



Metalloporphyrin-modified perovskite-type oxide for the electroreduction of oxygen



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HIGHLIGHTS

- We prepared cobalt octaethylporphyrin (Co-OEP)-modified perovskite/carbon catalysts.
- ORR activity of perovskite/carbon was enhanced by Co-OEP-modification.
- RRDE measurements suggested that the 2 + 2 electron reduction of O₂ is promoted.
- The porphyrin plays a role as a two-electron O₂ reduction catalyst to give HO₂⁻.
- HO₂⁻ is further reduced to OH⁻ by the perovskite-type oxide.

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ABSTRACT

Perovskite-type oxide-carbon (Vulcan XC72) mixture (La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O₃/C) was modified by a metalloporphyrin (cobalt octaethylporphyrin: Co-OEP) having two-electron O₂ reduction activity, and its electrochemical reduction activity for O₂ (ORR) was investigated in an alkaline solution by rotating ring disk electrode (RRDE) voltammetry. The Co-OEP/La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O₃/C catalyst showed improved ORR activity, with a positive shift of the onset potential. In addition, a decreased ring current compared to Co-OEP/C suggested that the quasi-four-electron reduction of O₂ was also enhanced. Further experiments showed that ORR activity was also enhanced by Co-OEP-modification of other types of carbon (Ketjen-black EC600JD, Denka Black) or perovskite-type oxide (La_{0.6}Ca_{0.4}Mn_{0.6}Fe_{0.4}O₃, La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O₃). In the case of the addition of other porphyrin complexes (cobalt tetraphenylporphyrin (Co-TPP), iron octaethylporphyrin (Fe-OEP)) to a La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O₃/C catalyst, the onset potential did not shift to the positive side due to the lower activity compared to Co-OEP.

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1. Introduction

The electrocatalytic oxygen reduction reaction (ORR) is an important process in energy-conversion technologies such as fuel cells and metal-air batteries. Compared to acid-based proton exchange membrane fuel cells, alkaline fuel cells (AFCs) have attracted attention because of the possibility of faster kinetics and the potential use of less costly non-precious metal catalysts [1–5].

The mechanism of the ORR in alkaline media has been reported

previously. In the ORR under alkaline conditions, there are two main pathways: a direct four-electron pathway (eq. (1)) and a two-by-two electron pathway (eq. (2) and (3)) which involves an alkaline-stabilized hydrogen peroxide intermediate (HO₂⁻) [6–8]:



Additionally, hydrogen peroxide can undergo disproportionation according to eq. (4):



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To date, various kinds of non-Pt-based catalysts that offer the possibility of faster kinetics in alkaline solution have been proposed, such as carbon material [9,10], non-Pt-metal [3,11–13], metal oxide (ex., manganese oxide [14,15], perovskite-type oxide [16–18]), metal macrocycles [19,20]. Among them, perovskite-type oxides are considered to be an attractive candidate for use as alkaline-resistant electrocatalysts with high ORR activity. Furthermore, the enhancement of ORR activity and durability are also expected to result from optimization of the constituent elements and their composition, since the perovskite-type structure is composed of a 12-coordinate cation (mainly, rare-earth or alkaline earth) site (A-site), and a tetrahedrally-coordinated transition metal cation site (B-site). For example, in La–Mn-based oxides, it has been shown that partial substitutions at the La^{3+} site by alkaline-earth metals (ex. Sr^{2+} , Ca^{2+}) and at the Mn^{3+} site by transition metals (ex. Fe^{3+}) can improve both the ORR activity and durability [21,22].

To apply a perovskite-type oxide as an electrocatalyst, conductive additive carbon is often added to the perovskite electrode since perovskite possesses relatively low electrical conductivity. Carbon also plays a role as a two-electron O_2 reduction catalyst to give a hydrogen peroxide intermediate (HO_2^-) in alkaline media (eq. (2)) [23,24]. Recently, the ORR activities of perovskite-type oxide thin film electrodes, for which can be neglected the contribution of carbon in ORR kinetics, have been studied, and it has been verified that perovskite thin films (La–Mn-based and La–Co-based oxide) possess faster kinetics for 2-electron HO_2^- reduction (eq. (3)) and/or disproportionation of H_2O_2 (eq. (4)) than for four-electron O_2 reduction (eq. (1)) [25]. Poux et al. [26] also reported that the La–Mn based perovskite ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$) and La–Co based perovskite (LaCoO_3) in a carbon supported catalyst contribute to the reduction and/or disproportionation of H_2O_2 . These studies suggest that O_2 reduction reaction to HO_2^- (eq. (2)) may be the rate-limiting process for a carbon-supported perovskite electrocatalyst. Therefore, it should be possible to promote the overall reaction on a carbon-supported perovskite catalyst by introducing a co-catalyst with high two-electron O_2 reduction activity.

As catalysts with two-electron reduction activity to generate HO_2^- from O_2 , metal complexes such as cobalt (or iron) porphyrin and phthalocyanine are well known [27–30]. So far, catalysts that combine these complexes with manganese oxides, which cause the disproportionation of H_2O_2 , have been reported [31]. This combined catalyst promotes the two-electron reduction reaction to give HO_2^- from O_2 (eq. (2)) and the subsequent chemical decomposition of H_2O_2 to O_2 and H_2O (eq. (4)) to achieve a pseudo four-electron reduction process.

From this background, it should be possible to enhance the ORR activity of a perovskite-type oxide based catalyst through modification with a metallocomplex having two-electron O_2 reduction activity. Up to now, catalysts using metalloporphyrin and perovskite-type oxide were reported; however, it was a heat-treated-product (at 700°C) and the effects and roles of metalloporphyrins remain unclear [32]. In this study, we prepared a porphyrin complex-modified perovskite-type oxide/carbon catalyst. The ORR activity and electron number of the catalyst was investigated in alkaline media by the rotating ring disk electrode (RRDE) method. The influence of the composition of the catalysts on the ORR activity was also examined by using several types of carbon black, porphyrin complexes, and perovskite-type oxides.

2. Experimental

2.1. Sample preparation

An increase in the specific surface area of a perovskite-type

oxide is considered to improve its catalytic activity. The polyvinyl pyrrolidone (PVP) method [33] was used to prepare nano-sized perovskite-type oxides. The perovskite-type oxides ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.6}\text{Fe}_{0.4}\text{O}_3$, $\text{La}_{0.6}\text{Ca}_{0.4}\text{Mn}_{0.6}\text{Fe}_{0.4}\text{O}_3$, and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_3$) were synthesized using PVP as follows. Stoichiometric amounts of the corresponding metal nitrates ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Wako, 99.9%; 1.2990 g (for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.6}\text{Fe}_{0.4}\text{O}_3$, $\text{La}_{0.6}\text{Ca}_{0.4}\text{Mn}_{0.6}\text{Fe}_{0.4}\text{O}_3$) or 1.7320 g (for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_3$)), $\text{Sr}(\text{NO}_3)_2$ (Aldrich, 99.95%; 0.4233 g (for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.6}\text{Fe}_{0.4}\text{O}_3$) or 0.2117 g (for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_3$)), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Aldrich, 99.9%; 0.4723 g), $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako, 99.9%; 0.8611 g), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako, 99.9%; 0.8731 g) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Wako, 99.9%; 0.8080 g) and PVP (ca. 6.0 g) were dissolved in ultrapure water (100 ml). The aqueous solutions were heated to vaporize water at 100°C , and the obtained precursors were fired in air at 600°C for 6 h. For calcination, the temperature was increased at a constant rate of $20^\circ\text{C min}^{-1}$.

The perovskite–carbon mixture (perovskite/C) was prepared by mechanical milling [34]. Perovskite-type oxide (0.24 g) and carbon black (Vulcan XC72, Ketjenblack EC600JD, Denka Black; 0.08 g) were mixed in a weight ratio of 3:1 in an agate pot at a rotation speed of 400 rpm for 30 min using a planetary ball milling apparatus (FRITTSCH GmbH, P-7).

Porphyrin complexes were adsorbed on perovskite/C by an evaporation-to-dryness method [35]. We used three porphyrin complexes with different molecular structures (Fig. 1(a)): cobalt octaethylporphyrin (Co-OEP; Aldrich ($[\text{Co}^{\text{II}}(\text{OEP})]$)), iron octaethylporphyrin (Fe-OEP; Aldrich ($[\text{Fe}^{\text{II}}(\text{OEP})(\text{Cl})]$)), and cobalt tetraphenylporphyrin (Co-TPP; Aldrich ($[\text{Co}^{\text{II}}(\text{TPP})]$)). The amount of porphyrin complex ($0.6 \mu\text{mol}$) on the perovskite/C support (30 mg) was constant at $20 \mu\text{mol g}_{\text{support}}^{-1}$. Fig. 1(b) shows a schematic illustration of the porphyrin-modified perovskite/carbon catalyst. In the present catalyst, both a porphyrin complex and a perovskite-type oxide were supported on carbon. The porphyrin (and carbon) acts as a two-electron O_2 reduction catalyst to give a hydrogen peroxide intermediate (HO_2^-), and the produced HO_2^- is then

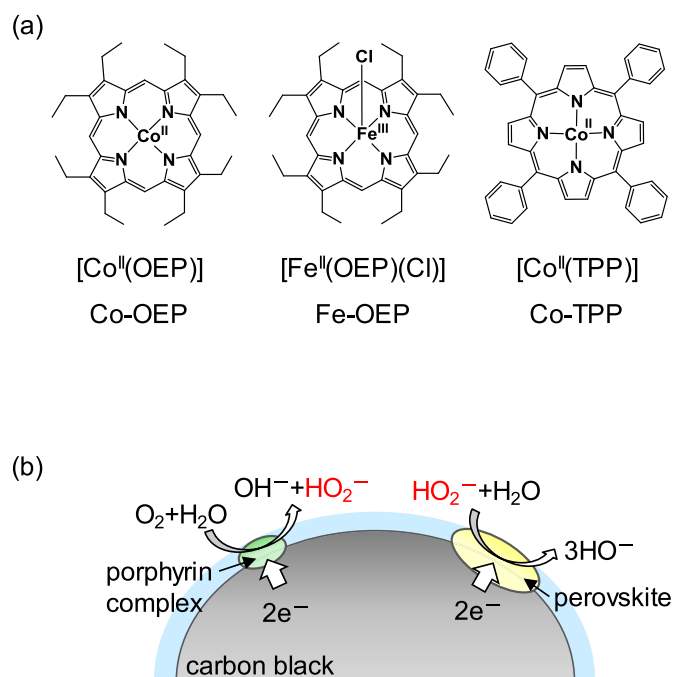


Fig. 1. Schematic illustration of the porphyrin-modified perovskite/carbon catalyst (a), and structures of the porphyrin complexes which used in this study (b).

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