Composition, valence and oxygen reduction reaction activity of Mn-based layered double hydroxides

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ABSTRACT
The oxygen reduction reaction (ORR) activity and cation valences of Mn-based Ni–Mn–Fe and Mg–Mn layered double hydroxides (LDHs) with various compositions were studied. The valences of the 3D transition metals (Mn, Fe, and Ni) were examined by X-ray absorption. The average valence of Ni was approximately 2, and that of Mn was approximately 3 in the LDHs investigated in this study. The valence of Fe decreased with increases in the Mn/Fe ratio. Increasing the amount of Mn enhanced the ORR activity, while the valences and surface areas of the LDHs had no significant effect on the activity.

1. Introduction
Alkaline fuel cells [1,2] and metal air batteries [3,4] have attracted significant attention as next-generation power sources. The oxygen reduction reaction (ORR) is an important electrochemical reaction occurring in the air electrodes of fuel cells and metal-air batteries. Pt and Pt-based nanoparticles can act as catalysts for ORRs, but these nanoparticles are very expensive. Development of a catalyst using 3D transition metals with small overpotential is consequently essential. Manganese compounds such as α-MnO2 [5], LaMnO3 [6], and Mn (O, N) [7] have been reported as Pt-free ORR catalysts in alkaline solutions. The correlation between electronic structures and ORR activity has been studied extensively, and a single electron in the antibonding state achieved by trivalent manganese in octahedral coordination, was determined to be favorable for high ORR activity [6,7].

Layered double hydroxides (LDHs) have the general formula [M2(1-x)AxA+x(OH)2]x[A−n/2+yn/H2O], where M2+ is divalent cations (Mg2+, Mn2+, Co2+, Ni2+, or Zn2+), M3+ is trivalent cations (Al3+, Cr3+, Fe3+, or Co3+), and A− is anions such as CO32− and Cl−. The conductivity of hydroxide ions [8–11] and a large specific surface area [12,13] are favorable factors for ORR in alkaline solutions. In addition, multiple metal ions occupying octahedral sites afford flexibility in their electronic structure. Thus, LDHs are interesting motifs for investigating the correlation between electronic structures and ORR activity.

The valence of transition metals in LDHs is mostly investigated by X-ray photoelectron spectroscopy (XPS) with Al or Mg X-ray sources under high-vacuum conditions [14]. Nonetheless, valence assignment in the bulk state is difficult because XPS is a surface-sensitive analysis and the spectra must be interpreted using overlapping signals with slightly different energies (typically <1–3 eV). XPS analysis of the surface relies on irradiated X-rays; moreover, since LDHs have low electronic conductivity, X-ray absorption spectroscopy is a powerful technique for examining the valence of metals in bulk states regardless of their electronic conductivity. This technique has sufficient energy resolution to estimate the valence and has been utilized to examine the correlation between electronic structures and catalytic activity in oxides and oxy nitrides [6,7,15].

Reports regarding ORR and oxygen evolution reaction (OER) catalysis by LDH have recently drawn attention. Since LDHs have low electron conductivity, their combination with an electronic conductor, typically carbon, is essential. The addition of Ni–Mn–Fe LDH to air electrodes enhanced the current generated by the ORR activity on Pt nanoparticles in Vulcan® carbon [16]. LDHs mixed with reduced graphene oxides (rGO) and multiwall carbon nanotubes (MWCNTs) such as Ni–Mn LDH/rGO [17], Ni–Mn LDH/MWCNTs, and Co–Mn LDH/MWCNTs [18] have shown excellent OER activity. Co–Mn–Ni LDH with rGO [19] and Ni–Fe–Mn LDH with carbon black [20] have been used as ORR catalysts. However, the influence of the Mn content and electronic state of LDHs on ORR activity has not yet been investigated.
In this study, we investigated the valences of the transition metals and ORR activity in Ni–Mn–Fe and Mg–Mn LDHs. We found that the average valence of Mn was approximately 3 in all LDHs investigated in the study. Their ORR catalytic activity was independent of the Mn valence but was enhanced by increasing the Mn ratio.

2. Experimental

2.1. Chemicals

The following chemicals were used without further purification: Mg(NO$_3$)$_2$·6H$_2$O (Wako Pure Chemical, 99.0%), Ni(NO$_3$)$_2$·6H$_2$O (Wako Pure Chemical, 98.0%), Fe(NO$_3$)$_3$·9H$_2$O (Wako Pure Chemical, 99.9%), Mn(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich, 98.0%), NaOH (Kanto Chemical, 97.0%), and Na$_2$CO$_3$ (Wako Pure Chemical, 99.8%).

2.2. Preparation

Ni–Mn–Fe LDH and Mg–Mn LDH were synthesized using the co-precipitation method. An aqueous solution with 0.05 M metal nitrates was dropped into a Na$_2$CO$_3$ solution under a nitrogen or ambient atmosphere to obtain precipitates. During the synthesis, NaOH solution was added dropwise to maintain the pH at 10. Thereafter, the mixed solution was kept at room temperature for 1 h for the Ni–Mn–Fe LDH sample and 18 h for the Ni–Fe LDH and Mg–Mn LDH samples. The precipitates were subsequently filtered, washed with distilled water, and dried under vacuum at room temperature for 18 h.

2.3. Characterization

X-ray diffraction (XRD) patterns were measured using an X-ray diffractometer (Rigaku, MiniFlex 600) with CuKα radiation ($\lambda = 0.15418$ nm). The morphology of the samples was observed with a field emission scanning electron microscope (FE-SEM, JEOL, JSM-6500F). The nitrogen adsorption isotherms were measured after the samples were dried at 80°C for one day. The composition of metals in the synthesized LDHs was determined by inductively coupled plasma (ICP, SHIMADZU ICPE-9000). The X-ray absorption spectra were measured in the transmission mode at BL5S1 and BL6N1 at the Aichi Synchrotron Radiation Center (Proposal number 201606008 and 201704041) to evaluate the valences of the transition metals in the LDHs.

2.4. Electrochemical measurement

A catalyst suspension was prepared by mixing 2.0 mg of LDH, 2.0 mg of Vulcan® (Cabot Corporation), 60 µL of 5.0 wt.% 1-propanol solution of anion exchange resin (Tokuyama), and 540 µL of C$_2$H$_5$OH (Kanto Chemical, 95.5%). After the suspension was sonicated for 30 minutes, thin-film electrodes on glassy carbon disks (4 mm in diameter) were prepared by five-times repeated pipetting and drying of 1.5 µL of the suspension. The above procedure yielded a catalyst density loading of 200 µg LDH/cm$^2$ disk.

Electrochemical measurements were performed using a three-electrode setup with a rotating disc electrode (RDE) device (BAS, RRDE-3A). A Hg/HgO electrode was used for the reference electrode, a Pt electrode was used for the counter-electrode, and an RDE was used for the working electrode. The reference potential was converted to reference the reversible hydrogen electrode (RHE) by applying the Nernst equation [7] as shown in Equation (1):

$$E_{\text{RHE}} = E_{\text{vol}} - 0.0980 + 0.0591 \times \text{pH} \quad (1)$$

1 M KOH solution was used as the electrolyte for the electrochemical measurements. Simultaneously with the application of the catalyst ink, oxygen gas was flowed into the electrolytic solution to induce an oxygen-saturated state. Subsequently, linear sweep voltammetry was performed at a scan rate of 5 mV s$^{-1}$.

The number of reaction electrons (n), a key parameter of ORR activity, was calculated based on the Koutecky–Levich (KL) equations [21] as shown in Equation (2):

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{J_L} + \frac{1}{J_B} \frac{1}{\omega^n} \quad (2)$$

where $J$ (mA cm$^{-2}$) is the measured current density; $J_K$ and $J_L$ (mA cm$^{-2}$) are the kinetic- and diffusion-limiting current densities, respectively; $\omega$ is the angular velocity ($\omega = 2\pi f$, where $f$ is rotation rate (rpm)); F is the Faraday constant (96,485 C mol$^{-1}$); $D_0$ is the diffusion coefficient ($1.80 \times 10^{-5}$ cm$^2$ s$^{-1}$); $v$ is the kinematic viscosity of the electrolyte ($1.0 \times 10^{-5}$ cm$^2$ s$^{-1}$); and $C_0$ is the bulk concentration of O$_2$ (7.8 $\times 10^{-7}$ mol cm$^{-3}$) [22].

3. Results

3.1. Structural characterization of LDHs

Figure 1 shows the XRD patterns of the LDHs. Since LDH peaks were observed in all the compositions, it was confirmed that LDHs were formed as the main phase in the samples. In Ni–Mn–Fe LDH, the diffraction peak 012 shifted to a lower angle as the Mn ratio increased, presumably due to a reduction in Fe ions, as described later. Weak peaks corresponding to Mn$_3$O$_4$ were also confirmed at $x = 0.80$. The stabilities of LDHs in 1.0 M KOH solution for 24 h were examined by XRD. While the XRD patterns (Figure
S1 in the supporting information) of LDHs with $x = 0–0.60$ showed the peaks assigned as LDHs, $\text{Mn}_3\text{O}_4$ was formed in the LDH with $x = 0.80$. Table 1 shows the compositions, lattice parameters, and specific surface areas of the tested LDHs. The chemical compositions of LDHs determined by ICP were nearly identical to the ratio of metal nitrates in the starting materials. In Ni–Mn–Fe LDH, the lattice parameters of the $a$-axis increased with increases in the Mn ratio, and those of the $c$-axis showed no clear trend. The surface areas of the samples ranged between 30 and 140 m$^2$ g$^{-1}$, and the lattice parameters of $\text{Mg}_{6.67–\text{Mn}_{0.33}}$ LDH were similar to the reported values [23].

Representative SEM images of the LDHs are shown in Figure 2. Characteristic plate-like structures were observed in every sample, with particle sizes ranging from 50 to 500 nm.

Figure 3 shows the X-ray absorption spectra of the LDHs for purposes of qualitative discussion concerning the valences of transition metals. We discuss the valence of transition metals by using references; the absorption edges in these references are similar to our results where Ni, Mn, and Fe LDH, the lattice parameters of the $a$-axis and $c$-axis were obtained by substituting the values of $d_{002}$ and $d_{012}$ obtained from the X-ray diffraction into the following equation: $d = \frac{2 \lambda}{\sqrt{h^2 + k^2 + l^2}}$. The current density at $-25 \mu A cm^{-2}$ showed a slight decrease in potential for 4 h, indicating moderate catalytic stability (Figure S2). However, further investigation of the stability of the crystal structures and valences of LDHs will be necessary.

### 3.2. ORR measurement

Figure 4(a) shows the linear sweep voltammetry results where $\text{Ni}_{0.75–\text{Fe}_{0.25}}$ LDH showed ORR activity as low as that for Vulcan® alone without LDH. The onset potential shifted in the direction of the noble metal potential, and the current density increased with increases in the Mn ratio. The Koutecky–Levich plots corresponding to a rotation rate of 400–2500 rpm and $-0.324$ V vs RHE were linear, and the number of reaction electrons was estimated to be 2.16 for $\text{Ni}_{0.60–\text{Mn}_{0.20}}–\text{Fe}_{0.20}$ LDH, 3.29 for $\text{Ni}_{0.20–\text{Mn}_{0.60}}–\text{Fe}_{0.20}$ LDH, and 3.88 for $\text{Mn}_{0.80–\text{Fe}_{0.20}}$ LDH (Figure 4(b)). Current density therefore increased in LDHs with a high Mn content, the valence of Fe was slightly higher than 3. Conversely, for samples with $x = 0.80$, the valence was lower than 3. In $\text{Mg}_{6.67–\text{Mn}_{0.33}}$ LDH, the average valence of Mn was almost 3, as estimated by the energy of the normalized absorption intensity of 0.5. This was consistent with the estimation in a previous report regarding Mg–Mn LDH [23,30].

### 4. Discussion

We examined the cation valences and ORR activities of various LDHs with different Mn ratios. The overpotential of the ORRs decreased with increases in the

### Table 1. Structural parameters of LDHs.

| Number | Mn ratio of cations | Composition* | Lattice constants/ nm$^b$ | Specific surface area/m$^2$ g$^{-1}$ | Onset potential/V (vs. RHE)$^c$ |
|--------|---------------------|--------------|--------------------------|---------------------------------|-------------------------------|
| 1      | $x = 0$             | Ni$_{0.75}$–Fe$_{0.25}$ | $a = 0.310, c = 2.32$   | 66                              | 0.818                         |
| 2      | $x = 0.20$          | Ni$_{0.60}$–Mn$_{0.20}$–Fe$_{0.20}$ | $a = 0.310, c = 2.28$   | 105                             | 0.832                         |
| 3      | $x = 0.40$          | Ni$_{0.40}$–Mn$_{0.40}$–Fe$_{0.20}$ | $a = 0.315, c = 2.35$   | 35                              | 0.846                         |
| 4      | $x = 0.60$          | Ni$_{0.20}$–Mn$_{0.60}$–Fe$_{0.20}$ | $a = 0.319, c = 2.32$   | 111                             | 0.849                         |
| 5      | $x = 0.80$          | Mn$_{0.80}$–Fe$_{0.20}$ | $a = 0.320, c = 2.28$   | 134                             | 0.863                         |
| 6      | $x = 0.33$          | Mg$_{6.67}$–Mn$_{0.33}$ | $a = 0.312, c = 2.33$   | 67                              | 0.843                         |

*Chemical composition of the cations was determined by ICP. $^b$The lattice parameters of the $a$-axis and $c$-axis were obtained by substituting the values of $d_{002}$ and $d_{012}$ obtained from the X-ray diffraction into the following equation: $d = \frac{2 \lambda}{\sqrt{h^2 + k^2 + l^2}}$. $^c$The current density at $-25 \mu A cm^{-2}$.
Mn ratio (Figure 4(a)). Assuming that the active site of an ORR is a hydroxide ion where Mn is present in the nearest metal site, the number of active sites should increase with increases in the specific surface area, resulting in higher activity. The influence of the Mn ratio and specific surface area on the onset potential was therefore examined in detail. In Figure 5, the onset potentials (vs RHE) of the LDHs are plotted as a function of the ratio of Mn to total cations, and specific surface area (Figure 5(a,b), respectively). A strong positive correlation between the Mn ratio and onset potential (Figure 5(a)) can be observed. On the other hand, there is no clear correlation between the specific surface area and the onset potential (Figure 5(b)). Because the actual Mn active site concentration can be expressed as the Mn ratio multiplied by the surface area, the onset potential was also plotted as a function of the product of the Mn ratio and specific surface area (Figure 5(c)). The correlation between the onset potential and the product of the Mn ratio and specific surface area is not as strong as the Mn ratio. This indicates that not all Mn on the surfaces of LDHs are highly active sites. The specific configurations of Mn, such as the edges, defects, and interfaces with carbon, likely play an important role in their catalytic activity. Further investigation is necessary.

Based on the X-ray absorption spectra in Figure 3(a,b), the valences of Mn$^{3+}$ and Ni$^{2+}$ ions were estimated to be constant. This indicated that the catalytic capabilities and electronic structures of Mn and Ni were unrelated to each other. On the other hand, because the valence of Fe varied with the Mn ratio, the onset potential was plotted as a function of the Fe–K edge in Figure 6(a). The Fe–K edge is related to the average valence of Fe and shows a strong correlation with the onset potential. With increases in the Mn ratio, the lattice parameter of the a-axis also increased, as shown in Table 1. The a-axis parameter is related to the distance between transition metal ions, and the correlation between the onset potential and a-axis parameter is shown in Figure 6(b). The lattice parameter of the a-axis and the onset potentials exhibit a weak correlation, which is lower than the correlation with the Mn ratio. The Mn ratio also affects the lattice parameters and Fe valence. We can therefore conclude that the Fe valence and lattice parameter of the a-axis are not essential to
ORR activity, and that the Mn ratio is the most important factor governing ORR activity. In LDHs with an Mn-rich composition \((x = 0.80)\), however, \(\text{Mn}_3\text{O}_4\) was formed. Further examination of their electrochemical stability will be necessary, since our results do not guarantee stability during and after the electrochemical reaction.

5. Conclusion

This study demonstrated that increasing the Mn ratio in LDH is an important factor for improving the ORR activity of the catalysts. The average valence of Ni was approximately 2, and that of Mn approximately 3 in Ni–Mn–Fe LDH. The average valence of
Fe decreased with increases in the Mn ratio, and the average valence of Mn in Mg\textsubscript{0.67}–Mn\textsubscript{0.33} LDH was 3. The correlation between the onset potential of the ORR and various parameters indicated that a high Mn ratio was important for reducing the overpotential of the ORR.

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