Soft X-ray Absorption Spectroscopic Study on Nickel Electrode for Alkaline Water Electrolysis

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Water electrolysis system for hydrogen production utilizing renewable energy is required to operate stably over a long period and in unstable energy supplying condition. Analysis of degradation mechanism of catalysis under electrochemical potential cycling will be useful for stable operation of water electrolysis. In this study, soft X-ray absorption spectroscopy (XAS) was utilized for the analysis of nickel catalyst used in a conventional alkaline water electrolysis system. Ni *L*-edge and O *K*-edge XAS were measured for the initial and electrochemical cycled nickel metal. In the initial state, the nickel(Ⅱ) oxide phase was present on the nickel metal surface. The electrochemical cycling caused the formation of nickel(Ⅲ) oxyhydroxide on the surface of the nickel metal. It was shown that the degradation mechanism can be analyzed at various depths by using XAS method for the catalyst of water electrolysis.

1. Introduction

The fluctuation of renewable energy supplying generally is one of the issues for energy storage. Hydrogen production used by water electrolysis is one of the attractive methods to store energy as chemical sources[1]. The wide spreading of water electrolysis combined with renewable energy system will be useful for the stable energy supplying and the decreasing CO_2 emissions[2]. In a water electrolysis cell, long time stability has to be maintained even in the load fluctuations for renewable energy supply. In order to improve the stability of water electrolysis, degradation mechanism for electrode catalysis should be understood. In our knowledge, there few reports for soft XAS study on the degradation mechanism of electrocatalysis for water electrolysis[3-5]. In this study, we analyzed the nickel metal electrode for potential cycling, which is a typical alkaline water electrolysis catalyst. The chemical state of the catalyst before and after potential cycling was analyzed by Ni *L*-edge and O *K*-edge XAS.
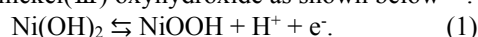
2. Experimental

Electrochemical potential cycling test was performed using a three-electrode cell. The purchased nickel metal plate was polished and washed with pure water and used as a working electrode. The counter electrode was a nickel wire, and the reference electrode was a self-made reversible hydrogen electrode (R.H.E.). 7 M KOH solution was used as an electrolyte. Cyclic voltammograms were measured at a scan rate of 100 mV / s, with a scan range of 0 V to 1.8 V. The nickel electrode after 10000 cycles was washed with pure water. As the initial sample, the polished and washed nickel metal was used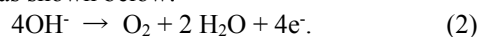. The samples were fixed on the sample holder and transferred to the vacuum chamber. Soft XAS measurements was performed at BL-2 and BL-11 at SR center, Ritsumeikan University. Ni L_3, L_2-edge and O *K*-edge were measured by total electron yield (TEY) mode, partial electron yield (PEY) mode, and partial fluorescence mode (PFY).

3. Result and Discussion

Figure 1 shows the cyclic voltammograms of nickel metal sheet measured in 7 M KOH. The redox peak is observed at around 1.3 V vs. RHE, which is close to the reaction potential of nickel(Ⅱ) hydroxide and nickel(Ⅲ) oxyhydroxide as shown below[6, 7]:

$$Ni(OH)_2 \leftrightarrows NiOOH + H^+ + e^-. \qquad (1)$$

Above 1.6 V, the oxidation current increases rapidly, which is derived from the oxygen evolution reaction, as shown below:

$$4OH^- \rightarrow O_2 + 2\,H_2O + 4e^-. \qquad (2)$$

In the reaction of water electrolysis using renewable energy, the supplied energy generated by power
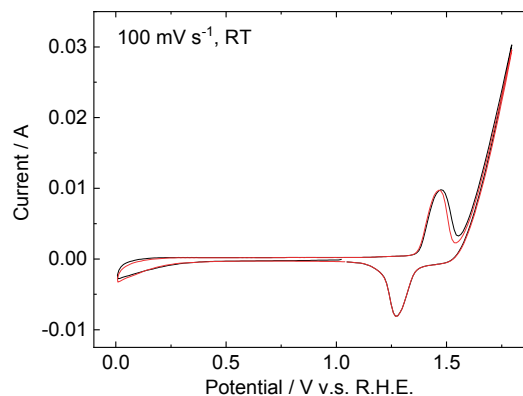

Fig. 1 Cyclic voltammogram of nickel sheet using 7 M KOH electrolyte. The scan rate is 100 mV / s.

generation is not constant, resulting in the electrochemical potential change of the electrode. This situation is similar to the electrochemical potential cycling in this study. That is, on the nickel catalyst for water electrolysis, the reaction between nickel(Ⅱ) hydroxide and nickel(Ⅲ) oxyhydroxide as shown in the formula (1) proceeds continuously, which may greatly affect the degradation of nickel catalysis.

The chemical state change of the nickel electrode induced by the electrochemical cycling was investigated by soft XAS. Figure 2 (a) shows Ni L_3, L_2-edge XAS of the nickel electrode before cycling. The PEY, TEY and PFY modes give information on the outermost surface, the surface, and the inside of the measured sample, respectively. The measurements in PEY and TEY modes results in the same spectral shape in all of Ni L_3, L_2-edge in the initial and after the cycle. The spectrum of the TEY mode shows a sharp peak around 854 eV. This peak position is equivalent to the reported absorption edge energy of NiO[8]. Although the nickel metal sheet was polished, the outermost surface is easily oxidized by oxygen in the air, indicating that a NiO surface film is formed. On the other hand, the spectrum of the PFY mode shows a broad peak around 853 eV, and the base spreads to the high energy side. This shape is equivalent to the spectrum of nickel metal[8], indicating that the nickel(Ⅱ) oxide does not form the inside.

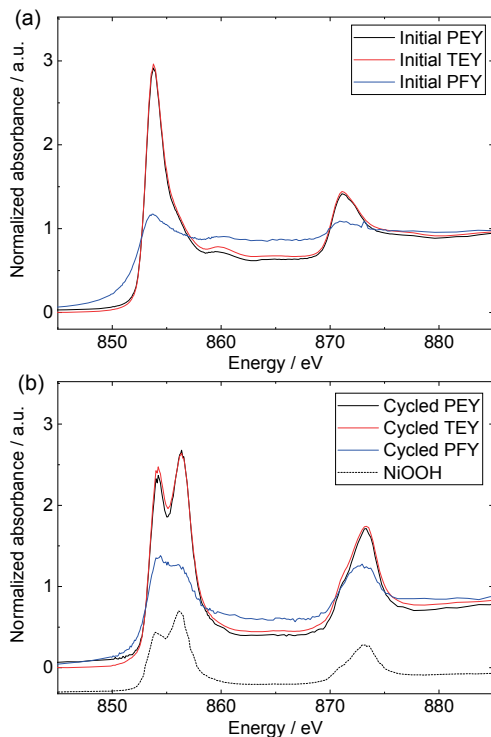The chemical state change of the nickel metal due to the potential cycle is discussed. Figure 2 (b) shows Ni L_3, L_2-edge XAS after the potential cycling. Two distinct peaks are confirmed around 854.2 and 856.5 eV in the spectrum from the TEY mode. The peak intensity of the latter is higher, and the shape of this spectrum is similar to the spectrum of nickel(Ⅲ) oxyhydroxide (NiOOH). On the other hand, in the spectrum of the PFY mode, the increased peak near 856.5 eV is observed as compared to that in the initial state. Since this energy corresponds to the main peak of the spectra for NiOOH, the spectra measured by the PFY mode is a mixed spectrum of Ni metal and NiOOH. While NiO did not form to the inside before the cycle, NiOOH grew the inside after the cycle. The spectrum of the TEY mode reflects the information of about 15 nm on the surface, while the X-ray transmission distance of Ni L-edge in the NiOOH is about 300 nm, which is the detection depth of the PFY mode. The formation of NiOOH by the potential cycling is estimated to have progressed to 100 nm. Since the products other than metallic nickel contain oxygen, the chemical state was analyzed by O K-edge XAS. Figure 3 (a) is the O K-edge XAS spectra in the initial state. The absorption peak at approximately 532 eV below the main peak is also observed in NiO[5], which is consistent with the result of Ni L_3-edge XAS showing the presence of NiO on the surface. The spectrum of the PFY mode reflecting the internal information was noisy, indicating the oxygen spicy exists dominantly on the surface.

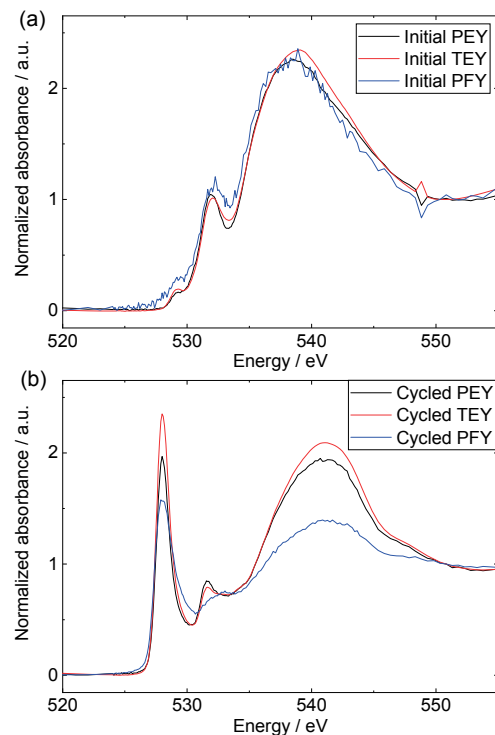After the cycle, the shape of O K-edge XAS changed significantly [Fig. 3 (b)]. In particular, the

Fig. 2 Ni L_3, L_2-edge XAS of the nickel electrode before cycling (a) and after cycling (b).

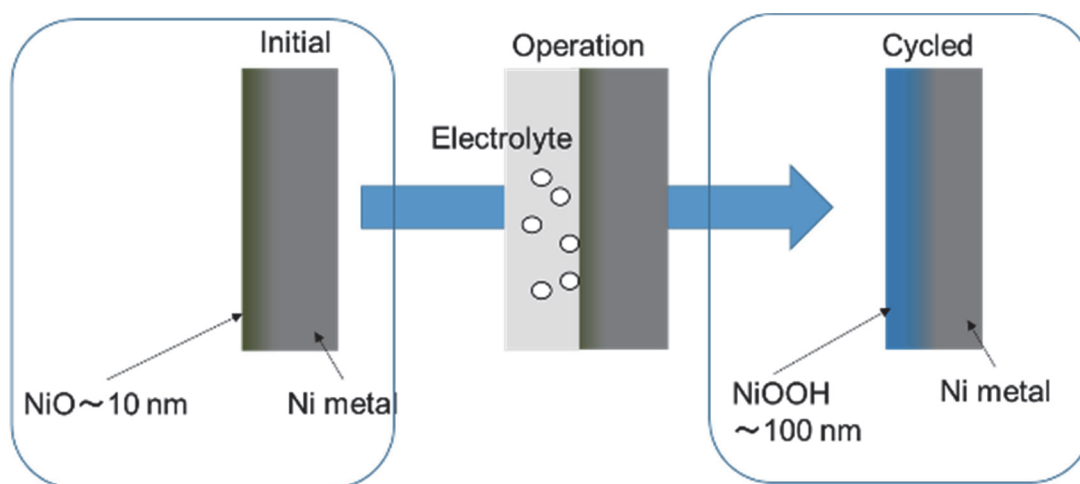**Fig. 3** O K-edge XAS of the nickel electrode before cycling (a) and after cycling (b).

Fig. 4 Proposed degradation mechanism of nickel catalyst for alkaline water electrolysis.

sharp and high-intensity peak appeared at 528 eV, and this peak is also observed in NiOOH[5]. The fluorescence spectrum is also little noisy, indicating that NiOOH has grown to the inside.

To summarize the information obtained, the reaction mechanism shown in Fig. 4 can be derived. In the initial state of nickel metal, nickel(II) oxide exists on the surface which thickness is about 15 nm, and most of the inside is nickel metal. On the other hand, NiOOH is formed by the potential cycling. By repeating the cycle, NiOOH grows to the inside, and its thickness reaches about 100 nm depending on the experimental conditions. The potential cycle changes the chemical state of the electrode surface greatly and influences the inner region. Soft XAS using TEY and PFY modes can separate the surface and the internal state in one measurement, and it is possible to analyze the degradation state of the water electrolysis catalyst at different depths.

4. Conclusion

In order to analyze degradation mechanism of nickel catalyst for alkaline water electrolysis, the three-electrode cell using a nickel sheet for the working electrode with 7 M KOH solution was prepared. The redox behavior between $Ni(OH)_2$ and NiOOH was confirmed by cyclic voltammetry measurement. For the electrode before and after the electrochemical potential cycling, soft XAS measurements at Ni L_3, L_2-edge and O K-edge were performed. In the initial state, a nickel(II) oxide phase was present on the nickel metal surface. On the other hand, nickel(III) oxyhydroxide was formed on the surface of nickel metal after degradation. Soft XAS can determine the degradation state according to the depth.

References

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