Oxygen Evolution Catalysis for Iron Oxides with Various Structures

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1. Introduction

Transition metal oxides crystallize in various structures, and their properties are dominated by crystal structures and resulting electronic states.1,2) For example, the various ABO3-type oxides are included in different structures such as perovskite,3,4) ilmenite,5,6) and lithium niobate types. The perovskite structures consist of vertex-sharing BO6 octahedra (B: d-block transition metals).3) In addition to the cubic perovskite, distorted perovskite structures achieved by adjusting ionic size balances, i.e., Goldschmidt tolerance factor, demonstrate fascinating structure-property relationships.8-10) The ilmenite structure with edge-face-sharing AO6 and BO6 octahedra can be transformed to perovskite ones under high pressure, which are unquenchable, thus the lithium-niobate-type structures are obtained under ambient pressure.11) The K2NiF4-type oxide, A2BO4, consisting of alternating perovskites and rock-salt structures, is known as a typical structure for high-temperature superconductivity.12)

For the above examples, the basic structure consists of BO6 octahedra, where the local environments around transition metal B ions are identical. The A2BO4-type oxides also crystallize in various structures: spinel,13) post-spinel,14) and stuffed-tridymite.15) The spinel consists of AO4 tetrahedra and BO6 octahedra, in which the neighboring octahedra are connected with mutual edges in three dimension (Fig. 1(a)). A variety of metals occupying the A and B sites for this family realize intriguing properties such as magnetism,16) thermoelectricity,17) and catalysis.13) The post-spinel structure, a high-pressure polymorph of spinel, consists of one-dimensional chain-like edge-sharing BO6 octahedra (Fig. 1(b)), differing from the three-dimensional octahedral connection for spinel. Several oxides crystallize in the identical structure as post-spinel under ambient pressure, being investigated as the oxidation catalyst for CO.14) The A2BO4-type oxides with BO4 tetrahedra are known as the stuffed-tridymite, in which the vertex-sharing BO4 tetrahedra form tridymite framework whereas the larger A ions fill the voids (Fig. 1(c)). A variety of crystal structures for A2BO4-type oxides arouse interest in fascinating structure-property relationship, but a systematic comparison has not been conducted.

In this study, we investigate catalytic activity on electrochemical oxygen evolution reaction (OER; 4OH− → O2 + 2H2O + 4e− in alkaline conditions) for the A2+Fe3+O4 oxides with different crystal structures: spinel ZnFe2O4, post-spinel CaFe2O4, and stuffed-tridymite BaFe2O4. These oxides, the Fe3+ ions in the different coordination polyhedra and polyhedral connections serve to activate OER, although the catalytically inert A2+ ions (Zn2+, Ca2+, and Ba2+) do not contribute to OER catalysis. Our electrochemical investigation reveals that the OER activity for BaFe2O4 and CaFe2O4 are much higher than ZnFe2O4, indicating that the structural differences influence OER activity.

2. Experimental Procedure

ZnFe2O4 was synthesized from the stoichiometric mixture of α-Fe2O3 (99.99%) and ZnO (99.9%) by calcination at 1273 K for 10 h. CaFe2O4 was obtained by heating the stoichiometric mixture of α-Fe2O3 (99.99%) and CaCO3 (99.95%) at 1273 K for 20 h. BaFe2O4 was synthesized by
using polymerized complex method.18) The mixture of Ba(NO₃)₂ (99.9%) and Fe(NO₃)₃·9H₂O (99.9%) at a molar ratio 1:2 was dissolved in nitric acid solution (ca. 5 M) respectively, to which a 5-fold excess of citric acid and one-fold excess of 1,2-ethanediol were added while stirring. The resulting solution was heated to 573 K, while stirring, and maintained at this temperature for 1 h to dry. Subsequently, the dried powder was calcined using a furnace at 673 K for 1 h and at 1373 K for 24 h in air with occasional grindings. The crystal structures of as-synthesized samples were characterized by using X-ray powder diffraction (XRD) with Cu-Kα radiation (Ultima IV, Rigaku, Japan). The XRD data were analyzed using the Rietveld refinement program Rietan-FP.19) Specific surface areas were determined by Brunauer-Emmett-Teller (BET) analysis20) of Kr gas adsorption data (BELSORP-max, MicrotracBEL, Japan). X-ray absorption near edge structure (XANES) spectra of Fe K-edges were collected in transmission mode at the BL14B2 beamline of SPring-8. Extended X-ray absorption fine structure (EXAFS) spectra were analyzed by using Athena program of the IFEFFIT package.21)

OER catalytic activities were evaluated by using rotating disk electrode system.22) A 5 mass% proton-type NaFon suspension, 0.1 M KOH aqueous solution, and tetrahydrofuran (THF) were mixed in a 2:1:97 volume ratio. The catalyst ink was prepared by mixing 5 mg of catalyst, 1 mg of acetylene black, and 1 mg of THF solution. A 6.4 µL of catalyst ink was taken with stirring and drop cast onto the glassy-carbon disk electrode. Electrochemical measurements were performed using a rotating-disk electrode in combination with a bipotentiostat. A Pt wire and an Hg/HgO electrode filled with a 0.1 M KOH aqueous solution were used as the counter and reference electrodes, respectively. The cyclic voltammetry was conducted at scan rate of 10 mV s⁻¹ in the potential range between 0.3 and 0.9 V versus Hg/HgO, which corresponds to 1.226 and 1.826 V versus reversible hydrogen electrode (RHE). The currents obtained by the electrochemical measurement was normalized by the BET specific surface area of the samples. The potential was corrected by IR compensation with R = 43 Ω after the measurement.

3. Results and Discussions

Figure 2(a) shows the XRD patterns of AFe₂O₄ oxides (A = Zn, Ca, and Ba). ZnFe₂O₄ and CaFe₂O₄ were obtained as almost single phases, although BaFe₂O₄ contains small amount of Ba₂Fe₂O₅ impurity phase. Rietveld analysis estimates the amount of Ba₂Fe₂O₅ impurity at about 9 mass%. The BET surface areas were 1.15 m² g⁻¹ for ZnFe₂O₄, 1.11 m² g⁻¹ for CaFe₂O₄, and 0.30 m² g⁻¹ for BaFe₂O₄. The valence states of Fe ions were evaluated by Fe K-edge XANES spectra (Fig. 2(b)). The absorption edge positions for all the oxides were identical and close to that for γ-Fe₂O₃ reference, confirming the trivalent states. The intense pre-edge peak at ~7110 eV observed in BaFe₂O₄

![Fig. 2](image) (a) XRD patterns for ZnFe₂O₄, CaFe₂O₄, and BaFe₂O₄. The black circles represent the Bragg reflections from Ba₂Fe₂O₅ impurity. (b) X-ray absorption spectra of Fe K-edge for AFe₂O₄ and γ-Fe₂O₃ (A = Ca, Zn, and Ba). (c) Fourier-transformed EXAFS curves of Fe K-edge for ZnFe₂O₄, CaFe₂O₄, and BaFe₂O₄.
The present study strengthens the importance of tetrahedral reactants absorbed to coordinately unsaturated metal sites to be the single-site adsorption. The OER mechanism of transition metal oxides is reported to demonstrate much higher activity than ZnFe$_2$O$_4$. The OER catalysts with different Fe-O bond lengths and coordination with shorter Fe atoms with the nearest neighboring oxygen atoms in the Fe-O polyhedra. The EXAFS data clarify that the tetrahedral coordination with shorter Fe-O bonds is predominant for BaFe$_2$O$_4$, whereas octahedral coordination with longer Fe-O bonds for CaFe$_2$O$_4$ and ZnFe$_2$O$_4$.

Figure 3 shows current density-disk potential curves measured in OER conditions. BaFe$_2$O$_4$ and CaFe$_2$O$_4$ demonstrated much higher activity than ZnFe$_2$O$_4$. The specific activity at 1.6 V vs. RHE was 8 and 11 times larger for BaFe$_2$O$_4$ (0.08 mA cm$^{-2}$) and CaFe$_2$O$_4$ (0.11 mA cm$^{-2}$) than ZnFe$_2$O$_4$ (0.01 mA cm$^{-2}$), respectively. The OER onset potentials of CaFe$_2$O$_4$ and ZnFe$_2$O$_4$, which were determined by the potentials exceeding 0.05 mA cm$^{-2}$, were both 1.58 V vs. RHE, which were about 0.1 V lower than that for ZnFe$_2$O$_4$ (1.68 V vs. RHE). The comparison of OER activities between perovskite-type alkaline-earth titanates was unexpectedly observed, because the previous study proposed that the OER activity is not solely predominated by the coordination polyhedra, but the difference in polyhedral interconnection significantly affects the OER activity. Further investigation on the effect of polyhedral connection is in press.

4. Conclusion

We compared the OER catalytic activities for trivalent Fe oxides with various structures such as spinel, post-spinel, and stuffed-tridymite. The FeO$_4$ tetrahedra in BaFe$_2$O$_4$ were active, which was different from the less contribution of AO$_4$ tetrahedra for spinel oxides. The manner of polyhedral connections also affects the OER activity; FeO$_6$ octahedra one-dimensional-chain connection for CaFe$_2$O$_4$ was more favorable than the three-dimensional octahedral connection of ZnFe$_2$O$_4$. This finding proposes a simple structure-activity relationship to contribute to design principle for highly active OER catalysts.

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