

Remarkable catalytic activity of brownmillerite-type $\text{Ca}_2\text{FeCoO}_5$ for oxygen evolution reaction of water splitting

Etsushi Tsuji,^{a,b} Ryosuke Nanbu,^a Yoshiki Degami,^a Kei Hirao,^a Teruki Motohashi,^{b,c} Yoshitaka Aoki,^b Hiroki Habazaki,^b Satoshi Suganuma^a and Naonobu Katada^a

^a Department of Chemistry and Biotechnology, Tottori University, Tottori, 680-8552, Japan

^b Division of Applied Chemistry, Hokkaido University, Sapporo, 060-8628, Japan

^c Department of Materials and Life Chemistry, Kanagawa University, Yokohama, 221-8686, Japan

*Corresponding author: Fax number +81-857-31-5257, E-mail address e-tsuji@chem.tottori-u.ac.jp

Abstract: The oxygen evolution reaction (OER) activity of brownmillerite (BM)-type $\text{Ca}_2\text{FeCoO}_5$ is beyond those of the perovskite (PV)-type $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and a precious-metal RuO_2 . The combination of tetrahedral/octahedral-sites in the BM structure plays a crucial role. In addition, the $\text{Ca}_2\text{Fe}_{2-x}\text{Co}_x\text{O}_5$ ultrafine particles with nano-metric dimension can be synthesized by reverse micelle (RM) method on TiO_2 nanoparticles. These facts make this oxide a promising OER electrocatalyst or cocatalyst used in energy conversion technologies such as hydrogen production from electrochemical/photocatalytic water splitting.

Keywords: brownmillerite, oxygen evolution reaction, ultrafine particles

1. Introduction

The increasing demand of hydrogen fuel production has promoted the development of effective OER catalysts used for electrochemical/photocatalytic water splitting. Although noble metal oxides such as RuO_2 and IrO_2 show relatively high catalytic activity for OER, the lack of precious metals prohibits their large-scale uses. Therefore, it is necessary to develop transition metal oxide catalysts such as PV-type oxides for OER. Suntivich et al. have proposed that the OER activity is high when the e_g electron number is close to unity¹. Based on this strategy, they found high OER activity in a cobalt/iron oxide BSCF. On the other hand, it has been suggested that the oxygen deficiencies also plays an important role in promoting OER². Therefore, in this study, we focused on BM-type $\text{Ca}_2\text{FeCoO}_5$, which is oxygen-deficient PV-type oxides (Figure 1a), for OER catalysts³.

2. Experimental

The $\text{Ca}_2\text{Fe}_{2-x}\text{Co}_x\text{O}_5$ ($0 \leq x \leq 1.0$) samples were synthesized by a solid-state reaction at 1100°C (CFCO_S1100) and by a wet-chemical reaction at 800°C (CFCO_W800) for electrochemical water splitting, or by a reverse micelle method with TiO_2 nanoparticles at 600°C (CFCO/ TiO_2 _RM600) as an OER cocatalyst for photocatalytic water splitting.

Electrochemical measurements were carried out using a conventional three electrode system. The catalyst ethanol ink ($\text{Ca}_2\text{Fe}_{2-x}\text{Co}_x\text{O}_5$: acetylene black: Nafion = 5: 1: 1) was dropped and dried on a glassy carbon electrode as a working electrode. A Pt plate and a Hg/HgO electrode were used as a counter and a reference electrode. 4 mol dm^{-3} KOH aqueous solution was used as an electrolyte. The crystallinity, morphology, particle size and chemical composition of them were characterized by XRD, XANES, SEM, TEM and EDS.

3. Results and discussion

All samples showed XRD patterns of BM-type $\text{Ca}_2\text{Fe}_{2-x}\text{Co}_x\text{O}_5$. The OER activity of CFCO_S1100 and W800 are compared with those of PV-type LFCO and BSCF, and RuO_2 as reference catalysts (Figure 1b). The OER current density of CFCO_S1100 and W800 is an order of magnitude larger than those of the reference catalysts at 1.60 V vs RHE. Also noticeably, the onset potential of OER clearly shifts to a negative direction, suggesting that the catalytic activity for OER of BM-type $\text{Ca}_2\text{FeCoO}_5$ is much higher than those of

the reference catalysts. To gain deeper insight into the role of Fe/Co in the OER activity, the BM-type $\text{Ca}_2\text{Fe}_{2-x}\text{Co}_x\text{O}_5$ was synthesized and characterized in the range of $0 \leq x \leq 1.0$. The overpotential for OER linearly decreases up to $x = 0.50$ and tends to be constant at $x = 0.50$. In addition, the magnitude of OER current systematically increases at $x \geq 0.50$. On the other hand, the relative intensity of the pre-edge peak of Fe K-edge XANES spectra of the $\text{Ca}_2\text{Fe}_{2-x}\text{Co}_x\text{O}_5$ samples attributable to tetrahedral (*Td*)-Fe is nearly constant for cobalt contents up to $x = 0.50$, and then starts to decrease upon further substitution. This implies that cobalt preferentially substitutes iron in the octahedral (*Oh*) layer for small substitution levels, and then in the *Td* layer at $x \geq 0.50$. Taking into account the experimental fact that the *Oh*- and *Td*-Co sites are likely to play distinct roles in the enhanced OER activity, i.e. the former mainly lowers the overpotential, and the latter enhances the OER current.

The particle size of CFCO_S1100 and W800 was more than several dozen nanometers. On the other hand, in the case of CFCO/TiO₂_RM600, spherical $\text{Ca}_2\text{FeCoO}_5$ ultrafine particles were loaded on the TiO₂ nanoparticles and the particle size of $\text{Ca}_2\text{FeCoO}_5$ evaluated by TEM was 5 ~ 7 nm. When $\text{Ca}_2\text{FeCoO}_5$ was synthesized by the RM method without TiO₂ nanoparticles at 600°C, the particle size was several dozen nanometers. These results suggest that $\text{Ca}_2\text{FeCoO}_5$ ultrafine particles can be formed by calcination of the precursors after loading on TiO₂ nanoparticles. Interaction between the precursors and TiO₂ surface is speculated to suppress aggregation of them during calcination. Furthermore, the ratio of cobalt to iron in the products can be controlled by selecting the mixing ratio in the starting solutions.

Figure 1. (a) Crystal structure of BM-type $\text{Ca}_2\text{FeCoO}_5$, (b) linear sweep voltammograms of CFCO_S1100, W800, LFCO, BSCF and RuO₂ for OER and (c) linear sweep voltammograms of $\text{Ca}_2\text{Fe}_{2-x}\text{Co}_x\text{O}_5$ ($0 \leq x \leq 1$) for OER.

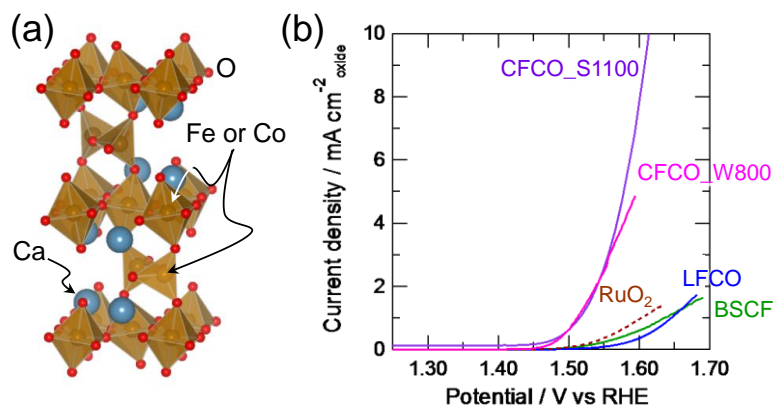


Figure 1. (a) Crystal structure of BM-type $\text{Ca}_2\text{FeCoO}_5$, (b) linear sweep voltammograms of CFCO_S1100, W800, LFCO, BSCF and RuO₂ for OER and (c) linear sweep voltammograms of $\text{Ca}_2\text{Fe}_{2-x}\text{Co}_x\text{O}_5$ ($0 \leq x \leq 1$) for OER.

4. Conclusions

BM-type $\text{Ca}_2\text{FeCoO}_5$ was found to exhibit remarkable OER catalytic activity. This oxide may be regarded as a promising catalyst for practical OER applications. Our systematic study on the $\text{Ca}_2\text{Fe}_{2-x}\text{Co}_x\text{O}_5$ suggests that the combination of *Td/Oh*-sites in the BM structure plays a crucial role. Also, BM-type $\text{Ca}_2\text{Fe}_{2-x}\text{Co}_x\text{O}_5$ ultrafine particles were synthesized by the RM method on TiO₂ nanoparticles. The particle size was 5 ~ 7 nm and the chemical composition was good consistent with the ratio of the starting solutions. It is necessary for forming such ultrafine particles to calcine after loading the precursors on TiO₂ nanoparticles.

Acknowledgments

Some parts of this work were supported by the RISING project of the NEDO and by the JSPS Grant-in-Aid for Young Scientists (B) (Grant Number 16K17968), Japan.

References

1. J. Suntivich, et al., *Science* **2011**, *334*, 1383-1385.
2. A. Ramirez et al., *J. Phys. Chem. C* **2014**, *118*, 14073.
3. E. Tsuji et al., *ChemSusChem*, **2017**, *10*, 2864-2868.

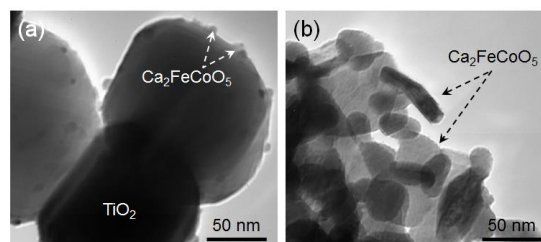


Figure 2. TEM images of $\text{Ca}_2\text{FeCoO}_5$ nanoparticles synthesized by reverse micelle method (a) with and (b) without TiO₂ nanoparticles.