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Oxygen K-edge X-ray Absorption Spectroscopy of $LaNiO_3$ and La_2NiO_4 for Oxygen Evolution Reaction Catalyst of Alkaline Water Electrolysis

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Oxygen evolution reaction (OER) activity and surface electronic structure of nickel-based perovskite oxide catalysts, $LaNiO_3$ and La_2NiO_4 was evaluated under alkaline water electrolysis conditions. Chronoamperometry measurements were carried out with 1 M KOH electrolyte, and electronic structural analysis was performed using O K-edge X-ray absorption spectroscopy (XAS). $LaNiO_3$ maintained OER activity with almost no change in its surface oxygen electronic structure, regardless of whether an alkaline treatment was applied. In contrast, La_2NiO_4 exhibited a disappearance of the O K-edge peak at 528 eV after alkaline treatment, accompanied by decrease in OER activity.

1. Introduction

Perovskite-type nickel oxide catalysts are among the candidate anode materials for alkaline water electrolysis. Previous studies have reported a correlation between the number of e_g electrons at the B-site cation of perovskite oxides and their OER overpotential [1]. In general, materials with an e_g electron count close to 1 tend to exhibit high OER activity. However, it is also known that the surface crystal and electronic structures of perovskite OER catalysts can change under OER operating conditions [2], meaning the bulk electronic state may not directly correlate with OER activity in some cases. A recent study using a rotating disk electrode (RDE) to evaluate $LaNiO_3$ and La_2NiO_4 reported that after an alkaline pretreatment, the OER current of La_2NiO_4 increased by a remarkable 45-fold compared to the untreated sample [3]. This suggests that surface modifications induced by alkaline treatment can have a significant impact on OER performance. In this study, we investigate $LaNiO_3$ and La_2NiO_4, focusing on how alkaline treatment affects their crystal structure, surface electronic structure, and OER activity. OER activity was evaluated in 1 M KOH using YNU electrochemical cell (with a binder-free catalyst electrode and a Zirfon separator membrane). Changes in bulk crystal structure were analyzed by X-ray diffraction (XRD), and changes in surface structure were investigated by O K-edge X-ray absorption spectroscopy (XAS) before and after alkaline treatment, as well as after OER durability testing.

2. Experimental

$LaNiO_3$ powder (Kojundo Chemical Lab. Co., Ltd.) was used as received, and La_2NiO_4 powder was synthesized via a sol-gel method. To perform alkaline treatment, each catalyst powder was immersed in 7 M KOH aqueous solution with oxygen gas bubbling, and stirred with a magnetic stirrer for more than 20 h. After the treatment, the powders were collected by filtration, thoroughly washed with deionized water to remove residual KOH, and then dried under vacuum at 80 °C. The OER activity of the catalysts was evaluated using the YNU cell [4] with 1 M KOH as the electrolyte. Each catalyst powder was applied to the electrode without any binder (forming a binder-free catalyst layer). A Zirfon® Perl UTP 500 porous diaphragm (Agfa-Gevaert) was employed as the separator. Chronoamperometry measurements were carried out to assess the OER performance, and an accelerated degradation test (ADT) of 200 cycles was conducted following a protocol reported in the literature [5]. During the chronoamperometry tests, current–time data were recorded and later used to show Tafel plots for comparison of catalytic activity.

XRD measurements were performed using a Rigaku Ultima IV diffractometer to examine the crystal structure of the samples before and after alkaline treatment. For surface electronic structure analysis, O K-edge XAS spectra were acquired at beamline BL-2 and BL-11 of Ritsumeikan University SR Center, in total electron yield (TEY) mode. O K-edge XAS measurements were conducted for each sample in three states: the powder samples before alkaline treatment, the powder samples after alkaline treatment, and the catalyst samples after the OER activity tests (post-ADT). Powder samples (before and after alkaline treatment) were mounted on a sample holder with carbon double-sided tape. For the post-ADT samples, each catalyst was subjected to three repeated ADT cycles; then the cell was disassembled and the portion of the Zirfon separator membrane with catalyst residue attached was cut out. These membrane pieces with adhering catalyst were mounted on a sample holder. XAS measurements in TEY mode primarily probe the top few nanometers of the sample surface, providing information on the surface oxygen species and electronic structure.

3. **Results and Discussion**

Fig. 1 shows the XRD patterns of $LaNiO_3$ and La_2NiO_4 powders before and after the alkaline treatment. All diffraction peaks can be assigned to the reported diffraction patterns [6,7], and no additional peaks or shifts were observed upon the alkaline treatment, indicating that the bulk crystal structure of both $LaNiO_3$ and La_2NiO_4 remains unchanged by the 7 M KOH treatment.

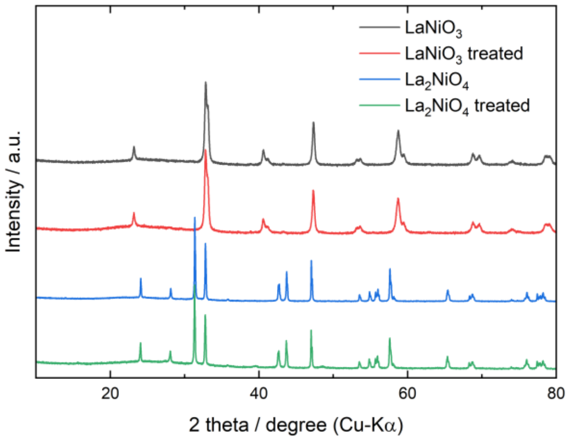

Fig. 1 XRD patterns of $LaNiO_3$ and La_2NiO_4 powders before and after the alkaline treatment.

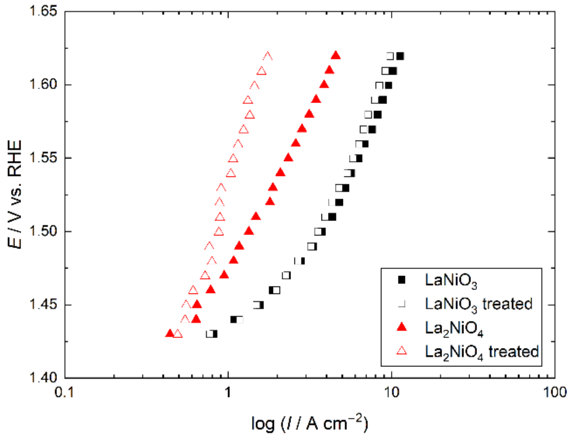

Fig. 2 Tafel plots derived from chronoamperometry of $LaNiO_3$ and La_2NiO_4 powders before and after the alkaline treatment.

Fig. 2 displays the OER activity of the catalysts as Tafel plots derived from chronoamperometry in 1 M KOH. In these plots, a catalyst that exhibits a curve positioned to the right is considered to have higher OER activity. It can be seen that $LaNiO_3$ delivers higher OER activity than La_2NiO_4 under all conditions tested. Moreover, the OER activity of $LaNiO_3$ shows little change due to the alkaline treatment, whereas for La_2NiO_4 the OER activity decreased after the treatment. These trends contrast with the earlier RDE-based study [3], which reported the enhancement of La_2NiO_4 activity after alkaline treatment. The alkaline treatment had no significant effect for $LaNiO_3$ and decreased OER activity for La_2NiO_4.

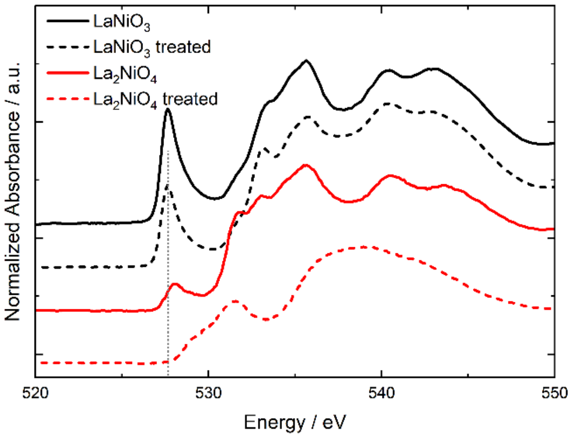

Fig. 3 O K-edge XAS of $LaNiO_3$ and La_2NiO_4 powders before and after the alkaline treatment.

Fig. 3 shows the O K-edge XAS spectra of $LaNiO_3$ and La_2NiO_4 powder samples before and after the alkaline treatment. A pre-edge peak is observed around 528 eV, which is attributed to transitions from O 1s core levels to unoccupied O 2p states that are hybridized with Ni 3d orbitals. The intensity of this peak provides insight into the occupancy of oxygen 2p–Ni 3d hybridized states which is related to surface oxygen species. The change in the oxidation state of nickel from +3 in $LaNiO_3$ to +2 in La_2NiO_4 may affect the hybridized state, which can potentially lead to changes in the spectral features. Changes in the intensity of this peak may correlate with OER-active surface oxygen sites. For $LaNiO_3$, the alkaline treatment causes only a slight reduction in the intensity of the peak at 528 eV. This minimal change suggests that the surface oxygen electronic structure of $LaNiO_3$ is stable even after exposure to concentrated KOH and oxygen bubbling. In contrast, La_2NiO_4 exhibits a pronounced change of O K-edge XAS after the alkaline treatment. The peak at 528 eV, which was initially present in the untreated La_2NiO_4, disappears completely following the alkaline pretreatment. The disappearance of this peak suggests that O 2p–Ni 3d hybrid states have been changed. La_2NiO_4 is known to be an oxygen nonstoichiometric compound, especially in high oxidation conditions where the interstitial oxygen can be incorporated into the lattice [8]. The fact that this peak vanishes after the treatment implies the surface structure change on La_2NiO_4. Whereas $LaNiO_3$ maintains a stable surface structure and OER activity, La_2NiO_4 undergoes surface restructuring upon alkaline treatment that correlates with a decline of OER activity. At this moment, the discrepancy of the previous report which demonstrated the drastically OER enhancement of La_2NiO_4 is not understood. This might be because the difference in the condition of the alkaline treatment and OER activity measurement and the further study is needed.

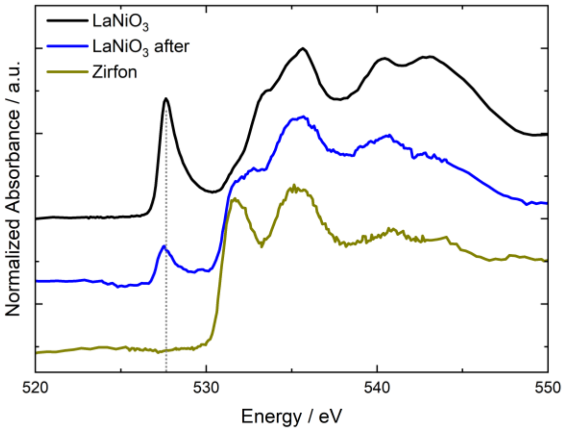

Fig. 4 O K-edge XAS of $LaNiO_3$ powder, $LaNiO_3$ electrode after the ADT, and Zirfon membrane.

O K-edge XAS were also obtained for the electrode sample after the 200-cycle ADT to investigate the surface state of the catalysts following OER durability testing. Fig. 4 presents a comparison of the O K-edge XAS spectra for the initial $LaNiO_3$ powder, the $LaNiO_3$ electrode after the ADT, and the Zirfon membrane. In the spectrum of the post-ADT $LaNiO_3$ electrode, a signal at 531 eV is observed, which is similar to the peak observed in the Zirfon membrane. This indicates that a considerable portion of the post-ADT spectrum is due to the membrane. The post-ADT $LaNiO_3$ spectrum shows a reduction in the intensity of the peak at 528 eV compared to the initial powder. This could imply that the OER cycling led to some modification of surface oxygen species on $LaNiO_3$. Nevertheless, due to the large background signal from the membrane, it is difficult to discuss a quantitative peak intensity. One way to improve the quality of post-test XAS data would be to increase the amount of catalyst loaded on the electrode, thereby yielding a stronger XAS signal from the catalyst relative to the membrane. However, simply increasing the catalyst loading could alter the OER performance, complicating the interpretation of OER activity. Further refinement of the experimental method will be necessary to accurately analyze the surface electronic state of catalysts after OER test.

4. Conclusions

$LaNiO_3$ retained OER activity after the alkaline treatment, with almost no change in its bulk crystal structure or surface electronic structure. This suggests that $LaNiO_3$ has a robust surface that remains stable in alkaline electrolytes, likely owing to an inherently stable electronic configuration. On the other hand, La_2NiO_4 was found to be more susceptible to surface modifications: the alkaline treatment caused the disappearance of the pre-edge peak in O K-edge XAS associated with surface O–Ni hybridized orbital, accompanied by a decrease in OER activity. Additionally, the post-ADT analyses highlighted an experimental challenge, which currently limits the quantitative comparison of catalyst surface states before and after OER durability test.

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