Highly active postspinel-structured catalysts for oxygen evolution reaction†

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The rational design principle of highly active catalysts for the oxygen evolution reaction (OER) is desired because of its versatility for energy-conversion applications. Postspinel-structured oxides, CaB2O4 (B = Cr3+, Mn1+, and Fe3+), have exhibited higher OER activities than nominally isoelectronic conventional counterparts of perovskite oxides LaBO3 and spinel oxides ZnB2O4. Electrochemical impedance spectroscopy reveals that the higher OER activities for CaB2O4 series are attributed to the lower charge-transfer resistances. A density-functional-theory calculation proposes a novel mechanism associated with lattice oxygen pairing with adsorbed oxygen, demonstrating the lowest theoretical OER overpotential than other mechanisms examined in this study. This finding proposes a structure-driven design of electrocatalysts associated with a novel OER mechanism.

Introduction

The oxygen evolution reaction (OER: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ in alkaline conditions) plays an essential role in energy-conversion applications such as water electrolysis and rechargeable metal-air batteries. Since this reaction intrinsically involves large overpotentials causing colossal energy loss, precious-metal oxides (e.g., RuO2 and IrO2) are presently utilized as typical OER catalysts. Despite their high performance, large-scale applications are restricted because of their scarcity and high cost. Accordingly, much effort has been directed toward the development of highly active transition metal oxide catalysts consisting of earth-abundant and low-cost elements. Most of the transition metal oxide catalysts, such as spinel and perovskite, comprise tetrahedral and octahedral metal–oxygen units. The perovskite-structured oxides, one of the most well-studied experimentally and theoretically catalyst systems, consist of vertex-sharing octahedra, in which a single-site adsorption/reaction mechanism is widely accepted as adsorbates evolution reaction (AEM). The reactants are adsorbed on coordinatively unsaturated sites (CUS) formed by the extraction of oxygen at an octahedral vertex. Since the neighboring transition metal sites in vertex-sharing octahedra are far from each other, the bridging adsorption of adsorbates on two active sites is disturbed.

Several structures in transition metal oxides possess particular geometric conditions such as smaller transition-metal interatomic distances than that of vertex-sharing octahedra in perovskite, inducing interactions between adsorbates and multiple sites on the catalyst surface. Accordingly, dual-site adsorption/reaction mechanisms that the reactant bound to the CUS is also connected to another atom in the surrounding polyhedra are manifested by experiments and theoretical calculations. For example, the dual-site reaction mechanism bridging $B$-site octahedral CUS metal and $A'$-site pseudosquare coordinated transition metal has been suggested in the $A$-site-ordered quadruple perovskite $(\text{AA}'_3\text{B}_4\text{O}_{12})$. The dual-site reaction mechanism has been experimentally and theoretically examined in the rutile-structured RuO2. RuO2 is composed of one-dimensional edge-shared RuO6 octahedral chains gathered by sharing vertices. The reaction mechanism reported in the RuO2(110) surface involves a reaction step where an oxygen atom adsorbed on the Ru CUS combines with the oxygen atom (O$\text{Ru}$) bridging two Ru atoms in the octahedral chain neighboring to CUS. Recently, Sugawara et al. reported that CaFeO2 exhibits higher OER activity than other Fe oxides, suggesting a novel reaction mechanism in which three Fe atoms...
OER activity of CaFe₂O₄ may be derived from the structural feature, the postspinel-related series of CaB₂O₄ (B = Cr and Mn) must exhibit higher OER catalytic activity than the spinel or perovskite oxides.

In this paper, we investigated the OER catalytic activities of postspinel-structured CaB₂O₄ (B = Cr, Mn, and Fe) and systematically compared activities with perovskite LaBO₃ and spinel ZnB₂O₄. Regardless of B-site transition metals, the OER activities in CaB₂O₄ oxides are monotonically superior to those of ZnB₂O₄ and LaBO₃ counterparts, which is supported by lower charge-transfer resistance in CaB₂O₄. We performed DFT calculations to reveal the origin of OER activity in CaFe₂O₄ by remodeling the regular 4-step reaction mechanism from the previously reported 3-step mechanism²¹ and compared with the comparison with several possible mechanisms. We eventually found a novel 4-step reaction mechanism with lower theoretical overpotential, where the adsorbed oxygen on the FeCUS and the adjacent O₃ surface were desorbed to generate oxygen. This finding suggests a new design principle for improving catalytic activity in multiple crystal structures of transition metal oxides.

**Experimental**

**Material synthesis**

CaCr₂O₄, CaMn₂O₄, and CaFe₂O₄ were obtained from the mixtures of CaCO₃ (99.95%) and Cr₂O₃ (99.9%), MnO₂ (99.9%), or Fe₂O₃ (99.99%) by calcining at 1473, 1473, and 1373 K, respectively, for 10–24 h for several times. ZnCr₂O₄ and ZnMn₂O₄ were synthesized from the mixtures of ZnO (99.9%) and Cr₂O₃ (99.9%) or MnO₂ (99.9%) by heating at 1273 and 1173 K for 5 and 10 h, respectively. ZnFe₂O₄ was obtained using the polymerized complex method. A mixture of ZnO (99.9%) and Fe(NO₃)₃·9H₂O (99.9%) at a molar ratio of 1 : 2 was dissolved in nitric acid solution (~5 M), to which a five-fold excess of citric acid and one-fold excess of 1,2-ethanediol were added to the solution with stirring. The resulting solution was heated for 573 K and maintained at this temperature for 1 h to dry. Subsequently, the dried powder was fire using a furnace at 673 K for 1 h and then 1273 K for 10 h in air with occasional grindings. LaCrO₃ and LaMnO₃ were also obtained using the polymerized complex method from mixtures of La(NO₃)₃·6H₂O and Mn(NO₃)₃·6H₂O, by combustion at 1273 and 1073 K for 5 and 10 h, respectively. LaFeO₃ was synthesized from a stoichiometric mixture of La₂O₃ and Fe₂O₃ by heating at 1673 K for 10 h.

**Basic characterization**

The as-synthesized samples were identified by X-ray powder diffraction (XRD) with Cu-Kα radiation (Ultima IV, Rigaku, Japan). The synchrotron XRD (SXRD) patterns were collected using a Debye–Scherrer camera installed at the BL02B2 beamline in SPring-8, Japan. The wavelength was determined as 0.49968 Å using CeO₂ as a reference. The SXRD data were analyzed using the Rietveld refinement program RIETAN-FP. Specific surface areas were determined by Brunauer–Emmett–Teller (BET) analysis of Kr gas adsorption data.
Electrochemical characterization

Working electrodes were prepared using the drop-casting method of inks containing catalysts on glassy carbon electrode, referred to previous papers.\(^{28}\) A 5 wt% proton-type Nafion suspension (Sigma-Aldrich), 0.1 M KOH aqueous solution (Nacalai Tesque, Inc., Japan), and tetrahydrofuran (THF, Sigma-Aldrich) were mixed at a ratio of 2:1:97 in volume. The catalyst ink was prepared by mixing 5 mg of catalyst, 1 mg of acetylene black (Denka Co., Ltd, Japan), and 1 mg of the THF solution. A 6.4 μL of catalyst ink was taken with stirring and drop cast onto the glassy-carbon disk electrode with 4 mm diameter.

Electrochemical measurements were conducted using a rotating-disc electrode rotator (RRDE-3 A, BAS Inc., Japan) and a bipotentiostat (model-2325, BAS Inc., Japan). We used a Pt wire electrode and a Hg/HgO electrode (International Chemistry Co., Ltd, Japan) filled with a 0.1 M KOH aqueous solution (Nacalai Tesque, Inc., Japan) as the counter and reference electrodes, respectively. All electrochemical measurements were conducted under O\(_2\) saturation at room temperature. This fixed the equilibrium potential of the O\(_2\)/H\(_2\)O redox couple to 0.304 V versus (vs.) Hg/HgO. The disk potential was controlled between 0.3 and 0.9 V vs. Hg/HgO at a scan rate of 10 mV s\(^{-1}\). The disk potential was represented in those vs. reversible hydrogen electrode (RHE), with IR-compensation (\(R = 43 \Omega\)). The capacitive effect was compensated by averaging the cathodic and anodic scans.

Chronoamperometry (CA) was conducted at 1.6 V vs. RHE, where IR-compensation was not made. The electrochemical surface area (ECSA) was determined by scanning non-faradaic region between 0.1 Hz to 1 MHz. Working electrodes were prepared using the drop-casting method of inks containing catalysts on glassy carbon electrode, referred to previous papers.\(^{12,22}\) Electrochemical impedance spectroscopy (EIS) measurement was conducted using an electrochemical analyzer (760E, BAS Inc., Japan) at 1.7 V vs. RHE at frequencies ranging from 0.1 Hz to 1 MHz.

Density-functional-theory calculation

Bulk model electronic structure

Spin-polarized DFT calculations were systematically performed for spinel and postspinel oxides, namely, CaFe\(_2\)O\(_4\), CaCr\(_2\)O\(_4\), CaMn\(_2\)O\(_4\), ZnCr\(_2\)O\(_4\), ZnMn\(_2\)O\(_4\), and ZnFe\(_2\)O\(_4\), using the plane-wave basis projector augmented wave (PAW) method as implemented in the Vienna \textit{ab initio} Simulation Package (VASP).\(^{21–23}\) The generalized gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof (PBE)\(^{26}\) were adopted to express exchange–correlation interactions. The strong on-site coulombic interactions on the localized 3d electrons were treated with the GGA + U approach.\(^{27}\) The \(U_{\text{eff}} = 3.5\), 4.0, and 3.9 eV were adopted for Cr, Mn, and Fe 3d orbitals, which were selected to reproduce the experimental oxidation enthalpy, as reported previously.\(^{28-29}\) The PAW potential data-set with radial cutoffs of 2.3 A for Ca, Cr, Mn, Fe, Zn, and 1.52 A for O were employed, where Ca-3s, 3p, 4s, Cr-3p, 3d, 4s, Mn-3p, 3d, 4s, Fe-3d, 4s, Zn-3s, 3p, 4s, 4p, 3d, O-2s, 2p were described as valence electrons. Table S11\(^{\dagger}\) summarizes the magnetic structures and nominal electron configurations considered in this work. The plane-wave cutoff energy was set to 500 eV for all calculations. The Brillouin zone was sampled using \(k_1 \times k_2 \times k_3\) mesh points according to the Monkhorst–Pack scheme.\(^{26}\) The mesh count for each direction was selected as the near natural number of 35 per lattice parameter (1 Å\(^{-1}\)). The lattice constants and internal coordinates were optimized until the total energy difference and residual forces converged to less than \(10^{-5}\) eV and \(10^{-2}\) eV Å\(^{-1}\), respectively. According to literature,\(^{31-37}\) oxygen 2p band centers and unoccupied 3d band centers of transition metal atoms were computed from the projected density of states (DOS) as follows:

\[
E_{2p} = \frac{\int_{E_F}^{E_{2p}} f_{2p}(E) \, dE}{\int_{E_F}^{E_{2p}} f_{2p}(E) \, dE},
\]

and

\[
E_{3d-un} = \frac{\int_{E_{3d-un}}^{E_{max}} f_{3d}(E) \, dE}{\int_{E_F}^{E_{max}} f_{3d}(E) \, dE},
\]

respectively. Here, \(f_{2p}(E)\) and \(f_{3d}(E)\) are DOS projected on O-2p and transition metal 3d orbitals, respectively; \(E_F\) is the Fermi energy; and \(E_{max}\) is the upper bound of unoccupied 3d bands. The \(E_{max}\) value was set as 10 eV higher than that of \(E_F\). The number of conduction bands was increased until the shapes of projected DOSs were converged.

Slab model surface energy and theoretical overpotential

The electronic structures of OER intermediates on the (001) surface of CaFe\(_2\)O\(_4\) terminated by exposed FeO\(_5\) pyramids were investigated using DFT calculations. The slab models in Fig. S6\(^{\dagger}\) were composed of doubled cells along the \(c\) and \(b\) axes for CaFe\(_2\)O\(_4\). The number of layers and the length of the vacuum layer in the slab models were carefully determined by checking the convergences of surface energies. For the (001) plane in CaFe\(_2\)O\(_4\), the slab models respectively consisted of 116 atoms with 8 layers. The lattice constants of slab models for CaFe\(_2\)O\(_4\) were 9.29 Å × 6.07 Å × 43.1 Å, including 20 Å vacuum layer to prevent interactions between surfaces in slab models. For these calculations, Brillouin zones were sampled with \(4 \times 4 \times 1\) grids for CaFe\(_2\)O\(_4\). We fixed the positions of 81 atoms in the middle of these models for CaFe\(_2\)O\(_4\) to evaluate bare surface energies (blue areas in Fig. S6b\(^{\dagger}\)). The atomic positions were optimized except for atomic layers in the bottom of slab models (magenta areas in Fig. S6b\(^{\dagger}\)) to calculate surface energies. The other computational conditions, including the PAW data-set, \(U_{\text{eff}}\) values, plane-wave cutoff energies, total energy differences, and residual forces, were identical with bulk calculations.
The surface energies of CaFe$_2$O$_4$ under the equilibrium conditions in OER were calculated according to the procedure proposed in the literature. The surface Gibbs free energy can be described for CaFe$_2$O$_4$ as follows:

$$I = \frac{1}{2A} [E_{\text{DFT}}(\text{slab}) - N_0\mu_0 - N_{Ca}\mu_{Ca} - N_{Fe}\mu_{Fe}].$$

(3)

where $E_{\text{DFT}}(\text{slab})$ is the total energy of the slab model using DFT calculations; $A$ is the surface area of the slab model. $N_2$ and $\mu_2$ (Z = Ca, Fe, and O) are defined as the amount of the atoms in the slab model and chemical potentials, respectively. The chemical potentials are determined under the equilibrium condition of water splitting. In agreement with the computational hydrogen potentials are determined under the equilibrium condition of CO$_2$ splitting.

$$\mu_{Ca} + 2\mu_{Fe} + 4\mu_{O}(pH, \phi) = E_{\text{DFT}}(\text{CaFe}_2\text{O}_4)$$

(5)

where $E_{\text{DFT}}(\text{CaFe}_2\text{O}_4)$ is the total energy of bulk CaFe$_2$O$_4$. By solving eqn (3) for $\mu_{Fe}$ and substituting it with eqn (4) into (3), the surface energy $I$ is obtained as a linear function dependent on $\mu_{Ca}$. In this work, we constructed reaction mechanisms from reported AEM$^{12,13}$ and lattice-oxygen-mediated mechanism (LOM)$^{14}$ and conducted surface calculations for the mechanisms listed in Tables S12 and S13$^{14}$ AEM–O$_{\text{BRI}}$, the LOM–O$_{\text{BRI}}$, AEM model, and dual-site AEM models referred by Sugawara $et al.$ In these reaction steps, the *X/*Y surface state of postspinel-structured CaFe$_2$O$_4$ is determined as using the binding state *X for Fe$_{\text{CUS}}$ and the binding state *Y for adjacent Fe$_{\text{CUS}}$ with O$_{\text{BRI}}$. The – bondings of *O–O$_{\text{BRI}}$ and *OOH–O$_{\text{BRI}}$ surfaces exhibit interactions between adsorbed oxygen and O$_{\text{BRI}}$. For each of the individual surfaces, the free energy change $\Delta G_{\text{X/Y}}$ (*X/*Y: adsorbed surfaces) was calculated using equations in Table S14$^{14}$. For each of the six reaction mechanisms, the free energy change $\Delta G_n$ ($n$: reaction steps) in the individual reaction was defined as each formula in Tables S15 and S16. Using the largest $\Delta G_n$ ($n$: reaction step), the value of theoretical overpotential ($\eta_n$) was calculated using the following equation:

$$\eta_n = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/e - 1.23 \text{ [V]}. $$

(6)

Results and discussion

Fig. 2 shows the XRD patterns of LaBO$_3$, ZnB$_2$O$_4$, and CaB$_2$O$_4$ ($B = \text{Cr, Mn, Fe}$). All samples crystallized in a single phase. CaB$_2$O$_4$ were assigned to orthorhombic phases, as reported previously. Rietveld refinement results obtained by using the SXRD data confirmed that the refined lattice parameters were similar to those previously reported in all samples (Fig. S1 and Table S1–S9$^{14}$). The computed bond valence sums (BVSs) indicate trivalent states of transition metal ions, as expected from the simple ionic models of La$^{+3}$B$^{+3}$O$_{3-}$, Zn$^{+2}$B$^{+3}$O$_{2-}$, and Ca$^{+2}$B$_2$O$_{4-}$. Fig. 3 shows the X-ray absorption spectra at K-edges of Cr, Mn, and Fe. The K-edge absorption positions of transition metals for perovskites, spinels, and postspinels are close to those of pure trivalent metal oxides (B$^{+3}$O$_3$) rather than aliovalent references (B$^{+2}$O and B$^{+4}$O$_3$), although the differences in local structures around the B sites appeared in shapes in higher energy ranges than absorption energies. The structural and spectroscopic analyses exclude the possible effects of valence on OER activities$^{14}$, thus the effects of crystal structure on activity can be investigated in this study.

Fig. 2 XRD patterns of LaBO$_3$, ZnB$_2$O$_4$, and CaB$_2$O$_4$ for B = Cr (green), Mn (magenta), and Fe (brown).
between 0.1 and 10 μm for all. The crucial differences in grain size were not observed between CaB₂O₄ and references containing the same B ion. The SEM observations roughly confirmed similar morphologies among all samples, compatible with BET and ECSA analyses.

Fig. 4 shows the linear sweep voltammograms for LaB₂O₄, ZnB₂O₄, and CaB₂O₄ (B = Cr, Mn, and Fe). Obviously, CaB₂O₄ series exhibited much higher activities than the LaB₂O₄ and ZnB₂O₄ counterparts in the identical transition metal element. Taking Cr oxides for instance, the overpotential of CaCr₂O₄ was η₀.₀₅ = 0.34 V, substantially lower than those of ZnCr₂O₄ (0.44 V) and LaCrO₃ (0.75 V) (see the inset of Fig. 4a and Table 1), where the overpotentials (η₀.₀₅) were determined at the onset potentials (Eᵋᵣ) exceeding the current density of 0.05 mA cm⁻²; η₀.₀₅ = Eᵋᵣ – 1.23 (V). The specific activity (a current density at 1.6 V vs. RHE) of CaCr₂O₄ was about 9 times higher than that of ZnCr₂O₄ or LaCrO₃. Fig. 5 and Table 1 summarize the specific activities and overpotentials for all samples. The superiority of CaB₂O₄ as OER catalyst were commonly observed in the activities normalized by disk areas, ECSA, and BET surface areas (Fig. 5). Regardless of the constituent transition metals, the lower overpotentials and larger activities reveal the intrinsic superiority of the postspinel structures. Especially, CaFe₂O₄ exhibited about 30 times larger specific activity and 0.15 V smaller η₀.₀₅ than ZnFe₂O₄. The improvement from spinel-structured ZnFe₂O₄ to postspinel-structured CaFe₂O₄ was the most remarkable among all comparisons.

Significant differences between postspinels and other structures were observed in Tafel plots and EIS analyses. Fig. 6 shows the Tafel plots for LaB₂O₄, ZnB₂O₄, and CaB₂O₄ (B = Cr, Mn, and Fe). The Tafel slope of CaFe₂O₄ (53 mV dec⁻¹) was much smaller than that of ZnFe₂O₄ (102 mV dec⁻¹) and LaFeO₃ (78 mV dec⁻¹). Clear differences in Tafel slopes between postspinel-structured oxides and counterparts were also observed in Cr and Mn oxides. Since the Tafel slope varies in dependent on the rate-determining step (RDS), the observed differences in Tafel slope indicate that the RDS is altered by crystal structures. Nyquist plots are displayed in Fig. 7 for LaB₂O₄, ZnB₂O₄, and CaB₂O₄ (B = Cr, Mn, and Fe). The semicircles around 1–100 Hz attributed to charge-transfer resistance (Rₜ) changed depending on the crystal structure. The Rₜ value of CaFe₂O₄ (≈150 Ω) was smaller than that of LaFeO₃ (≈400 Ω) and ZnFe₂O₄ (≈7000 Ω). CaCr₂O₄ (Rₜ ≈ 2000 Ω) and CaMn₂O₄ (≈800 Ω) exhibited lower Rₜ values than LaB₂O₄ and ZnB₂O₄ counterparts. The fact that the Rₜ values in CaCr₂O₄ and CaMn₂O₄ were larger than that in CaFe₂O₄ is probably associated with surface amorphizations in the formers, as shown in the HRTEM study later. The surface amorphizations disturb the charge transfer, deviating from the intrinsic nature of the crystalline surface. Consequently, the activated charge-transfer kinetics is consistently a primary origin for the enhanced OER activity in CaB₂O₄ for Cr, Mn, and Fe oxides.

We investigated the long-term stability and surface crystalline states of CaB₂O₄. Fig. 8 shows the CA currents normalized by initial currents in CaCrO₃, CaMn₂O₄, and CaFe₂O₄. CaFe₂O₄ exhibited no substantial degradation in OER activity. This
observation manifests the robustness of CaFe$_2$O$_4$ in OER conditions, whereas the sudden drops in initial states for CaCr$_2$O$_4$ and CaMn$_2$O$_4$ (Fig. 8) indicate instability of surface crystalline states. Fig. S3† displays HRTEM images of CaCr$_2$O$_4$, CaMn$_2$O$_4$, and CaFe$_2$O$_4$. CaFe$_2$O$_4$ retained the crystalline surface after CA, as well as the pristine and as-cast powders. In contrast, CaCr$_2$O$_4$ demonstrated severe surface amorphization.

Table 1  Specific surface area from BET analysis and electrochemical surface area (ECSA) for LaBO$_3$, ZnB$_2$O$_4$, and CaB$_2$O$_4$ ($B =$ Cr, Mn, Fe). Overpotential ($\eta_{0.05}$), specific activity normalized by BET surface area at 1.6 V vs. RHE, and Tafel slope for these catalysts

| Compound     | Specific surface area (m$^2$ g$^{-1}$) | ECSA (m$^2$ g$^{-1}$) | $\eta_{0.05}$ (V) | Specific activity (mA cm$^{-2}$) oxide | Tafel slope (mV dec$^{-1}$) |
|--------------|--------------------------------------|-----------------------|-------------------|---------------------------------------|-----------------------------|
| LaCrO$_3$    | 2.49                                 | 27.3                  | 0.75              | 0.004                                 | 230                         |
| LaMnO$_3$    | 1.52                                 | 26.6                  | 0.51              | 0.010                                 | 163                         |
| LaFeO$_3$    | 1.32                                 | 20.5                  | 0.42              | 0.015                                 | 78                          |
| ZnCr$_2$O$_4$| 1.84                                 | 15.3                  | 0.47              | 0.008                                 | 248                         |
| ZnMn$_2$O$_4$| 1.57                                 | 21.3                  | 0.48              | 0.005                                 | 101                         |
| ZnFe$_2$O$_4$| 1.15                                 | 10.9                  | 0.45              | 0.009                                 | 103                         |
| CaCr$_2$O$_4$| 1.15                                 | 18.2                  | 0.31              | 0.068                                 | 138                         |
| CaMn$_2$O$_4$| 1.32                                 | 17.5                  | 0.39              | 0.012                                 | 84                          |
| CaFe$_2$O$_4$| 1.11                                 | 10.3                  | 0.33              | 0.111                                 | 53                          |

Fig. 4  Linear sweep voltammograms for LaBO$_3$, ZnB$_2$O$_4$, and CaB$_2$O$_4$ for $B =$ (a) Cr, (b) Mn, and (c) Fe. The insets represent the magnified data in the vicinity of the OER onset potential.

Fig. 5  Comparison of OER (a) overpotential ($\eta_{0.05}$) and activities at 1.6 V vs. RHE for LaBO$_3$, ZnB$_2$O$_4$, and CaB$_2$O$_4$ ($B =$ Cr, Mn, and Fe) normalized by (b) disk area (0.126 cm$^{-2}$), (c) ECSA, and (d) BET surface area.
even in the as-cast sample and further evolution of the amorphous layer after CA (Fig. 8). CaMn$_2$O$_4$ also possessed the amorphous surface in the as-cast sample, which is probably the cause of the initial degradation in CA. Gradual increases in current density were observed for several oxides (CaMn$_2$O$_4$ and CaFe$_2$O$_4$), but the origin was unclear at the present stage. Since CaFe$_2$O$_4$ did not exhibit severe amorphization, the intrinsic feature of the crystalline surface is predominantly reflected in the electrochemical analyses.

![Fig. 6 Tafel plots of LaBO$_3$ (black), ZnB$_2$O$_4$ (blue), and CaB$_2$O$_4$ (red) for B = (a) Cr, (b) Mn, and (c) Fe.](image)

![Fig. 7 Nyquist plots of LaBO$_3$ (black), ZnB$_2$O$_4$ (blue), and CaB$_2$O$_4$ (red) for B = (a) Cr, (b) Mn, and (c) Fe, measured at 1.7 V vs. RHE. The insets represent the magnified data in Fe oxides. Blank circles display points observed between 1–100 Hz.](image)

Our electrochemical experiments elucidated that the OER catalytic activities in postspinel CaB$_2$O$_4$ (B = Cr, Mn, and Fe) are superior to those of perovskites LaBO$_3$ and spinels ZnB$_2$O$_4$, irrespective of B metal ions. The commonly observed properties in CaB$_2$O$_4$ suggest that the edge-sharing one-dimensional octahedra in postspinel structures predominate the reaction mechanism. We conducted DFT calculations to discuss the reaction mechanism on the surface of CaB$_2$O$_4$ associated with the geometric feature of the coordination polyhedra, in addition to the bulk electronic factors possibly affecting the OER catalysis. Fig. S4† shows the DOS generated from bulk-model DFT.
The free energies $\Delta G_{\text{rxn,1}}$ at each reaction step of the above-examined models are listed in Table S17† defined with formulae in Table S14.† The value of $\Delta G_{\text{rxn,1}}$ tended to increase in correspondence with the number of adsorbed atoms in the *X/*Y surface state. We calculated the values of energy change $\Delta G_n$ of each reaction steps and $\eta_{\text{th}}$ for the six reaction mechanisms (Table S18†) as following calculations in formulae in Tables S15 and S16.† Fig. 10 shows the energy diagrams for each reaction mechanism. In Fig. 10, the thick lines represent the potential determining steps (PDSs) with the largest $\Delta G_n$ in each mechanism, accompanied by $\eta_{\text{th}}$ values calculated from $\Delta G_n$ at these PDSs. The PDSs for AEM–OBRI ($\eta_{\text{th}} = 1.33$ V) and LOM–OBRI ($\eta_{\text{th}} = 0.85$ V) were assigned to step 3 (*O–OBRI + OH$^-$ \rightleftharpoons *OOH–OBRI + e$^-$) and step 4 (*OH + OH$^-$ \rightleftharpoons */+ H$_2$O + e$^-$), respectively. In contrast, step 2 with a significant large $\eta_{\text{th}}$ (2.04 V) was the PDS in the AEM (*OH/* + OH$^-$ \rightleftharpoons *O/* + H$_2$O + e$^-$). LOM–OBRI demonstrated the lowest $\eta_{\text{th}}$ among the 4-step mechanisms. Due to the high variation in surface structures and types of adsorbed species in PDSs, we could not identify any consistency in adsorption states of PDSs among the three reaction mechanisms. The PDSs of LOM–OBRI and AEM were categorized as transforming steps from *OH to *O, whereas the PDSs of AEM–OBRI were assigned to adsorption processes of the reactant OH$^-$. We conclude that the LOM–OBRI with the lowest $\eta_{\text{th}}$ (0.85 V) examined in the present DFT calculation is the most probable mechanism to explain the high OER activity of postspinel-structured oxides.

We compared theoretical overpotential in the mechanisms reported in previous studies with LOM–OBRI, which is the most probable reaction mechanism among our reaction mechanisms described above. We validated two types of 4-step mechanisms, dual-site AEM (1)–(2) in Fig. 9d and e, which are reformulations of the 3-step model, and dual-site AEM (3) (Fig. 9f), proposed by Sugawara et al. The OH$^-$ adsorbates are sequentially bonded with two FeCUS sites in the 4-step reaction with two procedures ($*/ \rightarrow$ *OH$/*$ \rightarrow $*$OH/*OH$^-$ \rightarrow $*$OH$/*$ (Fig. 9d) or $*$/*$ \rightarrow $*/+OH$^-$ \rightarrow $*$OH/*OH$^-$ \rightarrow $*$OH$/*$ (Fig. 9e)), in contrast to the simultaneous OH$^-$ adsorption in the previous 3-step reaction in Fig. 9f ($*/ \rightarrow$ *OH$/*$ \rightarrow *OH$/*$O). In dual-site AEMs, depending on the initial position of *OH species, the PDSs were determined at adsorption of step 2 in dual-site AEM (1) ($\eta_{\text{th}} = 1.11$ V, *OH$^+$ + OH$^-$ \rightleftharpoons *OH/*OH$^-$ + e$^-$), and step 1 in dual-site AEM (2) ($\eta_{\text{th}} = 0.88$ V, */ + OH$^-$ \rightleftharpoons *OH$/*$ + e$^-$). The calculation using the 3-step mechanism “dual-site AEM (3)” referred to the previous study** demonstrated simultaneous adsorptions of reactants (step 1) was assigned to the PDS ($\eta_{\text{th}} = 1.00$ V, */* + 2OH$^-$ \rightleftharpoons *OH/*OH$^-$ + 2e$^-$). The present calculations revealed that the PDSs in three subpaths of dual-site AEMs are assigned in adsorptions steps of OH$^-$ species to the surface, differing from the charge-transfer PDS in the previous study,** whereas the original PDS reaction (*OH/*OH + OH$^-$ \rightleftharpoons *OH$^+$ + H$_2$O + e$^-$) was stabilized in our calculations. Since the repulsive energies between the two OH$^-$ species were not considered, the theoretical overpotential (0.58 V)$^*$ in the previous 3-step reaction mechanism would be underestimated.
Fig. 9  Schematics of surface structures of CaFe₂O₄ after structural relaxations for mechanisms of (a) AEM–OBR, (b) LOM–OBR, (c) AEM, and dual-site AEMs. In dual-site AEM, calculated mechanisms start from the surface of (d) */OH, (e) *OH/*, and (f) *OH/*OH.
Conclusion

In summary, we investigated the OER catalytic activity in the postspinel-structured oxides \( \text{Ca}_B \text{O}_4 \) (\( B = \text{Cr}, \text{Mn}, \) and \( \text{Fe} \)), revealing higher OER activities and smaller charge-transfer resistances than the perovskite- and spinel-structured counterparts. The DFT calculation on the surface of \( \text{CaFe}_2\text{O}_4 \) elucidates that a novel reaction mechanism with the lowest theoretical overpotential, where \( \text{O}_{\text{BRI}} \) and \( \text{O}_{\text{ad}} \) are combined to generate oxygen, is more probable than the 3-step reaction mechanism with simultaneous adsorption of \( \text{OH}^- \) proposed in the previous study. Consequently, the geometric configurations around adsorption sites tolerating additional bonding are another factor to activate OER beyond the conventional single-site OER mechanism.

Conflicts of interest

There are no conflicts to declare.

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