Enhancement of Oxygen Evolution Activity of Ruddlesden-Popper-Type Strontium Ferrite by Stabilizing Fe$^{4+}$

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**Abstract**

Development of active iron based water oxidation for designing an ideal artificial photosynthesis devices operating under benign neutral pH is highly demanded. We investigated the electrocatalytic activity of Ruddlesden-Popper-type strontium ferrite (Sr$_3$Fe$_2$O$_7$) toward the oxygen evolution reaction (OER). Owing to the temperature-dependent efficiency of the charge disproportionation of Fe$^{4+}$, the OER activity of Sr$_3$Fe$_2$O$_7$ varied with the temperature, and the onset potential for the OER at a neutral pH underwent a negative shift of approximately 200 mV by increasing the temperature for the stabilization of Fe$^{4+}$. When metal substitution was made to Sr$_3$Fe$_2$O$_7$ for stabilizing Fe$^{4+}$ at room temperature, the temperature dependence of the OER activity disappeared and the OER was driven at a small overpotential without increasing the temperature, indicating that the stabilization of Fe$^{4+}$ is substantially important for achieving high OER activity.

**Keywords**

Oxygen Evolution, Charge Disproportionation, Water-Splitting, Sr$_3$Fe$_2$O$_7$

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**1. Introduction**

The ever-growing global energy consumption has triggered considerable interest in addressing the challenge of storing renewable energy in a chemical form [1] [2]. One promising solution to this issue is to produce hydrogen (H$_2$) by using solar energy to split water into H$_2$ and oxygen (O$_2$) [3] [4] [5]. As a four-electron transfer reaction, the O$_2$ evolution reaction (OER, 2H$_2$O $\rightarrow$ O$_2$ + 4H$^+$ + 4e$^-$), which is a half-reaction of water splitting, suffers from sluggish kinetics...
owing to a large overpotential and has been considered to be the efficiency-limiting step of water splitting. Therefore, extensive research has been devoted to developing O₂ evolution catalysts [6]-[15]. Iridium oxide (IrO₂) and ruthenium oxide (RuO₂) are effective OER catalysts for solar water splitting as they exhibit high turnover frequencies under neutral pH conditions [6] [7] [8]; however, their high cost and scarcity render their use impractical for large-scale applications. Thus, it is important to develop active OER catalysts using earth-abundant elements.

In the past few decades, many earth-abundant metal oxides have been investigated [9] [10] [11] as potential OER catalysts to replace IrO₂ and RuO₂. Among them, iron (Fe) oxide is attractive because Fe is the most abundant first-row transition metal on Earth and nontoxic. Several Fe-based OER catalysts have been reported to show excellent activity [12] [13] [14] [15]. For example, Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃δ and CaCu₃Fe₄O₁₂ have high activity comparable to that of IrO₂ and RuO₂ in an alkaline solution [12] [13]. Despite these achievements; however, substantial improvements in the design and preparation of catalysts are still needed because few Fe-based OER catalysts function effectively under neutral pH conditions [16] [17] [18]. Therefore, for the successful application of Fe-based catalysts as components for solar fuel production systems, improvement of their OER activity under neutral pH conditions is essential.

Recently, numerous studies have been conducted to investigate the mechanism of the OER on Fe oxides by using various spectroelectrochemical techniques [18] [19] [20] [21] [22]. On the basis of the results of in situ UV-vis measurement, we have reported that Fe⁴⁺ is the intermediate species of the OER on a hematite (α-Fe₂O₃) electrode [18] [19]. Hamann et al. observed a potential-dependent infrared absorption peak, which they attributed to a high-valent Fe⁴⁺-oxo species, and proposed that the rate-determining step of the OER is Fe⁴⁺-OH → Fe⁴⁺ = O + e⁻ + H⁺ [20]. Chen et al. conducted in situ Mössbauer measurements and observed signals indicating that the formation of Fe⁴⁺ proceeds on NiFe hydroxide during the electrocatalysis of the OER [21]. Concerning a descriptor for OER activity, Suntivich et al. reported that near-unity occupancy of the eg orbitals of transition-metal ions at the B-site of perovskites (formula ABO₃) is essential to obtain high OER activity [12]. Notably, the Fe⁴⁺ ion that is formed on metal oxides has the high-spin d⁴ configuration of t₂g⁴e₈ [23] [24], and its formation satisfies the conditions required for high OER activity. On the basis of these reports, we hypothesize that the accessibility to Fe⁴⁺ is a possible descriptor for the OER activity of Fe-based catalysts [25]. Ruddlesden-Popper-type strontium ferrite (Sr₃Fe₂O₇) contains Fe⁴⁺ which is unstable and consumed by charge disproportionation (CD) (2Fe⁴⁺→ Fe³⁺ + Fe⁵⁺) [26]. Notably, the CD of Fe⁴⁺ in Sr₃Fe₂O₇ can be suppressed by regulating the temperature and its chemical composition [26] [27] [28].

Thus, to examine the validity of the hypothesis that the accessibility to Fe⁴⁺ is a descriptor for the OER activity of Fe-based catalysts, we have investigated the OER activities of Sr₃Fe₂O₇ and its La- or Ti-substituted compounds at different
temperatures using electrochemical measurements. By increasing the temperature or substituting the foreign elements to suppress the CD of Fe⁴⁺, the enhancement of the OER activity was observed.

2. Experimental Section

2.1. Preparation of Electrodes

Sr₃Fe₂O₇ powder was synthesized by a solid-state reaction [26]. Stoichiometric amounts of α-Fe₂O₃ (Kojundo Chemical Lab., 99.9%) and strontium carbonate (SrCO₃, Kojundo Chemical Lab., 99.9%) were ground in a ball mill and calcinated in air at 900°C for 9 h. The resulting powder was pressed into pellets and sintered in air at 1300°C for 24 h. When Sr₂.₆La₀.₄Fe₂O₇ and Sr₃FeTiO₇ were prepared, stoichiometric amounts of lanthanum oxide (La₂O₃, Kanto Chemical, 98.0%) and titanium dioxide (TiO₂, Kanto Chemical, 98.0%) were added to the starting materials as reported in the literature [27] [28]. All chemical reagents were used without further purification.

Electrodes were prepared using a spray deposition method as reported previously [25]. Briefly, 300 mg of the synthesized powder sample was suspended in 200 mL of ethanol. The suspension was sprayed onto a clean conducting glass substrate (FTO-coated glass, resistance: 20 Ω/square; SPD Laboratory Inc.) at 170°C using an automatic spray gun (Lumina, ST-6; Fuso Seiki Co., Ltd.). After coating, the resultant transparent black film was calcinated at 500 °C in air for 2 h.

2.2. Characterization

The crystal structures of the electrocatalysts were analyzed by X-ray diffraction (XRD) using a PW-1700 X-ray diffractometer (PANalytical) with monochromatic Cu Kα radiation. XRD patterns were recorded from 15˚ to 80˚ in 2θ with a step size of 0.02˚ and a scan rate of 0.25˚/min. Scanning electron microscopy (SEM) inspection was performed using a scanning electron microscope (JSM-6500F, JEOL).

2.3. Electrochemical Measurements

Polarization curves were obtained with a commercial potentiostat and potential programmer (HZ-5000, Hokuto Denko). A platinum wire was used as a counter electrode. All potentials were measured against a silver/silver chloride reference electrode (Ag/AgCl/KCl(sat.)) and converted to the standard hydrogen electrode (SHE) reference scale using the equation \( U(\text{versus SHE}) = U(\text{versus Ag/AgCl/KCl (sat.)}) + 0.197 \). The electrolyte solution used for all experiments was 0.1 M sodium sulfate (Na₂SO₄) aqueous solution, which was prepared from highly pure Milli-Q water (18 MΩ-cm) and Na₂SO₄ (Kanto Kagaku, 99.0%). The pH was adjusted to 7 using 0.1 M sulfuric acid (H₂SO₄, Kanto Kagaku, 96.0%) and 0.1 M sodium hydroxide (NaOH, Kanto Kagaku, 97.0%). No agent for pH buffering was added to the electrolyte solution to avoid effects from the adsorption of multivalent anions. Prior to the measurement, the electrolyte was maintained at
a certain temperature and bubbled with argon gas for at least 15 min. Polarization curves were measured by sweeping the electrode potential from the rest potential to 1.5 V at a scan rate of 10 mV/s and the concentration of O₂ dissolved in the electrolyte was monitored during the potential sweep using a needle-type O₂ microsensor (Microx TX3-trace, PreSens). The current density was normalized to the geometric surface area of the electrode.

3. Results and Discussion

3.1. Characterization of the Prepared Electrodes

Figure 1 shows the XRD patterns of Sr₃Fe₂O₇ and its substituted materials Sr₂.6La₀.4Fe₂O₇ and Sr₂FeTiO₇. All materials exhibited XRD patterns indexed to the tetragonal space group I4/mmm as reported in the literature [26] [27] [28], and no peaks assignable to other crystal phases were detected. The peak position of the prepared Sr₃Fe₂O₇ (Figure 1(a)) matched with a reference data (Figure 1(b), ICSD no. 163173). In contrast, the intensity of the diffraction peaks corresponding to (00h) planes was particularly intense for our prepared Sr₃Fe₂O₇. This can be understood by the preferred orientation of the Sr₃Fe₂O₇ particles which have plate-like shapes (Figure 2(a)) owing to its two-dimensional (2-D)

![Figure 1](image)

**Figure 1.** XRD patterns of synthesized crystalline powder ((a) Sr₃Fe₂O₇; (b) Sr₂.6La₀.4Fe₂O₇ and (c) Sr₂FeTiO₇) and (d) reference data (Sr₃Fe₂O₇, ICSD no. 163173). Peaks marked with (▲) in trace (a) correspond to (00h) diffraction peaks. (e) Shift of diffraction peaks to a lower angle upon substituting metal ions.
layered crystal structure composed of stacked rock salt and perovskite layers with the sequence of SrO-(SrFeO$_3$)$_2$. For Sr$_{2.6}$La$_{0.4}$Fe$_2$O$_7$ and Sr$_3$FeTiO$_7$, shifts of the diffraction peaks to lower angles were observed (Figure 1(e)), confirming that cationic substitution had taken place. The peak shift was larger for Sr$_3$FeTiO$_7$ as the expansion of the crystal lattice has been reported to be more prominent for Sr$_3$FeTiO$_7$ than Sr$_{2.6}$La$_{0.4}$Fe$_2$O$_7$ [27] [28].

Figure 2 shows SEM images of the prepared film electrodes. The Sr$_3$Fe$_2$O$_7$ particles had a diameter ranging from 1 μm to 8 μm (Figure 2(a)). In contrast, the particle sizes of Sr$_{2.6}$La$_{0.4}$Fe$_2$O$_7$ and Sr$_3$FeTiO$_7$ were approximately from 0.3 μm to 1.2 μm (Figure 2(b) and Figure 2(c)). All the samples were uniformly deposited on the electrodes. From the cross-section image in Figure 2(d), the thickness of the deposited film was found to be approximately 500 nm.

3.2. Electrocatalytic Activity of Sr$_3$Fe$_2$O$_7$ Electro catalysts

Figure 3 shows polarization curves of a Sr$_3$Fe$_2$O$_7$ film electrode measured at pH 7. Irrespective of the temperature, we observed simultaneous increases in the anodic current and O$_2$ concentration while neither of them was observed at this potential by using a bare FTO electrode (data not shown). In contrast to the typical polarization curves for OER, Sr$_3$Fe$_2$O$_7$ showed a slight decrease in the anodic current upon sweeping the electrode potential. This decrease is because a part of Sr$_3$Fe$_2$O$_7$ transformed to Sr$_3$Fe$_2$(OH)$_{12}$ during the measurements by intercalation of water molecules between its two rock-salt-type SrO layers [29].

However, because this transformation causes no anodic current and O$_2$ formation, we can consider that the observed results indicate that the OER was electrocatalyzed on Sr$_3$Fe$_2$O$_7$.

Notably, when the temperature of the electrolyte was increased from 30°C to 70°C, the anodic current showed a negative shift of the onset potential of approximately 200 mV. Since the onset potential for O$_2$ formation was similarly
shifted, these results indicate that the OER activity of Sr$_3$Fe$_2$O$_7$ is improved by increasing the temperature. As demonstrated in a solid oxide electrolysis cell (SOEC), the OER is thermodynamically more favorable at a high temperature and the standard potential of the OER becomes more negative with increasing temperature owing to a decrease in the Gibbs free energy required for the OER [30]. However, the potential shift due to the change in the Gibbs free energy is estimated to be at most only 40 mV at 70°C because of the small temperature difference between 30°C and 70°C. Thus, the observed improvement of the OER activity should originate from a temperature-dependent property of Sr$_3$Fe$_2$O$_7$.

As described in the introduction, Fe$^{4+}$ is considered to play an important role in the OER on Fe-based catalysts; however, Fe$^{4+}$ is unstable against CD and rapidly disappears in usual [26] [28] [29] [31] [32] [33]. According to the literature, the efficiency of CD is closely related to the electronic bandwidth of $\sigma^*$ bonding composed of Fe-3d and O-2p$\sigma^*$ orbitals, and CD occurs when the bandwidth of $\sigma^*$ bonding is narrow [31] [32]. For Fe-based perovskite compounds, the bandwidth broadens at high temperatures because with increasing temperature, the Fe-O-Fe bond angle increases and the electronic interaction between Fe and O strengthens [31] [32]. Kuzushita et al. investigated the temperature dependence of the Fe$^{4+}$ stability by performing Mössbauer measurements and found that there is a critical temperature for the CD of Sr$_3$Fe$_2$O$_7$ at 70°C ± 10°C, indicating that CD is suppressed above 70°C [26]. Therefore, the observed enhancement of OER activity at 70°C is considered to be due to the suppression of the CD of Fe$^{4+}$.

To examine the validity of the interpretation that the stabilization of Fe$^{4+}$ leads to the enhancement of the OER activity of Sr$_3$Fe$_2$O$_7$, we also investigated the effect of Fe$^{4+}$ stability on the OER activity using the metal-substituted materials. **Figure 4(a)** shows the polarization curves of Sr$_{2.6}$La$_{0.4}$Fe$_2$O$_7$ measured at 30°C and 70°C. Unlike Sr$_3$Fe$_2$O$_7$, the anodic current initiated to increase from essentially the same potential for both temperatures, which is consistent with the
Figure 4. Polarization curves of (a) Sr$_{2.6}$La$_{0.4}$Fe$_2$O$_7$ and (b) Sr$_3$FeTiO$_7$ electrodes measured at 70˚C (red line) and 30˚C (black line).

fact that the substitution of Sr with La suppresses CD at room temperature and that Fe$^{4+}$ in Sr$_{2.6}$La$_{0.4}$Fe$_2$O$_7$ is stable at both 30˚C and 70˚C [27]. When the OER was conducted with Sr$_3$FeTiO$_7$, in which Fe$^{4+}$ is stably contained at room temperature [28], the onset potential was independent of temperature. Thus, the stabilization of Fe$^{4+}$ is an effective means of enhancing the OER activity of Fe oxide. As shown in Figure 4(a) and Figure 4(b), a higher current density was observed at 70˚C.

Although the reason for this is unclear, it is assumed to be due to the greater convection of the electrolyte. Notably, the onset potentials observed with these substituted materials were almost the same as that observed for Sr$_3$Fe$_2$O$_7$ at 70˚C, indicating that the efficient formation of Fe$^{4+}$ on Sr$_3$Fe$_2$O$_7$ derivatives enables the initiation of the OER around this potential. From a comparison of the polarization curves (Figure 3, Figure 4(a) and Figure 4(b)), the current density of Sr$_3$Fe$_2$O$_7$ at 70˚C was larger than those of metal substituted derivatives at the same temperature. This is likely to be due to higher concentration of Fe$^{4+}$ in Sr$_3$Fe$_2$O$_7$.

From the above results, the OER activity of Sr$_3$Fe$_2$O$_7$ derivatives is considered to be determined by the efficiency of Fe$^{4+}$ formation, and the suppression of CD was found to be effective for designing active OER catalysts. CD is known to take place not only with Fe$^{4+}$ but also with other first-row transition-metal ions [31] [32]. Previously, one of the authors (T. T.) showed that the CD of Mn$^{3+}$ is the primary origin of the pH-dependent OER activity of MnO$_2$ and succeeded in enhancing OER activity under a neutral pH by suppressing CD [34] [35] [36]. Thus, by analogy with Fe$^{4+}$ and Mn$^{3+}$, the stabilization of other first-row transition-metal ions by suppressing CD is likely to be a promising approach for the development of active OER catalysts made from abundant elements. Fe ions introduced in layer-structured metal (hydr) oxides have been reported to form Fe$^{4+}$ without causing CD [37] [38]. The application of Fe-doped layered materials to the OER is currently underway in our laboratory.
4. Conclusion

In this study, the OER activity of Sr$_3$Fe$_2$O$_7$ was investigated at 30˚C and 70˚C under neutral pH conditions. The onset potential for the OER of a Sr$_3$Fe$_2$O$_7$ electrode was found to be dependent on the temperature and shifted by approximately 200 mV in the negative direction with increasing temperature. This enhancement of the OER activity is considered to be due to the fact that Fe$^{4+}$ is stably formed by suppressing CD at 70˚C, and the stabilization of Fe$^{4+}$ by metal substitution enabled efficient OER catalysis at room temperature. Unfortunately, Sr$_3$Fe$_2$O$_7$ derivatives underwent the transformation in aqueous solution; however, these findings will provide insights for designing Fe oxide OER catalysts that can evolve O$_2$ efficiently under neutral pH conditions.

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