edge structure (XANES) spectra of (a) the Co K edge and (b) the Mn K edge from the CoMnON/G 550 °C catalyst measured in 0.1 M KOH at four different potentials. Neither spectrum from this electrocatalyst showed any discernible changes with an increase in potential over the range of 0.28-0.80 V, revealing that both atomic and electronic structures of Co and Mn remain unchanged over the potential range of the ORR. Only at the highest potential (1.05 V) did we observe a slight increase in the absorption edge energy, which is considered to be a consequence of the oxidation of both elements. Compared with CoMnO/G (Figure S5), CoMnON/G is clearly less potential dependent; the nitriding indeed contributes to the stability of CoMnON/G, which is one of the origins of enhanced ORR performance for this electrocatalyst. For example, as shown in Pourbaix diagrams,^[13] manganese exists as MnO at 0.28 V in a solution at pH 13; MnO is oxidized to Mn₃O₄ at 0.46 V and Mn₂O₃ at 0.69 V. However, no oxidation of Mn in CoMnON/G is observed up to 0.80 V. This suggests that nitrogen doping markedly inhibits the oxidation of the Mn phase. The cyclic voltammetry for CoMnON/G also exhibited the inhibition of surface oxidation up to 0.82 V, while that for CoMnO/G initiated oxide formation above 0.6 V (Figure S4d).

In order to determine the oxidation states of Co and Mn in the CoMnON catalyst, the half step energy values ($U_{1/2}$) of reference Co and Mn oxides (at 0.5 of the normalized absorption in XANES shown in Figures 4a and 4b) are plotted as a function of their valence states (ψ) to establish the linear correlations (Figures 4c and 4d). Accordingly, the valences of Co and Mn in the CoMnON catalyst at a potential of 0.28 V are determined to be 2.17 and 1.97, respectively, which are basically close to those of CoO and MnO.

The extended X-ray absorption fine structure (EXAFS) analysis revealed that the peaks of Co and Mn K edge spectra of the CoMnON catalyst at a low R-range are located at slightly higher R positions (1.75 Å and 1.77 Å, respectively) than those of CoO and MnO due to Co-O and Mn-O bonds (1.71 Å and 1.74 Å, respectively), as shown in the insets in Figure 4c and 4d (also see Figure S6). We consider that the increase in peak position is caused by nitrogen-doping in the oxide phases. The results are in line with the XRD observations (Figure 1).

The Fourier-transformed EXAFS spectra of the Co and Mn K edges between 2.0 Å and 3.3 Å from the CoMnON catalyst are very different from those from CoO and MnO

(Figure S6). The differences are caused by multiple-bonds of Co-Co and Co-Mn for Co, and Mn-Mn and Mn-Co for Mn in CoMnON, respectively, while CoO and MnO have only Co-

Co and Mn-Mn bonds, respectively. More interestingly, as shown in Figure 5, the Fourier-transformed EXAFS spectra of the Co and Mn K edges observed on the CoMnON 550°C catalyst are similar to each other. This indicates that the local atomic structure deduced from the Co K edge spectrum could be similar to that from the Mn K edge spectrum; the EXAFS analysis also supports the existence of an oxynitride phase that consists of homogeneously mixed nitrogen-doped CoO and MnO.

The XANES analysis revealed that CoMnON/G annealed at 550 °C shows a similar oxidation state of MnO. On the other hand, the Mn K-edge XANES from CoMnO/G is similar to that of a spinel compound of Mn₃O₄ (Figure S5b). It is known that the ORR activity of MnO is much lower than that of spinel Mn₃O₄ in alkaline media.^[14] Nevertheless, the activity of CoMnON/G becomes higher than that of CoMnO/G, suggesting that the presence of nitrogen-doped MnON may lead to the

Figure 5. Fourier-transformed EXAFS spectra of Co K edge and Mn K edge from CoMnON in 0.1 M KOH at a potential of 0.28 V.

enhancement of the ORR activity.

The nitriding temperatures are crucial for changing the electrochemical performance of these electrocatalysts. RDE measurements (Figure S7) were carried out to study the ORR activity of CoMnON/G as a function of nitriding temperature. The $E_{1/2}$ for the ORR increases when the nitriding temperature is raised up to 550 °C and then decreases significantly for the catalyst nitrided at 700 °C. The CoMnO catalyst before nitriding has the spinel structure of $\text{Co}_2\text{Mn}_1\text{O}_{4.5}$ and the basic structure appeared to remain similar at 300 °C. At 550 °C the structure transformed to the oxynitride phase of $\text{Co}_{2.1}\text{Mn}_1\text{O}_3\text{N}_{0.4}$, which showed the highest activity for the ORR. When the temperature is further increased to 700 °C, however, the oxynitride decomposed to the two separate phases of MnO (PDF#07-0230) and metallic Co (PDF#15-0806) as shown in the XRD (Figure S2). The existence of Co and MnO in the catalyst nitrided at 700°C was also identified by the XAS analysis (Figure S8). Metallic Co is known to have poor ORR activity.^[8e] This demonstrates that nitrogen-doped CoON is another constituent for the enhanced ORR activity of the system, which would be easily recognized by other studies showing that both Co_xN and CoO possess good ORR activity.^[7d, 8e] We envisage that the metal sites of Co–(O, N) and Mn–(O, N) are active sites for the ORR while the nitrogen incorporation increases their electrochemical performance markedly. Further investigation involving a theoretical study is needed to clarify possible changes in electronic configurations of the metals by nitrogen-doping as well as a synergistic interaction between CoON and MnON.

We also used carbon black (Vulcan XC72 (C)) as a carbon support to prepare CoMnO/C and CoMnON/C for comparison of their ORR performances with CoMnO/G and CoMnON/G (Figure S9). CoMnO/C and CoMnON/C showed lower activity than CoMnO/G and CoMnON/G, respectively. Recently we have shown that graphene supports enhanced catalytic activity and stability of non-precious-metal catalysts comprising some non-precious-metal nitrides.^[15] It has been suggested that electronic interaction between the metal d -orbital and the π -orbital of the underlying graphene may alter the charge-transfer rate, thereby leading to the enhancement of the catalytic activity.^[16]

Nitrogen-doped carbon materials could act as an effective metal-free electrocatalysts for the ORR.^[17] Nitrogen-doping into graphene by thermal annealing in a NH_3 -containing gas requires high temperatures above 800 °C at atmospheric pressure.^[18] Since the annealing temperatures for the nitriding in the present study were only up to 700 °C, we consider that nitrogen is not involved in the graphene supports for the CoMnON catalysts. Figure S10 shows TEM pictures of the CoMnON/G 550°C catalyst; the insets in the high resolution images show the fringes of graphene sheet supports with a (0 0 1) spacing of 0.67 nm, which is identical to that of graphite reported in the literature.^[19] It is known that nitrogen-doping to graphene leads to an increase in interlayer spacing by the intercalation of nitrogen atoms into its graphitic planes (for example, from 0.67 nm to 0.682 nm).^[17] Thus, the TEM observation in Figure S10 clearly demonstrates that nitrogen is not incorporated in the graphene supports for the CoMnON catalysts. Dai *et al* demonstrated that nitrogen-doped reduced graphene oxide sheets could enhance the ORR activity of spinel MnCo_2O_4 nanoparticles significantly.^[7d] As mentioned above, the $\text{Co}_x\text{N}/\text{NHCS}$ catalyst is the only carbon-doped non-precious-metal nitride that showed higher ORR activity than the present CoMnON/G catalyst (Table S1). The NHCS showed a reasonably high ORR activity as a

consequence of nitrogen-doping, and thus the high activity of the $\text{Co}_x\text{N}/\text{NHCS}$ catalyst originates in part from the support. These studies imply that the electrochemical performance of the present oxynitride nanoparticles could also be further improved by controlling the catalyst–support interaction using nitrogen-doped carbon supports.

The OER polarization curves of CoMnO, CoMnON, and RuO_2 in an O_2 -saturated 0.1 M KOH electrolyte are shown in Figure 6. Graphene supports were not used for these catalysts to avoid the activity loss caused by dissolution of carbon or partial oxidation of graphene at high potentials. The CoMnON catalyst gave a lower overpotential η (0.47 V at a current density of 10 mA/cm^2) for the OER than that of CoMnO ($\eta = 0.54$ V). (The value of 10 mA/cm^2 was chosen as the point of reference because under 1 Sun of AM 1.5 illumination, the solar photon flux produces a charge-carrier flux of 10–20 mA/cm^2 to a planar electrode surface using typical photovoltaic conditions.^[20]) RuO_2 is known to be the most active catalyst for the OER in both acids and bases.^[21] The present measurements demonstrate that both the onset potential and the η at 10 mA/cm^2 (0.34 V) for the OER of the RuO_2 catalyst are lower than those observed using the CoMnON and CoMnO catalysts. However, at higher current densities above 17 mA/cm^2 , the OER activity of RuO_2 becomes comparable to that of the CoMnON catalyst. These results again strengthen the case for nitrogen-doped modification of CoMnO, which can enhance the catalysts' electrochemical performance and enables CoMnON as an active bifunctional catalyst for both oxygen reduction and water oxidation. To the best of our knowledge, this is the first time that the OER activity of oxynitride catalysts has been reported. We note that the OER activities of other spinel compounds could also be considerably enhanced by nitrogen doping with concomitant phase transformation with similar nitriding treatments.^[22]

The stability of the CoMnO and CoMnON catalysts at high potentials was analyzed by 200 potential cycles between 0.9 V and 1.8 V at a scan rate of 10 mV/s (Figure S11). The high potential cycling reduced the initial OER activity by 35% at 1.75 V for both electrodes. The current loss may be attributed to oxide formation or dissolution at such high potentials, thereby blocking or loss of active sites, although the morphology of the CoMnON catalysts did not change much after the hash potential cycling test as shown in Figure S12. The comparison of activity and stability with other OER electrocatalysts under a benchmarking protocol with different conditions^[21] will be performed in the near future.

In conclusion, the results presented herein reveal that CoMnON is an active and stable bifunctional catalyst for both the ORR and OER. The nitrogen doping coupled with the phase

Figure 6. OER polarization curves for CoMnO, CoMnON, and RuO_2 catalysts in O_2 -purged 0.1 M KOH at a sweep rate of 10 mV/s. Loadings: 69 $\mu\text{g}_{\text{Co+Mn}}/\text{cm}^2$ for CoMnO and CoMnON, 50 $\mu\text{g}_{\text{Ru}}/\text{cm}^2$ for RuO_2 .

transformation is responsible for the enhancement of the electrochemical activity and stability. This approach further facilitates new opportunities to prepare non-precious-metal oxynitrides having high electrochemical performance by a properly designed nitriding treatment.

Experimental Section

Experimental details and additional data can be found in the Supporting Information.

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Keywords: oxynitride • spinel • nitriding • oxygen reduction • oxygen evolution

Notes and references

- [1] a) M. Mamlouk; K. Scott; J. A. Horsfall; C. Williams, *Int. J. Hydrogen Energ.* **2011**, 36, 7191-7198; b) T. Sakamoto; K. Asazawa; J. Sanabria-Chinchilla; U. Martinez; B. Halevi; P. Atanasov; P. Strasser; H. Tanaka, *J. Power Sources* **2014**, 247, 605-611.
- [2] K. B. Kokoh; E. Mayousse; T. W. Napporn; K. Servat; N. Guillet; E. Soyeze; A. Grosjean; A. Rakotondrainibe; J. Paul-Joseph, *Int. J. Hydrogen Energ.* **2014**, 39, 1924-1931.
- [3] a) A. A. Gewirth; M. S. Thorum, *Inorg. Chem.* **2010**, 49, 3557-66; b) A. Ramirez; P. Bogdanoff; D. Friedrich; S. Fiechter, *Nano Energy* **2012**, 1, 282-289; c) C. X. Zhao; H. T. Yu; Y. C. Li; X. H. Li; L. Ding; L. Z. Fan, *J. Electroanal. Chem.* **2013**, 688, 269-274.
- [4] a) H. A. Gasteiger; S. S. Kocha; B. Sompalli; F. T. Wagner, *Appl. Catal. B-Environ.* **2005**, 56, 9-35; b) M. K. Debe, *Nature* **2012**, 486, 43-51.
- [5] Y. Lee; J. Suntivich; K. J. May; E. E. Perry; Y. Shao-Horn, *J. Phys. Chem. Lett.* **2012**, 3, 399-404.
- [6] a) L. Dai; Y. Xue; L. Qu; H.-J. Choi; J.-B. Baek, *Chem. Rev.* **2015**, 115, 4823-4892; b) Y. Nie; L. Li; Z. Wei, *Chem. Soc. Rev.* **2015**, 44, 2168-2201; c) X. Ge; A. Sumboja; D. Wu; T. An; B. Li; F. W. T. Goh; T. S. A. Hor; Y. Zong; Z. Liu, *ACS Catal.* **2015**, 5, 4643-4667.
- [7] a) A. C. Queiroz; F. H. B. Lima, *J. Electroanal. Chem.* **2013**, 707, 142-150; b) N. C. Cheng; R. Kutz; C. Kemna; A. Wieckowski, *J. Electroanal. Chem.* **2013**, 705, 8-12; c) Y. Y. Liang; Y. G. Li; H. L. Wang; J. G. Zhou; J. Wang; T. Regier; H. J. Dai, **2011**, 10, 780-786; d) Y. Liang; H. Wang; P. Dia; W. Chang; G. Hong; Y. Li; M. Gong; L. Xie; J. Zhou; J. Wang; T. Z. Regier; F. Wei; H. Dai, *J. Am. Chem. Soc.* **2012**, 134, 15849-15857.
- [8] a) F. Charreter; F. Jaouen; S. Ruggeri; J. P. Dodelet, *Electrochim. Acta* **2008**, 53, 2925-2938; b) D. J. Ham; J. S. Lee, *Energies* **2009**, 2, 873-899; c) Y. Wu; Q. Shi; Y. Li; Z. Lai; H. Yu; H. Wang; F. Peng, *J. Mater. Chem. A* **2015**, 3, 1142-1151; d) T. Sun; Q. Wu; R. Che; Y. Bu; Y. Jiang; Y. Li; L. Yang; X. Wang; Z. Hu, *ACS Catal.* **2015**, 5, 1857-1862; e) X. Zhong; L. Liu; Y. Jiang; X. Wang; L. Wang; G. Zhuang; X. Li; D. Mei; J.-g. Wang; D. S. Su, *ChemCatChem* **2015**, 7, 1826-1832; f) K. Zhang; L. Zhang; X. Chen; X. He; X. Wang; S. Dong; P. Han; C. Zhang; Shan Wang; L. Gu; G. Cui, *J. Phys. Chem. C* **2013**, 117, 858-865.
- [9] a) G. Wu; K. L. More; C. M. Johnston; P. Zelenay, *Science* **2011**, 332, 443-7; b) K. Strickland; E. Miner; Q. Jia; U. Tylus; N. Ramaswamy; W. Liang; M.-T. Sougrati; F. d. r. Jaouen; S. Mukerjee, *Nat. Commun.* **2015**, 6, 7343.
- [10] a) M. Chisaka; A. Ishihara; K. Ota; H. Muramoto, *Electrochim. Acta* **2013**, 113, 735-740; b) E. Rios; S. Abarca; P. Daccaretti; H. N. Cong; D. Martel; J. F. Marco; J. R. Gancedo; J. L. Gautier, *Int. J. Hydrogen Energ.* **2008**, 33, 4945-4954.
- [11] a) X. Cao; C. Jin; F. Lu; Z. Yang; M. Shen; R. Yanga, *J. Electrochem. Soc.* **2014**, 161, H296-H300; b) Y. Zhang; J. Rosen; G. S. Hutchings; F. Jiao, *Catal. Today* **2014**, 225, 171-176; c) F. Y. Cheng; J. A. Shen; B. Peng; Y. D. Pan; Z. L. Tao; J. Chen, *Nat. Chem.* **2011**, 3, 79-84.
- [12] a) B. F. Cao; G. M. Veith; R. E. Diaz; J. Liu; E. A. Stach; R. R. Adzic; P. G. Khalifah, *Angew. Chem. Int. Ed.* **2013**, 52, 10753-10757; b) Z. Xia; L. An; P. Chen; D. Xia, *Adv. Energy Mater.* **2016**, 6, 1600458, DOI: 10.1002/aenm.201600458; c) A. Miura; C. Rosero-Navarro; Y. Masubuchi; M. Higuchi; Shinichi Kikkawa; K. Tadanaga, *Angew. Chem. Int. Ed.* **2016**, 55, 7963-7967; d) L. An; W. Huang; N. Zhang; X. Chenc; D. Xia, *J. Mater. Chem. A* **2014**, 2, 62-65.
- [13] M. Pourbaix, in *Atlas of Electrochemical Equilibria in Aqueous Solutions*. CEBELCOR: Oxford: Brussels, 1966; p pp330-342, pp373-377.
- [14] F. H. B. Lima; M. L. Calegaro; E. A. Ticianelli, *J. Electroanal. Chem.* **2006**, 590, 152-160.
- [15] a) W.-F. Chen; S. Iyer; S. Iyer; K. Sasaki; C.-H. Wang; Y. Zhu; J. T. Muckerman; E. Fujita, *Energ. Environ. Sci.* **2013**, 6, 1818-1826; b) W.-F. Chen; J. M. Schneider; K. Sasaki; C.-H. Wang; J. Schneider; S. Iyer; S. Iyer; Y. Zhu; J. T. Muckerman; E. Fujita, *ChemSusChem* **2014**, 7, 2414-2418.
- [16] C. Gong; G. Lee; B. Shan; E. M. Vogel; R. M. Wallace; K. Cho, *J. Appl. Phys.* **2010**, 108, 123711-123718.
- [17] L. Qu; Y. Liu; J.-B. Baek; L. Dai, *ACS Nano* **2010**, 4, 1321-1326.
- [18] a) D. Geng; Y. Chen; Y. Chen; Y. Li; R. Li; X. Sun; S. Yeb; S. Knights, *Energy Environ. Sci.* **2011**, 4, 760-764; b) Q. Wei; X. Tong; G. Zhang; J. Qiao; Q. Gong; S. Sun, *Catalysts* **2015**, 5, 1574-1602; doi:10.3390/catal5031574.
- [19] Y. Gogotsi; J. A. Libera; N. Kalashnikov; M. Yoshimura, *Science* **2000**, 290, 317-320.
- [20] M. G. Walter; E. L. Warren; J. R. McKone; S. W. Boettcher; Q. X. Mi; E. A. Santori; N. S. Lewis, *Chem. Rev.* **2010**, 110, 6446-6473.
- [21] C. C. L. McCrory; S. Jung; F. I. M.; S. M. Chatman; J. C. Peter; T. F. Jaramillo, *J. Am. Chem. Soc.* **2015**, 137, 4347-4357.
- [22] F. Meng; K. A. Kuttivel; K. Sasaki; J. T. Muckerman, E. Fujita, in preparation.
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A nitriding treatment to generate graphene-supported cobalt manganese oxynitride nanocatalysts (CoMnON/G) from spinel compound CoMnO, increases the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) activities considerably. The most active material catalyzes the ORR with only a 30 mV half-wave potential difference from the commercial carbon-supported platinum (Pt/C) in alkaline media. The catalyst also exhibits intrinsic stability that outperforms Pt/C.

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