

# In-situ/Operando X-ray Spectroscopic Study of Cobalt Oxide Electrocatalysts During Oxygen Evolution Reaction

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## Abstract

The exact effect of defect structure in transition metal-based electrocatalysts on the oxygen evolution reaction (OER), which is a highly dynamic process, has not been clearly determined yet. During this electrochemical reaction, determination of electronic structure of the catalyst and the structure-activity relationship of the defective electrocatalyst under *operando* conditions is very important for unraveling the reaction mechanism.  $\text{Co}_3\text{O}_4$  with rich oxygen vacancy ( $\text{V}_\text{O}$ ) has been reported to efficiently catalyze OER. However, the stability of  $\text{V}_\text{O}$ , especially under the highly oxidizing conditions of the OER, is a concern. Stabilizing  $\text{V}_\text{O}$  in  $\text{Co}_3\text{O}_4$  while retaining excellent electrocatalytic activity is a real challenge. In this study, pure spinel  $\text{Co}_3\text{O}_4$  and  $\text{V}_\text{O}\text{-Co}_3\text{O}_4$  are investigated by in situ x-ray absorption spectroscopy. The defect formation mechanism is revealed through various operational conditions, and the dynamic behavior of defect sites in the electrocatalytic OER process is also examined. Soft X-ray spectroscopy was used to track the valence and spin states of Co ions in these  $\text{Co}_3\text{O}_4$  in operational OER condition. It is suggested that  $\text{V}_\text{O}$  can initialize the surface reconstruction of  $\text{V}_\text{O}\text{-Co}_3\text{O}_4$  before the OER process. The oxygen vacancies are firstly filled with  $\text{OH}^-$ , promoting the formation of  $\text{V}_\text{O}\text{-Co}_3\text{O}_4$  and the pre-oxidation of Co with low charge state, and causing the formation of intermediate  $\text{Co-OOH}^-$ . A large proportion of Co ions undergo a voltage-dependent transition from  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$ . Highly oxidized  $\text{Co}^{4+}$  sites, instead of  $\text{Co}^{3+}$  sites or oxygen vacancies, are mostly responsible for high OER activity. The dynamic evolution of the surface structure of the defective electrocatalyst was observed and the active sites in the electrocatalysis process were identified. Accordingly, the effect of defective and active sites on  $\text{Co}_3\text{O}_4$  for OER was thus revealed in this study.