

Fe⁴⁺-based quadruple perovskite catalyst for oxygen evolution reaction

The oxygen evolution reaction (OER) is an essential electrochemical reaction for energy conversion in various applications such as rechargeable metal-air batteries and water electrolysis for hydrogen production. Highly active and durable OER catalysts are required to reduce high overpotential, which causes a huge loss of energy. Precious-metal-based oxides such as RuO₂ and IrO₂ are widely used as OER catalysts, but alternative OER catalysts consisting of earth-abundant elements are desired. Transition metal oxide catalysts with the perovskite structure are extensively investigated because of their flexible chemical compositions and electronic states. Cobalt-based perovskite oxides such as Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) and R_{0.5}Ba_{0.5}CoO₃ (R = rare-earth metals) are considered promising candidates for OER catalysis materials. Suntivich *et al.* proposed that the occupancy of e_g orbitals of B-site metal ions for ABO₃ perovskite is related to catalytic activity for OER [1], in which B-site ions with e_g^{~1} configuration show the highest catalytic activity. Furthermore, the energy level of the oxygen 2p band center was proposed as another descriptor of OER catalytic activity [2]. However, the design principle for highly active and durable catalysts has not been established.

Fe⁴⁺-based oxides with the nominal electron configuration of t_{2g}³e_g¹ are also expected to be good candidates for highly active OER catalysts, but their catalytic properties have not been carefully investigated yet probably because of their severe synthesis conditions such as high pressures (several GPa) and high temperatures. Recently, we have reported that the quadruple perovskite oxide CaCu₃Fe₄O₁₂ (CCFO) containing Fe⁴⁺ ions demonstrate very high OER catalytic activity [3]. We also found that CCFO has higher stability under OER conditions than the simple perovskites AFe⁴⁺O₃ (A = Ca, Sr). The electron density distribution analysis based on synchrotron X-ray powder diffraction indicates that the increased stability of CCFO under OER conditions is derived from the covalent bonding network incorporating multiple transition metal ions such as Cu²⁺ and Fe⁴⁺, and we propose a new guideline to achieve both catalytic activity and durability.

Figures 1(a) and 1(c) show the crystal structures of SrFeO₃ and CCFO. SrFeO₃ crystallizes in a simple cubic perovskite structure, whereas CCFO crystallizes in an AA'₃B₄O₁₂-type quadruple cubic perovskite structure, in which A-site Ca²⁺ and A'-site Cu²⁺ ions are spatially ordered because of the differences in ionic size and coordination preference. Both CCFO

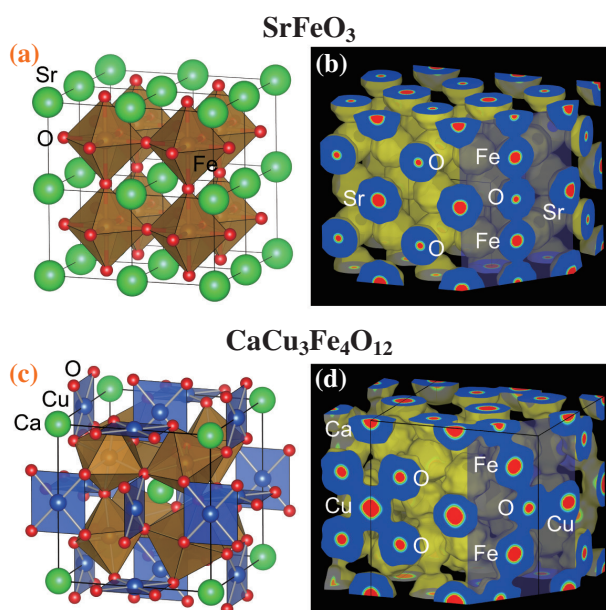


Fig. 1. Crystal structures of Fe⁴⁺-perovskites (a) SrFeO₃ and (c) CaCu₃Fe₄O₁₂. Electron density mapping obtained by the maximum entropy analysis of synchrotron X-ray powder diffraction data for (b) SrFeO₃ (equidensity level: 0.4 Å⁻¹) and (d) CaCu₃Fe₄O₁₂ (equidensity level: 0.5 Å⁻¹).

and SrFeO_3 can be synthesized under high-pressure and high-temperature conditions of above several GPa and approximately 1000°C.

Figure 2(a) shows the linear sweep voltammograms of various transition metal oxides under OER conditions. CCFO shows the lowest onset potential (lowest overpotential) and a rapid increase in current density, indicating a high catalytic activity, which exceeds those of the state-of-the-art catalysts BSCF and RuO_2 . It should also be noted that CaFeO_3 has a higher catalytic activity than LaMnO_3 with Mn^{3+} in the electron configuration of $t_{2g}^3e_g^1$, nominally identical to Fe^{4+} . The superiority of Fe^{4+} in OER catalysis is attributed to its unique electronic state. It is considered that ligand holes in oxygen 2p orbitals are predominant in unusual high-valence Fe^{4+} ions because of the deeply lying Fe 3d orbitals; thus, electron configuration of Fe^{4+} is close to $t_{2g}^3e_g^2\bar{L}^1$ (\bar{L} ligand hole), not to conventional $t_{2g}^3e_g^1$. The above finding indicates that the oxygen 2p band is lifted up close to the Fermi level in Fe^{4+} -oxides, satisfying the descriptor suggested by Grimaud *et al.* [2].

It is also notable that CCFO has relatively higher stability than simple Fe^{4+} -perovskites. Figure 2(b) shows cyclic voltammograms of CaFeO_3

and CCFO in 100 cycles. CaFeO_3 shows serious degradation in the 100th sweep and its current density markedly decreases during the cycles. On the other hand, CCFO shows no degradation after 100 cycles, retaining a high current density and a low overpotential. The high stability of CCFO under OER conditions was investigated in terms of chemical bonding. Synchrotron X-ray powder diffraction data were collected at BL02B2 beamline. Figures 1(b) and 1(d) show the electron density distributions of SrFeO_3 and CCFO. A certain electron density is observed between Fe and O ions for SrFeO_3 , which is attributed to the high covalency of the Fe–O bond. In contrast, Sr ions are separated from neighboring O ions because of its ionic characteristic. This probably leads to the dissolution of Sr ions. Together with Fe–O bonds, substantial electron densities are also confirmed between neighboring Cu and O ions for CCFO (Fig. 1(d)), resulting in a widespread covalent bonding network which inhibits the degradation in a number of OER cycles.

In summary, we demonstrate that Fe^{4+} -based perovskite oxides synthesized under high-pressure and high-temperature conditions have high catalytic activities for OER. The stability under OER conditions of CCFO is much higher than those of simple Fe^{4+} -perovskites. A widespread covalent bonding network consisting of Cu, Fe, and O ions is determined by the electron density distribution analysis of synchrotron X-ray powder diffraction, which is a key to realizing robust and highly active OER catalysts.

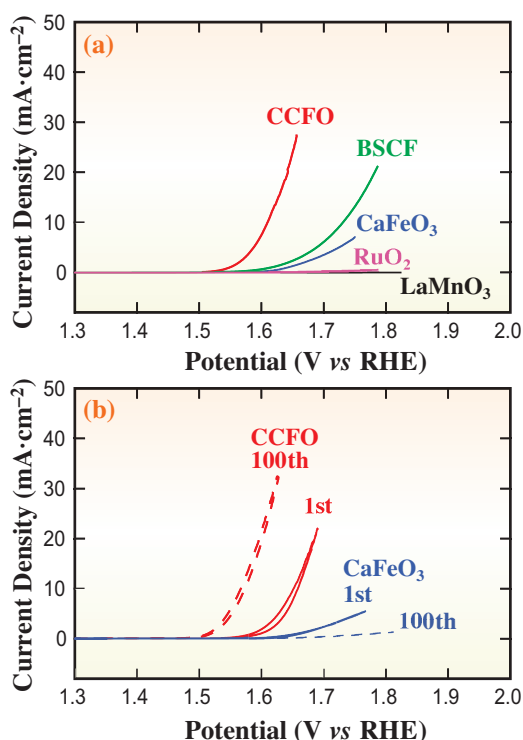


Fig. 2. (a) Linear sweep voltammograms of various transition metal oxides for OER. (b) Cyclic voltammograms of CaFeO_3 and $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ during continuous 100 cycle OER measurements.

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References

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