## Supporting Information for "Enhancement of the Oxygen Evolution Reaction in Mn<sup>3+</sup>-based Electrocatalysts: Correlation between Jahn-Teller Distortion and Catalytic Activity"

Shigeto Hirai,\*a Yagi Shunsuke,<sup>b</sup> Akihiro Seno,<sup>b</sup> Masaya Fujioka,<sup>c</sup> Tomoya Ohno<sup>a</sup> and Takeshi Matsuda<sup>a</sup>

<sup>a</sup> Department of Materials Science and Engineering, Kitami Institute of Technology, 165
Koen-cho, Kitami 090-8507, Japan

<sup>b</sup> Nanoscience and Nanotechnology Research Centre, Osaka Prefecture University, Osaka 599-8570, Japan

 <sup>c</sup> Laboratory of Nano-Structure Physics, Research Institute for Electronic Science, Hokkaido University, Sapporo 001-0021, Japan

Corresponding Author:

\* hirai@mail.kitami-it.ac.jp

The variation of lattice parameters with composition in the  $Mn_{3-x}Co_xO_4$  (x = 0, 0.3, 0.6, 0.9, 1.2, 1.5) samples is shown in Fig. S3. The *a*-axis length remains almost constant, whereas the reduction in *c*-axis length is accelerated where  $0 \le x < 1$ . The cell volume and the indicator of Jahn-Teller distortion ( $c/\sqrt{2}a$ ) follow the trend of the *c*-axis length. Since the tetrahedral site remains undistorted, the value of the Jahn-Teller distortion indicator reflects the Mn<sup>3+</sup>O<sub>6</sub> octahedral distortion. Although the octahedral site of Mn<sub>3</sub>.  $_xCo_xO_4$  (x = 0, 0.3, 0.6, 0.9) remains occupied only by the Mn<sup>3+</sup> ions, the tetrahedral site contracts due to the replacement of Mn<sup>2+</sup> (ionic radius = 0.066 nm)<sup>S1</sup> by a smaller Co<sup>2+</sup> (ionic radius = 0.058 nm),<sup>S1</sup> and thereby the octahedral site undergoes an anisotropic contraction (the two longer Mn<sup>3+</sup>-O bonds are softer and therefore contract more than the four shorter Mn<sup>3+</sup>-O bonds).

We have determined the value of *x* in Mn<sub>3-*x*</sub>Co<sub>*x*</sub>O<sub>4</sub> on the basis of lattice constants. In this study, we focused on the Jahn-Teller distortion indicator:  $c/\sqrt{2a}$  which decreases with the increase of the Co content. Since the precise values of lattice constant *a* and *c* were obtained by Rietveld refinement for Mn<sub>3-*x*</sub>Co<sub>*x*</sub>O<sub>4</sub> samples ( $0 \le x \le 1.5$ ), the values of  $c/\sqrt{2a}$  were plotted towards the *x* (calculated using the initial molar ratio in the starting material) in addition to those obtained by neutron diffraction studies in Bordeneuve et al.<sup>17</sup> (Fig. S3(d)). Our values of  $c/\sqrt{2a}$  are consistent with those of Bordeneuve et al.<sup>17</sup>. Therefore, we describe the synthesized samples using the initial molar ratio of 3-x/x(Mn/Co).

We chose the scan rate of 10 mV/s for the RRDE measurements referring to the scan rate of Grimaud et al.<sup>S2</sup>. As a test of scan rate dependence, we measured the OER activity of  $Mn_{2.1}Co_{0.9}O_4$  at different scan rates (= 10, 20, 50, 100, 200, 500 and 1000 mV/s). Fig. S4(e) shows variation of the specific OER activity at 1.76 V vs. RHE towards

the scan rate. The OER activity remains almost constant for these scan rates, implying that the oxygen evolution reaction (OER) is not a diffusion controlled process. We understand this in the following way. The OH- consumed by the oxygen evolution reaction (OER) is immediately provided by the autodissociation of water, which is abundant in the KOH aqueous solution as the solvent. This situation is maintained regardless of the scan rate. For these reasons, our results are legitimate at the scan rate of 10 mV/s.

The prepared  $Mn_{3-x}Co_xO_4$  (x = 0, 0.3, 0.6, 0.9) samples exhibited comparable Brunauer, Emmett, and Teller (BET) surface areas of 60 m<sup>2</sup>/g (x = 0), 70 m<sup>2</sup>/g (x = 0.3), 65 m<sup>2</sup>/g (x = 0.6), and 74 m<sup>2</sup>/g (x = 0.9). This result suggests that Co-substituted samples have slightly larger surface areas than the Co-free sample, yet no correlation between Co content and surface area was observed for the Co-substituted samples. **Fig. S1**: Fitted powder X-ray diffraction profiles of  $Mn_{3-x}Co_xO_4$  nanoparticles for (a) x = 0, (b) x = 0.3, (c) x = 0.6, (d) x = 0.9, (e) x = 1.2, and (f) x = 1.5. The green open circles are the experimental XRD intensities. The red curve is the calculated XRD intensity, and the blue curve is the mismatch between experimental and calculated XRD intensities. The black tick marks indicate the calculated Bragg peak positions.

(a)



(b)



(c)







(f)



**Fig.S2**: (a) Variation in Co concentration on the A and B sites for  $Mn_{3-x}Co_xO_4$ . (b) Variation in electrical conductivity for  $Mn_{3-x}Co_xO_4$ . These results are taken from the neutron diffraction studies of Bordeneuve et al.<sup>17</sup>.



(b)



**Fig.S3**: Variations of the tetragonal lattice parameter (a) a, (b) c, (c) unit cell volume (V), and (d)  $c/\sqrt{2a}$  (an indicator of Jahn-Teller distortion in the Mn<sup>3+</sup>O<sub>6</sub> octahedra) for Mn<sub>3-</sub> <sub>x</sub>Co<sub>x</sub>O<sub>4</sub> nanoparticles of this study (x = 0, 0.3, 0.6, 0.9, 1.2, 1.5) with the data taken from the neutron diffraction studies of Bordeneuve et al. <sup>17</sup>. The squares denote the data of this study, and the open squares denote the data of Bordeneuve et al. <sup>17</sup>. Standard deviation for the data is reflected by the point size.









(d)



**Fig.S4**: (a) The specific OER activities (cycles 1-10) of  $Mn_{3-x}Co_xO_4$  (x = 0, 0.3, 0.6, 0.9) at -1.76 V vs. RHE. (b) Variation of the overpotentials (cycles 1-10) for  $Mn_{3-x}Co_xO_4$  (x = 0, 0.3, 0.6, 0.9). The overpotential ( $\eta$ ) was determined from the onset potential ( $E_{onset}$ ) at 0.5 mA/cm<sup>2</sup><sub>disk</sub> by  $\eta = E_{onset} - 1.23$  V. (c) The OER specific activities (cycles 1-10) of  $Mn_{3-x}Co_xO_4$  (x = 0, 0.3, 0.6, 0.9) at 1.76 V vs. RHE divided by the normalized BET surface area  $s_x = S_x/S_0$ .  $S_x$  and  $S_0$  denote the BET surface area of  $Mn_{3-x}Co_xO_4$  and  $Mn_3O_4$ , respectively. (d) Variation of the OER specific activities (cycles 1-10) divided by the normalized BET surface area  $s_x$  for  $Mn_{3-x}Co_xO_4$  (x = 0, 0.3, 0.6, 0.9) against the Jahn-Teller distortion indicator,  $c/\sqrt{2a}$ . (e) Variation of the Specific OER activities (cycles 1-10) of  $Mn_{2.1}Co_{0.9}O_4$  towards the scan rate of the RRDE measurements. The horizontal axis in logarithmic scale is guide for the eye.





**Fig.S5**: (a) Specific OER activities of  $Mn_{3-x}Co_xO_4$  (x = 0-1.5) at 1.76 V vs. RHE. (b) Variation of Tafel slopes for  $Mn_{3-x}Co_xO_4$  (x = 0-1.5). (c) Variation of the overpotentials (cycles 1-10) for  $Mn_{3-x}Co_xO_4$  (x = 0-1.5). (a)



**Fig.S6**: Linear sweep voltammetry curves of the OER (cycles 10 and 100) for  $Mn_{2.1}Co_{0.9}O_4$  and  $Co_3O_4$  in aqueous 0.10 M KOH solution at 10 mV/s. The OER activity of  $Mn_{2.1}Co_{0.9}O_4$  is compared per unit mass with the highly OER active  $Co_3O_4$  to demonstrate its OER performance.<sup>S3</sup>



## **References:**

(S1) R. D. Shannon, Acta Cryst., 1976, A32, 751.

(S2) A. Grimaud, K. J. May, C. E. Carlton, Y. L. Lee, M. Risch, W. T. Hong, J. Zhou and Y. Shao-Horn, *Nature Commun.*, 2013, 4, 2439.

(S3) I. Nikolov, R. Darkaoui, E. Zhecheva, R. Stoyanova, N. Dimitrov and T. Vitanov,

J. Electroanal. Chem., 1997, 429, 157.