Hybrid structure analysis: precise structure determination of electrocatalysts by the combination of X-ray diffraction and absorption

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The structure parameters such as bond length, bond angle, and occupancy of each atomic site greatly affect the performance of the activity of solid catalysts and the physical properties of electronic and magnetic materials. Precise structure analysis including accurate estimation of these parameters by powder X-ray diffraction (PXRD) is very important in the development of materials. Generally, occupancy is highly correlated with atomic displacement parameters, making it difficult to determine accurate values by PXRD, especially, in the case that atoms with close atomic numbers share the same site. Here, we will present a precise structure analysis of an electrocatalyst, spinels \( \text{Co}_3\text{O}_4 \) and \( \text{Co}_2\text{MnO}_4 \), by “hybrid structure analysis” combining the advantages of both PXRD and X-ray absorption fine structure (XAFS).

We chose \( \text{Co}_3\text{O}_4 \) as an example to prove the concept of “hybrid structure analysis.” The structure parameters were shared between PXRD and XAFS, and refined alternately and iteratively to afford a more reliable result. Both of calculated PXRD pattern and FT-EXAFS spectrum matched the experimental ones well. We successfully obtained the final structure parameters including occupancies through the hybrid structure analysis, indicating the effectiveness of this method.

This method was further applied to a real material as an electrocatalyst, \( \text{Co}_2\text{MnO}_4 \). It is one of the most stable electrocatalysts for oxygen evolution reactions of water electrolysis among non-noble catalysts [1]. It was difficult to determine the distribution and occupancy of metals only by PXRD data due to their close atomic numbers of Co and Mn. The hybrid structure analysis enabled the elucidation of the accurate occupancy of each atom in \( \text{Co}_2\text{MnO}_4 \) before and after the electrolysis, showing that the metal at the tetrahedral A site was easier to leach than at the octahedral B site. The result was consistent with that of the DFT calculations, clarifying the stabilization mechanism of this catalysis.

Figure 1. The results of the hybrid structure analysis of \( \text{Co}_3\text{O}_4 \). (a) Rietveld analysis and (b) EXAFS fitting at the final step.


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