Oxygen Evolution Reaction Driven by Charge-Transfer from Cr-complex to Co-Containing Polyoxometalate in a Porous Ionic Crystal

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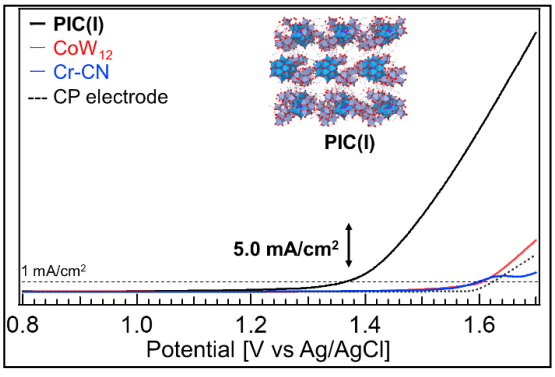
Considerable efforts have been devoted to developing oxygen evolution reaction (OER) catalysts based on transition metal oxides. Polyoxometalates (POMs) can be regarded as model compounds of transition metal oxides, and cobalt-containing POMs (Co-POMs) have received significant interest as candidates. Nanocomposites based on Co-POMs have been reported to show high OER activity due to synergistic effects among the components, while the role of each component is unclear due to its complex structure. Herein, we utilize porous ionic crystals (PICs) based on Co-POMs, which enable the establishment of a composition–structure–function relationship to understand the origin of the synergistic catalysis. Specifically, a Keggin-type POM $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$ and a Cr-complex $[Cr_3O(OOCCH_2CN)_6(H_2O)_3]^{+}$ are implemented as building blocks of PIC for OER under non-basic conditions. The PIC exhibits efficient and sustained OER catalytic activity while each building block is inactive. Electrochemical and spectroscopic studies clearly show that the synergistic catalysis originates from the charge transfer from the Cr-complex to $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$; the increased electron density of $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$ may increase its basicity and accelerate proton abstraction as well as enhance electron transfer to stabilize reaction intermediates adsorbed on $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$.

Keywords : Oxygen evolution reaction, Polyoxometamate, Ionic crystal, electrochemical catalysis, Porous materials

遷移金属酸化物を用いた酸素発生反応（Oxygen Evolution Reaction, OER）触媒の開発が盛んに行われている。Polyoxometalate（POM）は、アニオン性の遷移金属酸化物クラスターであり、特にコバルト含有 POM（Co-POM）は OER 触媒の候補として注目されている。Co-POM を用いたナノコンポジット材料が構成ユニット間の相乗効果により高い OER 活性を示すことが報告されているが、その複雑な構造から各成分の役割は不明である。本研究では、組成-構造-機能の関係を確立できる Co-POM をベースにした多孔性イオン結晶（Porous Ionic Crystal、PIC）を利用し、相乗的な触媒作用の起源を理解することを目指した。Keggin 型 POM $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$ とクロム錯体 $[Cr_3O(OOCCH_2CN)_6(H_2O)_3]^{+}$ を構成ユニットとした PIC で相乗的な OER 触媒活性が発現することを見出した。電気化学的および分光学的研究により、この相乗的な触媒活性は Cr 錯体から $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$ への電荷移動に起因することを明らかにした。



1) **Shimoyama Y.**; Ogiwara N.; Weng Z.; Uchida S., Oxygen Evolution Reaction Driven by Charge-Transfer from Cr-Complex to Co-Containing Polyoxometalate in a Porous Ionic Crystal. ***J. Am. Chem. Soc., accepted.***