

# Summary of Doctoral Dissertation

## Mechanistic Aspect of Water Splitting Activity by Observing Local Structure in Electrocatalysts (電極触媒の局所構造観測による水分解活性の メカニズム解明)

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# Summary

Hydrogen is gaining attention as a clean energy source with a low environmental impact. However, the predominant method of hydrogen production at present is steam reforming, which relies on fossil fuels. Achieving a sustainable energy supply will require harnessing natural energy sources for water splitting and using stored hydrogen on demand and the development of efficient water-splitting catalysts is therefore crucial. In particular, the focus should be on the development of OER catalysts, as the oxygen production reaction is often the rate-limiting step in the water splitting process. Additionally, it will be essential to utilize inexpensive and abundant transition metals for the design of catalysts and so understanding the associated reaction mechanisms is also vital.

This thesis work comprised a series of studies concerning transition metal-based OER catalysts, with a focus on operando XAFS observations providing real-time insights into reaction mechanisms. The primary elements of this research included operando XAFS observations of manganese catalysts containing alkali metals, the development and XAFS analysis of manganite mineral-based catalysts, the design of diamine-doped nickel catalysts and subsequent assessments using operando UV-vis spectroscopy and XAFS and the elucidation of the effects of phosphate ion adsorption on CoOOH catalysts in phosphate electrolyte solutions by operando XAFS.

This work determined that  $\text{MnO}_x$  catalysts containing alkali metal ions within their layers exhibited excellent water-splitting activity. This effect is attributed to the ability of these alkali metal ions to stabilize  $\text{Mn}^{3+}$ . The activity of the  $\text{MnO}_x$  catalysts was also observed to vary depending on the specific alkali metal ion incorporated into the material. Specimens containing potassium, sodium or cesium were synthesized and evaluated to assess electrochemical catalytic performance. Among these, a cesium-containing  $\text{MnO}_x$  catalyst demonstrated particularly high water-splitting activity. Operando XAFS observations indicated that the alkali metal ions formed hydration complexes within the catalyst structure and interacted with the  $\delta\text{-MnO}_2$  layer, thereby stabilizing  $\text{Mn}^{3+}$  and increasing structural strain. The data also suggested that cesium, in particular, provided a stronger stabilizing effect.

A water-splitting catalyst was also produced by ball-milling a naturally occurring manganese ore having the formula  $\text{MnOOH}$ . Surface defects on the milled material were found to play a crucial role by providing active sites for water splitting. The water splitting activity of this catalyst was demonstrated by carrying out electrochemical tests. XAFS data were acquired and the surface and bulk structures of the ball-milled  $\text{MnOOH}$  catalyst were compared. This assessment confirmed that surface defects created during the ball-milling process were present on the catalyst surface and were responsible for the observed water-splitting activity. These data demonstrated that this mineral, when subjected to ball-milling, can serve as an effective water-splitting catalyst primarily due to the formation of surface defects.

In other work,  $\text{NiO}_x$  catalysts incorporating various diamines were synthesized. These materials were found to contain Ni with an oxidation state of approximately +3.6 and exhibited a distorted local structure that provided active sites for water splitting. Operando XAFS observations indicated that, following the incorporation of EDA, the catalyst adopted a  $\gamma$ - $\text{NiOOH}$ -type structure. These findings suggest that the introduction of organic molecules such as EDA induces structural distortion within the catalyst, thereby creating or enhancing active sites crucial for water splitting.

Lastly, the water splitting characteristics of  $\text{CoO}_x$  catalysts in phosphoric acid electrolyte solutions were investigated. The adsorption of phosphate ions on the catalyst surface was shown to disrupt its structure, thereby enhancing the activity of the material. Cobalt phosphate catalysts electrodeposited from phosphoric acid solutions exhibited high water splitting activity according to electrochemical tests. Operando XAFS data provided insights into this phenomenon and indicated that phosphoric acid was adsorbed onto the catalyst surface, leading to a disruption of the  $\text{CoOOH}$  structure. This disruption resulted in a higher cobalt oxidation state. These findings suggest that the adsorption of phosphate ions induces changes in the local structure of the catalyst, which in turn increase its catalytic activity for water splitting.

These results underscore the significant impact that local structural distortions within a catalyst have on the performance of the material. Controlling the local structure of the catalyst, whether through mechanical manipulation or chemical modification, is a crucial aspect of developing highly active catalysts. As an example, the addition of various cations and anions to the catalyst matrix can introduce the desired structural changes, leading to enhanced catalytic performance. Therefore, strategies that focus on fine-tuning these local structural aspects hold promise for the development of highly efficient catalysts.