Electrocatalytic Activity of Tetravalent Fe–Co Mixed Oxide for Oxygen and Hydrogen Evolution Reactions

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Electrochemical water splitting is a useful way for sustainable hydrogen production, whereas sluggish kinetics of oxygen/hydrogen evolution reactions (OER/HER) limits the efficiency; thus, active electrocatalysts to reduce overpotentials are desired. Mixing of multiple transition-metal elements is a promising way to enhance electrochemical catalysis. In the present study, we investigated the OER and HER catalytic activities of tetravalent Fe–Co mixed perovskite oxide $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$. $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ demonstrated a higher OER activity than those of the parent compounds CaFeO_3 and CaCoO_3 . In contrast, the HER activity of $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ was not significantly enhanced. These observations suggest that the mixing of Fe^{4+} and Co^{4+} ions is an efficient way to activate OER. [doi:10.2320/matertrans.MT-MN2019032]

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1. Introduction

Electrochemical water splitting is a useful method for sustainable hydrogen production,¹⁾ although sluggish kinetics of oxygen/hydrogen evolution reactions (OER/HER) disturbs efficient energy conversions.^{2,3)} Fundamental understanding of the mechanism of OER/HER is necessary to develop efficient catalysts. Platinum-group metals and their oxides (e.g. Pt, IrO_2 , RuO_2) have been widely utilized as practical catalysts for OER and HER to suppress intrinsic large overpotentials and resulting energy loss.^{4–6)} On the other hand, transition-metal oxides have been extensively investigated because of their earth abundance and low cost.⁷⁾ Exploration of novel catalysts for OER and HER has been eagerly conducted among perovskite oxide family (ABO_3), some of which display high catalytic activity.^{8–10)}

Mixing of multiple transition-metal elements is a promising way to enhance catalytic activity, which is considered as a synergistic effect between mixed elements. For example, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSCF) is proposed as a highly active OER catalyst⁸⁾ and further mixing of multiple transition metals enhances stability.¹⁰⁾ However, the origin of the synergistic effect has not been elucidated well because of complex chemical compositions and crystal structures including substantial amount of oxygen deficiency.¹¹⁾ Suntivich *et al.* also proposed electron occupancy in the e_g orbital of the transition metal ion at *B* site in the perovskite structure can be a simple descriptor; the catalytic activity of BSCF ($e_g \sim 1.2$) locates at the top of the volcano-like plot as a function of e_g electron number.⁸⁾ On the other hand, it has been recently suggested that the oxygen deficiencies in the perovskite-related phases also play an important role in promoting OER.⁹⁾ A brownmillerite oxide $\text{Ca}_2\text{FeCoO}_5$ consisting of randomly mixed Fe and Co ions displays a high catalytic activity for OER,^{12–14)} implying that tetrahedral ($\text{Fe}^{3+}/\text{Co}^{3+}$) O_4 and octahedral ($\text{Fe}^{3+}/\text{Co}^{3+}$) O_6 units affect

catalytic activity for OER in addition to the mixing of Fe^{3+} and Co^{3+} ions. It is expected that the mixing of intrinsically active ions such as Fe^{4+} and Co^{4+} further improves the electrochemical catalysis of perovskite oxides for OER,¹⁵⁾ but detailed study has not been conducted yet because of the difficulty in synthesis of high-valent metal oxides under ambient conditions. In the present study, we synthesized CaBO_3 ($B = \text{Fe}, \text{Co}, \text{and } \text{Fe}_{0.5}\text{Co}_{0.5}$) under high-pressure and high-temperature conditions at 8 GPa and 1373 K to examine the coexistence effects of randomly mixed Fe^{4+} and Co^{4+} ions on OER and HER catalysts. The OER catalytic activity was significantly improved by mixing Fe^{4+} and Co^{4+} ions in $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ whereas a smaller enhancement was observed for HER. This finding proposes the mixing of high-valent Fe^{4+} and Co^{4+} ions is a useful way for activating OER rather than HER.

2. Experimental Procedure

The powder sample of $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ was synthesized from its stoichiometric mixture, which was prepared by complex polymerized method in advance.¹⁶⁾ High-pressure and high-temperature treatment (8 GPa and 1373 K) with an oxidizing agent KClO_4 was utilized to stabilize Fe^{4+} and Co^{4+} valence states for CaBO_3 ($B = \text{Fe}, \text{Co}, \text{and } \text{Fe}_{0.5}\text{Co}_{0.5}$) without oxygen deficiency. X-ray powder diffraction patterns at room temperature were collected using a X-ray diffractometer with Cu $\text{K}\alpha$ radiation (Ultima IV, Rigaku, Japan). Specific surface area was estimated by the Brunauer-Emmett-Teller (BET) analysis of Kr gas adsorption data. Specific surface area was determined by BET analysis of Kr-gas absorption data. Oxidation states of the constituent transition metal ions were determined by iodometric titration with Hiranuma automatic titrator (COM-1700A, Hiranuma, Japan).

OER catalytic activity was evaluated by using rotating disk electrode system (RRDE-3A, BAS, Japan) in the same manner as the previous studies.^{15,17,18)} Electrochemical

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Fig. 1 Observed XRD pattern of $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ and the Rietveld refinement result. The circles and solid lines represent observed and calculated patterns, respectively. The difference between the observed and calculated patterns is shown at the bottom. The vertical marks indicate the Bragg reflection positions.

measurements were conducted in 1 M KOH solution under O_2 saturation (for OER) and N_2 saturation (for HER) at room temperature.

3. Results and Discussions

Figure 1 shows the XRD pattern and Rietveld refinement result of $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$. All the Bragg reflection peaks were indexed with the GdFeO_3 -type orthorhombic perovskite structure with the space group of $Pnma$ (No. 62). Based on the refinement, the lattice constants were determined to be $a = 5.3106(5) \text{ \AA}$, $b = 7.4850(7) \text{ \AA}$, $c = 5.2921(5) \text{ \AA}$. The calculated unit cell volume ($210.36(3) \text{ \AA}^3$) for $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ was an intermediate value between CaFeO_3 ($214.97 \text{ \AA}^3$) and CaCoO_3 ($207.65 \text{ \AA}^3$), confirming that the obtained oxide is the 1:1 solid solution of CaFeO_3 and CaCoO_3 .^{19,20} $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ probably consists of Fe^{4+} ($t_{2g}^3e_g^1$ configuration) and Co^{4+} ($t_{2g}^4e_g^1$ configuration) ions as well as the parent compounds.^{19,20} Since there was no sign of additional peaks attributed to atomic ordering, Fe and Co ions are distributed randomly at the same crystallographic sites. Oxygen content for $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ was determined to be about 2.98 by iodometric titration, confirming the tetravalency of the transition metals.

Figure 2 shows linear sweep voltammograms in OER conditions for CaBO_3 ($B = \text{Fe}, \text{Co}, \text{and Fe}_{0.5}\text{Co}_{0.5}$). Current densities per surface area of oxides (in a unit of $\text{mA cm}^{-2}_{\text{oxide}}$) were adopted to evaluate the intrinsic catalytic activities. The OER onset potentials (E_{OER}) were determined using the potentials reaching 1 mA cm^{-2} , and OER overpotentials (η_{OER}) were calculated as follows: $\eta_{\text{OER}} = E_{\text{OER}} - 1.23 \text{ V}$. The overpotential of CaFeO_3 ($\eta_{\text{OER}} = 0.39 \text{ V}$) for OER was superior to that of CaCoO_3 ($\eta_{\text{OER}} = 0.47 \text{ V}$) as well as the previous study measured in 0.1 M KOH conditions.¹⁸ $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ exhibited a lower overpotential ($\eta_{\text{OER}} = 0.31 \text{ V}$) than both CaFeO_3 and CaCoO_3 , clearly indicating a significant Fe^{4+} – Co^{4+} mixing effect on OER activity. It is notable that the present result cannot be explained by other descriptors such as e_g electron configuration and oxygen deficiency because the e_g electron for $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ is

Fig. 2 Linear sweep voltammograms in OER conditions for CaBO_3 ($B = \text{Fe}, \text{Co}, \text{and Fe}_{0.5}\text{Co}_{0.5}$). The disk potential was controlled between 0.3 and 0.9 V versus Hg/HgO at a scan rate of 10 mV s^{-1} and the disk rotation rate was set at 1600 rpm.

Fig. 3 Linear sweep voltammograms in HER conditions for CaBO_3 ($B = \text{Fe}, \text{Co}, \text{and Fe}_{0.5}\text{Co}_{0.5}$). The disk potential was controlled between -0.9 and -1.5 V versus Hg/HgO at a scan rate of 10 mV s^{-1} and the disk rotation rate was set at 1600 rpm.

retained in the mixture of Fe^{4+} ($t_{2g}^3e_g^1$) and Co^{4+} ($t_{2g}^4e_g^1$) with identical e_g electron number.

Figure 3 shows linear sweep voltammograms in HER conditions for CaBO_3 ($B = \text{Fe}, \text{Co}, \text{and Fe}_{0.5}\text{Co}_{0.5}$). HER overpotentials (η_{HER}) were determined based on the absolute values of the onset potentials reaching at -1 mA cm^{-2} (E_{HER} ; $\eta_{\text{HER}} = |E_{\text{HER}}|$), as well as η_{OER} . The HER overpotential of CaCoO_3 for HER ($\eta_{\text{HER}} = 0.26 \text{ V}$) was lower than that of CaFeO_3 ($\eta_{\text{HER}} = 0.35 \text{ V}$) in contrast to OER overpotentials. The disagreement between OER and HER activity implies that the descriptors for each reaction are different. Since systematic trend in HER activity for perovskite oxides has not been elucidated yet, we do not focus on the detailed HER mechanism in this study. $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ exhibited a lower overpotential ($\eta_{\text{HER}} = 0.22 \text{ V}$) than CaFeO_3 , but almost the same as CaCoO_3 . This is apparent from the result that both the voltammograms of $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ and CaCoO_3 are

almost overlapping. These observations indicate that the synergistic effect of the Fe^{4+} – Co^{4+} mixing is subtle on HER activity in contrast to the significant increase in the OER activity of $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$.

4. Conclusion

We successfully synthesized the Fe^{4+} – Co^{4+} mixed oxide $\text{CaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ using a high-pressure synthesis method, exhibiting that the OER catalytic activity is significantly improved by mixing Fe^{4+} and Co^{4+} ions. This work first demonstrated the synergistic effect between Fe^{4+} and Co^{4+} on the OER activity. In contrast, the HER activity was slightly enhanced by Fe^{4+} – Co^{4+} mixing. This finding suggests a simple and new design principle to enhance the OER catalysis rather than HER catalysis.

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REFERENCES

- 1) M. Carmo, D.L. Fritz, J. Mergel and D. Stolten: *Int. J. Hydrogen Energ.* **38** (2013) 4901–4934.
- 2) W.T. Hong, M. Risch, K.A. Stoerzinger, A. Grimaud, J. Suntivich and Y. Shao-Horn: *Energy Environ. Sci.* **8** (2015) 1404–1427.
- 3) R. Subbaraman, D. Tripkovic, D. Strmcnik, K.C. Chang, M. Uchimura, A.P. Paulikas, V. Stamenkovic and N.M. Markovic: *Science* **334** (2011) 1256–1260.
- 4) R.R. Rao *et al.*: *Energy Environ. Sci.* **10** (2017) 2626–2637.
- 5) Y. Lee, J. Suntivich, K.J. May, E.E. Perry and Y. Shao-Horn: *J. Phys. Chem. Lett.* **3** (2012) 399–404.
- 6) S. Trasatti: *Electrochim. Acta* **29** (1984) 1503–1512.
- 7) A.A. El-Moneim, N. Kumagai and K. Hashimoto: *Mater. Trans.* **50** (2009) 1969–1977.
- 8) J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough and Y. Shao-Horn: *Science* **334** (2011) 1383–1385.
- 9) K.J. May, C.E. Carlton, K.A. Stoerzinger, M. Risch, J. Suntivich, Y.L. Lee, A. Grimaud and Y. Shao-Horn: *J. Phys. Chem. Lett.* **3** (2012) 3264–3270.
- 10) Y. Zhu, W. Zhou, Z.G. Chen, Y. Chen, C. Su, M.O. Tadé and Z. Shao: *Angew. Chem. Int. Ed.* **54** (2015) 3897–3901.
- 11) I. Yamada, T. Odake, K. Asai, K. Oka, S. Kawaguchi, K. Wada and S. Yagi: *Mater. Chem. Front.* **3** (2019) 1209–1217.
- 12) E. Tsuji, T. Motohashi, H. Noda, D. Kowalski, Y. Aoki, H. Tanida, J. Niikura, Y. Koyama, M. Mori, H. Arai, T. Ioroi, N. Fujiwara, Y. Uchimoto, Z. Ogumi and H. Habazaki: *ChemSusChem* **10** (2017) 2864–2868.
- 13) K. Nakayama, R. Ishikawa, A. Kuwabara, S. Kobayashi, T. Motohashi, N. Shibata and Y. Ikuhara: *Inorg. Chem.* **58** (2019) 10209–10216.
- 14) D. Kowalski, H. Kiuchi, T. Motohashi, Y. Aoki and H. Habazaki: *ACS Appl. Mater.* **11** (2019) 28823–28829.
- 15) I. Yamada, A. Takamatsu, K. Asai, T. Shirakawa, H. Ohzuku, A. Seno, T. Uchimura, H. Fujii, S. Kawaguchi, K. Wada, H. Ikeno and S. Yagi: *J. Phys. Chem. C* **122** (2018) 27885–27892.
- 16) M. Kakihana: *J. Sol-Gel Sci. Technol.* **6** (1996) 7–55.
- 17) S. Yagi, I. Yamada, H. Tsukasaki, A. Seno, M. Murakami, H. Fujii, H. Chen, N. Umezawa, H. Abe, N. Nishiyama and S. Mori: *Nat. Commun.* **6** (2015) 8249.
- 18) I. Yamada, A. Takamatsu, K. Asai, H. Ohzuku, T. Shirakawa, T. Uchimura, S. Kawaguchi, H. Tsukasaki, S. Mori, K. Wada, H. Ikeno and S. Yagi: *ACS Appl. Energy Mater.* **1** (2018) 3711–3721.
- 19) P.M. Woodward, D.E. Cox, E. Moshopoulou, A.W. Sleight and S. Morimoto: *Phys. Rev. B* **62** (2000) 844–855.
- 20) T. Osaka, H. Takahashi, H. Sagayama, Y. Yamasaki and S. Ishiwata: *Phys. Rev. B* **95** (2017) 224440.