Chapter V: Heterogeneous Catalysis for Oxygen Evolution

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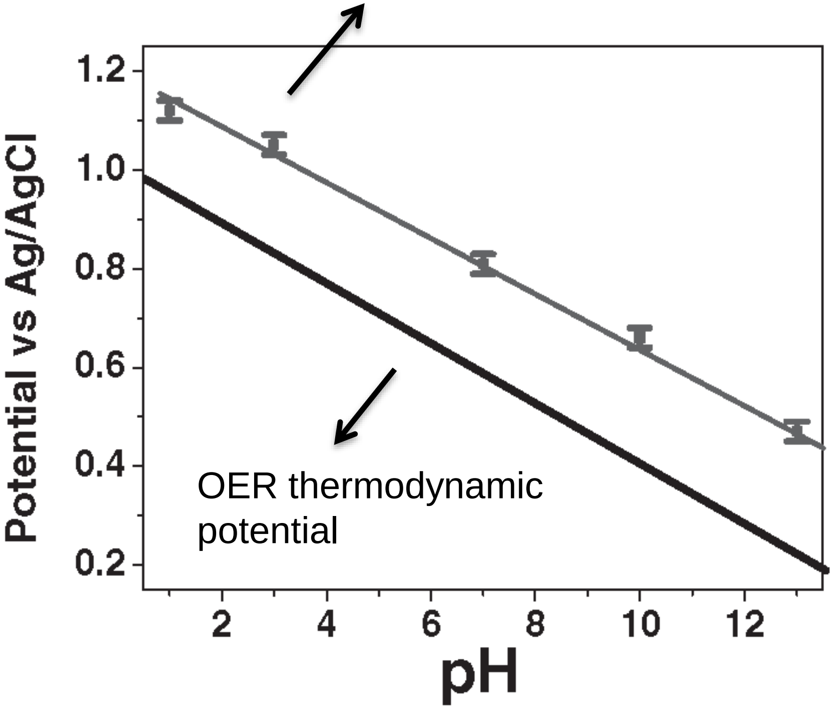
Best catalysts: IrO_2; RuO_2; (not Pt)
Conditions: Acidic (pH = 0 to 1) or alkaline (pH = 13-14) or neutral (pH = 7).

Many metal oxides are catalysts in alkaline conditions; however, they are not stable in acidic solutions. IrO_2 nanoparticles are used in acidic membrane electrolyzers due to its higher stability than RuO_2, and higher activity than Pt.

$$\text{M-O} \xrightarrow{H^+} \text{M-OH} \xrightarrow[-H_2O]{H^+} M^{2+} \quad \text{dissolution in solution.}$$

Metal oxide is unstable in acid

Performance of IrO_x



The potential for J = 1.5 mA/cm_2
using an IrO_x film as catalyst (10^{-7} mol/cm^2)

OER thermodynamic
potential

This graph shows that IrO_x is a catalyst at various pH; the overpotential to achieve a current density of 1.5 mA/cm^2 is the same at different pHs; it is 200 mV.

Mallouk, et al. Small 2011, 14, 2087.

Mechanism of OER: Bimetallic (e.g. on iridium oxide)

In acidic or neutral water:

$$\mathrm{cat} + \mathrm{H_2O} \longrightarrow \mathrm{cat{-}OH} + \mathrm{H^+} + \mathrm{e} \qquad \text{(A1-1)}$$

$$\mathrm{cat{-}OH} \longrightarrow \mathrm{cat{-}O} + \mathrm{H^+} + \mathrm{e} \qquad \text{(A1-2)}$$

$$\mathrm{cat{-}O} + \mathrm{cat{-}O} \longrightarrow 2\ \mathrm{cat} + \mathrm{O_2} \qquad \text{(A1-3)}$$

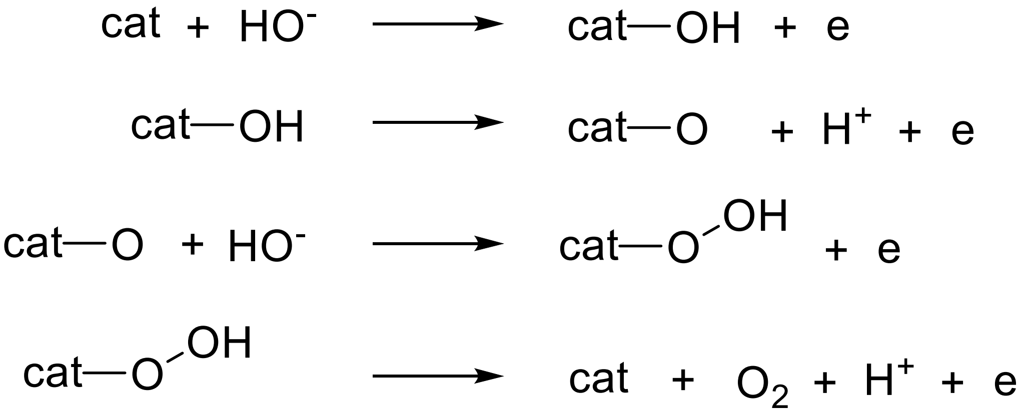
In alkaline water:

$$\mathrm{cat} + \mathrm{HO^-} \longrightarrow \mathrm{cat{-}OH} + \mathrm{e} \qquad \text{(B1-1)}$$

$$\mathrm{cat{-}OH} + \mathrm{HO^-} \longrightarrow \mathrm{cat{-}O} + \mathrm{H_2O} + \mathrm{e} \qquad \text{(B1-2)}$$

$$\mathrm{cat{-}O} + \mathrm{cat{-}O} \longrightarrow 2\ \mathrm{cat} + \mathrm{O_2} \qquad \text{(B1-3)}$$

General mechanism of OER :

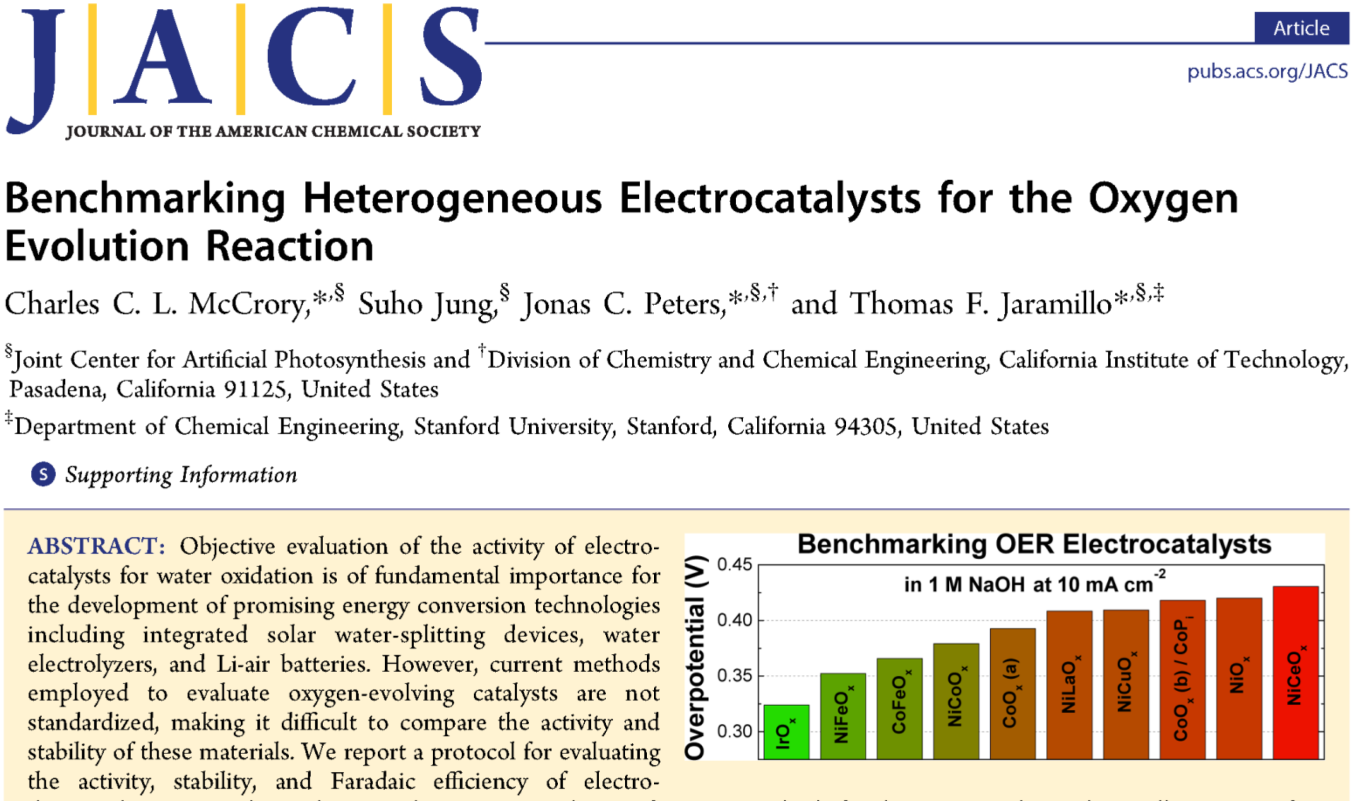


$$\text{cat} + HO^- \longrightarrow \text{cat—OH} + e \qquad \text{(C-1)}$$

$$\text{cat—OH} \longrightarrow \text{cat—O} + H^+ + e \qquad \text{(C-2)}$$

$$\text{cat—O} + HO^- \longrightarrow \text{cat—O—OH} + e \qquad \text{(C-3)}$$

$$\text{cat—O—OH} \longrightarrow \text{cat} + O_2 + H^+ + e \qquad \text{(C-4)}$$



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Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction

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Supporting Information

ABSTRACT: Objective evaluation of the activity of electrocatalysts for water oxidation is of fundamental importance for the development of promising energy conversion technologies including integrated solar water-splitting devices, water electrolyzers, and Li-air batteries. However, current methods employed to evaluate oxygen-evolving catalysts are not standardized, making it difficult to compare the activity and stability of these materials. We report a protocol for evaluating the activity, stability, and Faradaic efficiency of electro-

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Perspective

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Transition Metal Oxides as Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Solutions: An Application-Inspired Renaissance

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ABSTRACT: Water splitting is the essential chemical reaction to enable the storage of intermittent energies such as solar and wind in the form of hydrogen fuel. The oxygen evolution reaction (OER) is often considered as the bottleneck in water splitting. Though metal oxides had been reported as OER electrocatalysts more than half a century ago, the recent interest in renewable energy storage has spurred a renaissance of the studies of transition metal oxides as Earth-abundant and nonprecious OER catalysts. This Perspective presents major progress in several key areas of the field such as theoretical understanding, activity trend, in situ and operando characterization, active site determination, and novel materials. A personal overview of the past achievements and future challenges is also provided.

The technological need of OER catalysts has motivated intense research efforts on the development of catalysts that are solely composed of Earth-abundant elements.[4,6,7,9−12] These catalysts might be classified into two categories: homogeneous, molecular complexes and heterogeneous, inorganic solids.[10,11] Molecular catalysts[13] have uniform and easy-to-identify active sites; they are readily characterized by spectroscopy and X-ray crystallography. Their properties can be finely turned by ligand modification. The mechanistic understanding of molecular OER catalysis is more advanced than its heterogeneous counterparts. Notwithstanding these desirable features, molecular catalysts suffer from their low long-term stability under the harsh conditions of OER and the difficulty to integrate them into electrochemical and photoelectrochemical devices. In this regard, heterogeneous inorganic catalysts are more practical. They often exhibit notable stability at OER potentials. Many of them have been deposited onto electrodes to catalyze OER

Conclusions

Iridium oxide and ruthenium oxide are the benchmark catalysts. They are among the few catalysts that work in both acidic and basic solutions.

Oxygen evolution is mechanistically complex as it is a four-electron reaction.

A number of metal oxides without precious metals are reasonably active in alkaline conditions. They might be further improved following various approach to design catalysts by using descriptors, and by rational experimental and computational screening.

To reach a desired current density of about > 100 mA/cm^2 for OER, even the best catalysts require a large overpotential (> 300 mV).