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).

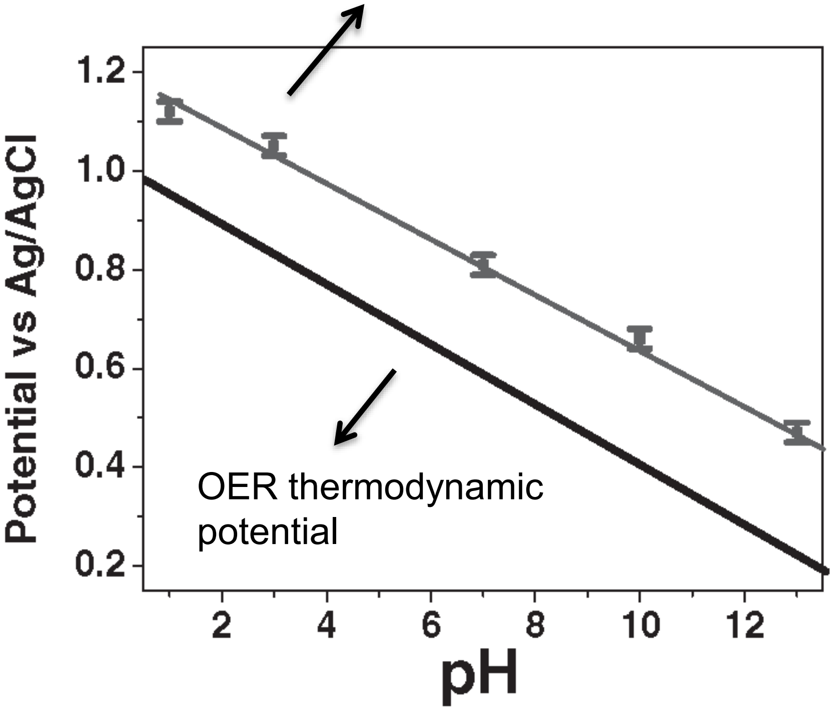
Many metal oxides are catalysts in alkaline conditions; however, they are not stable in acidic solutions. IrO_2 nanoparticles are used in acidic membrane electrolyzers due to its higher stability than RuO_2, and higher activity than Pt.

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

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:

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

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

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

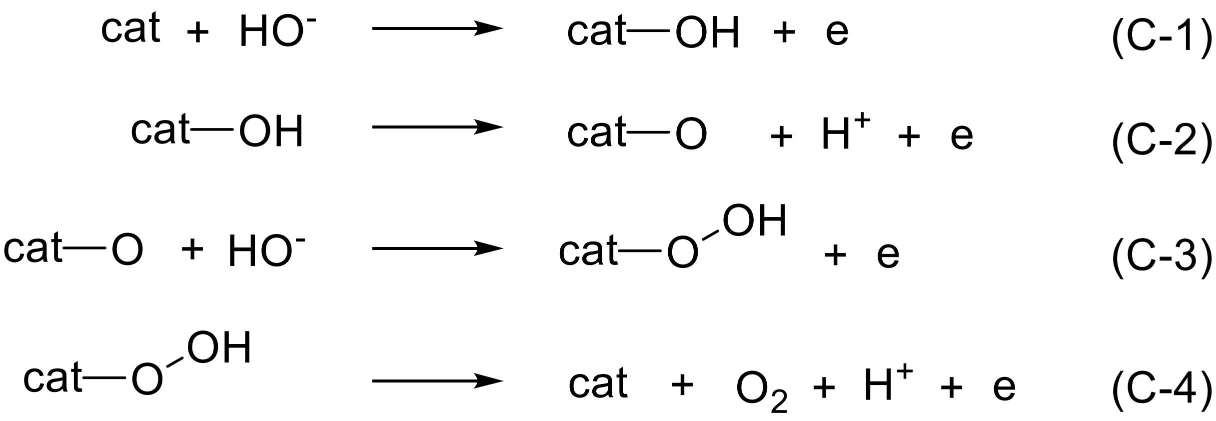
In alkaline water:

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

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

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

General mechanism of OER : Monometallic



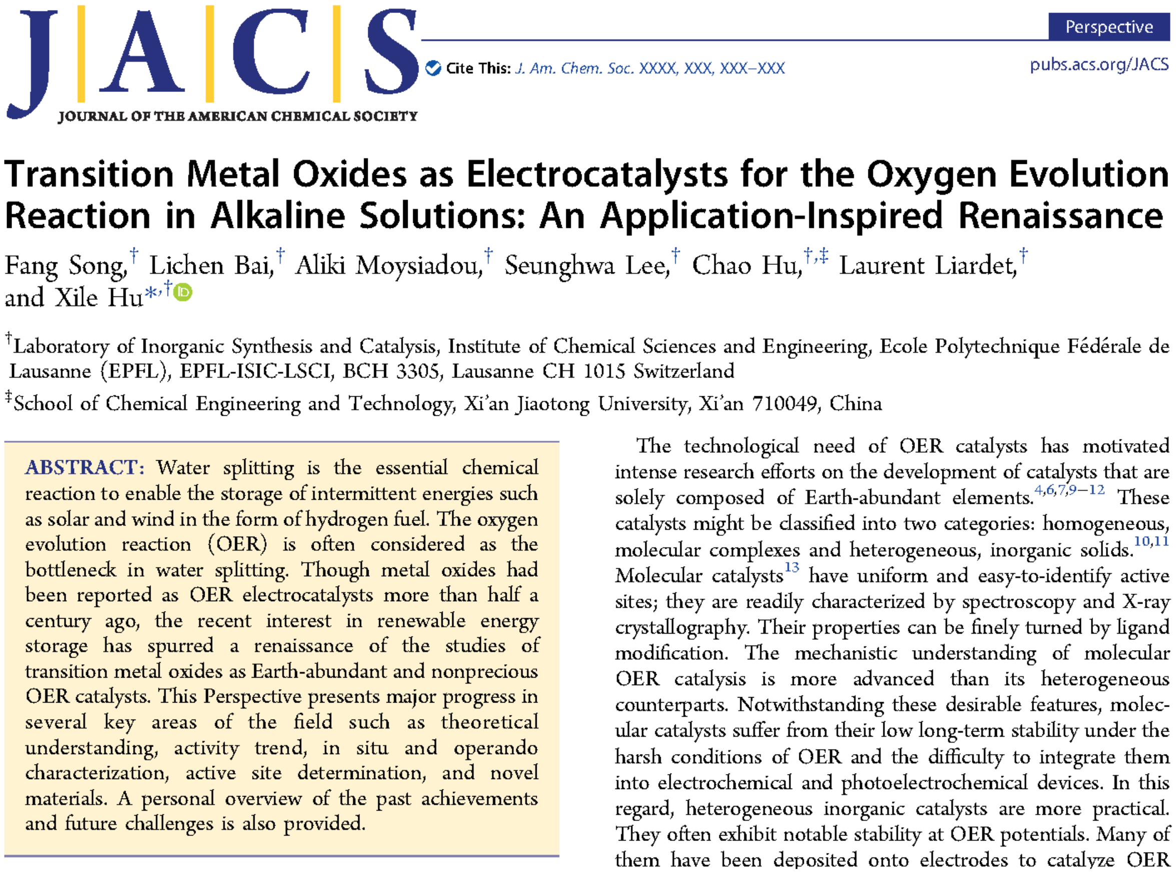
$$\text{cat} + HO^- \longrightarrow \text{cat—OH} + e \qquad \text{(C-1)}$$

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

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

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

Chapter 1, 2, 4, 8, 10 of this paper



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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

1. When did the studies of metal oxides for OER start?

Scholarly studies of Co-, Ni-, Fe- and Mn-based oxides or hydroxides in OER dated back to more than half a century ago

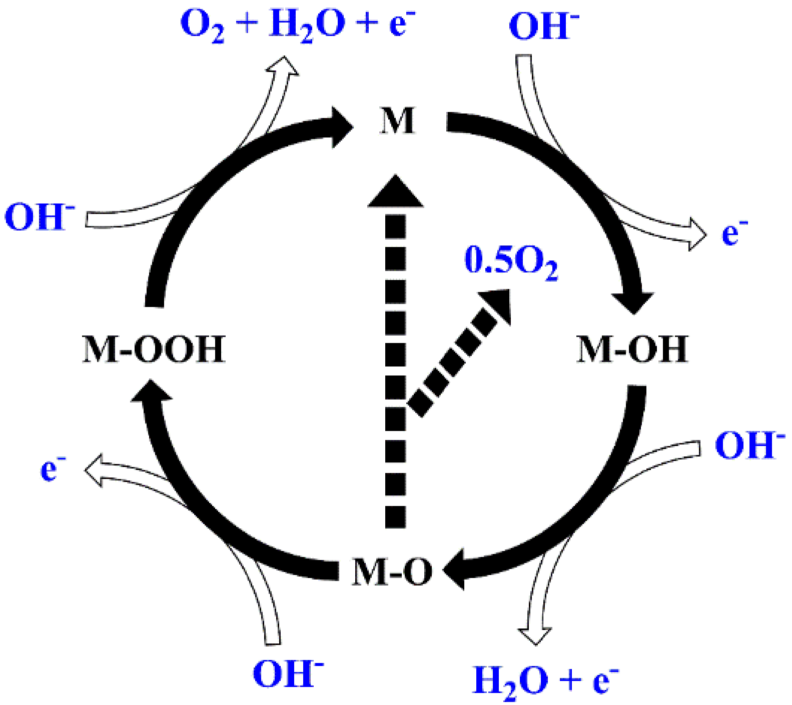
2. What are the limitations of early studies?

The samples used in these early studies were either bulk oxides or electrochemically deposited films. Sample purity and structural homogeneity were not strictly controlled. The characterization was largely limited to electrochemical measurements. As a result, mostly phenomenal findings were reported and the field progressed slowly.

3. What are the reasons that make the recent renassicance possible?

- Thanks to developments in nanoscience and nanotechnology, it is now possible to synthesize a wide range of metal oxides with controlled composition, morphology, size, structure, and surface areas.
- Modern analytical tools in spectroscopy and microscopy, especially the access to in situ and operando techniques, provide unprecedented fundamental information about the catalytic sites.
- Progress in density functional theory (DFT) computations makes it possible to calculate the properties and even catalytic activity of metal oxides with a reasonable accuracy.

OER is a four-electron four proton step



Tafel equation: $\eta = a + b \log j$

For a 1-electron reaction: $b = -(2.3RT/\alpha F)$ or about 120 mv/dec if α is 0.5

How about more than 1 electron transfer like in OER? Well, we will then focus only on the rate determining step.

$$b = \frac{ə\,\eta}{ə\,logj} = \frac{2.303RT}{\alpha_a nF}$$

n = 1

$$\alpha_a = n_r\beta + \frac{n_b}{v}$$

n_b is the number of electrons transferred before the RDS, *v* is the number of rate-determining steps (1 in most cases), n_r is the number of electrons that participate in the rate-determining step (1 in most cases), and β is the transfer coefficient of the RDS (0.5 most of the case)

Thus, b is typically lower than 120. Can be 40 or 30.

Activity metrics are required to quantitatively compare the activity of different OER catalysts.

4. What activity metrics are suggested?

Turnover frequencies (TOFs), specific current density (J_s), geometric current density (J_g), and overpotential (η).

a. In principle TOF is the best measure of the intrinsic catalytic activity. However, accurate determination of TOF is not straightforward because the true active sites of heterogeneous catalysts are very difficult to determine. A more realistic method to calculate TOF is to consider all relevant metal sites as active sites. The TOFs determined in this way surely represent only a lower limit of the true TOFs, nevertheless, they enable a fair and consistent comparison among catalysts prepared by different groups.

b. The specific current density (J_s) is an alternative metric for the intrinsic activity of electrocatalysts. J_s is defined as the current density at a specific overpotential normalized by the active surface area of the catalyst. This metric complements the TOF metric as inaccessible bulk sites are no longer counted.

c. In part due to substantial work required for the measurement of TOF and J_s, researchers in the field tend to employ two other, more easily determined metrics to compare OER activity: geometric current density (J_g) at a specific overpotential and overpotential (η) for a specific geometry current density.

For water electrolysis, the relevant current densities are from 300 mA/cm2 to 2000 mA/cm2.

d. The Tafel slope alone is not a recommendable activity metric.

5. What is a commonly used method to study the stability of OER catalyst? What is its limitation?

In the literature, the stability of a metal oxide catalyst is commonly studied by potentiodynamic, chronoamperometric, or chronopotentiometric(these are all electrochemical measurements to determine the I-V curves) experiments during a few hours. The activity profile of the catalyst is then used as an indication of its stability.
Limitation: activity stability is not directly related to catalyst stability. Catalyst can degrade while stability is similar for a short period of time.

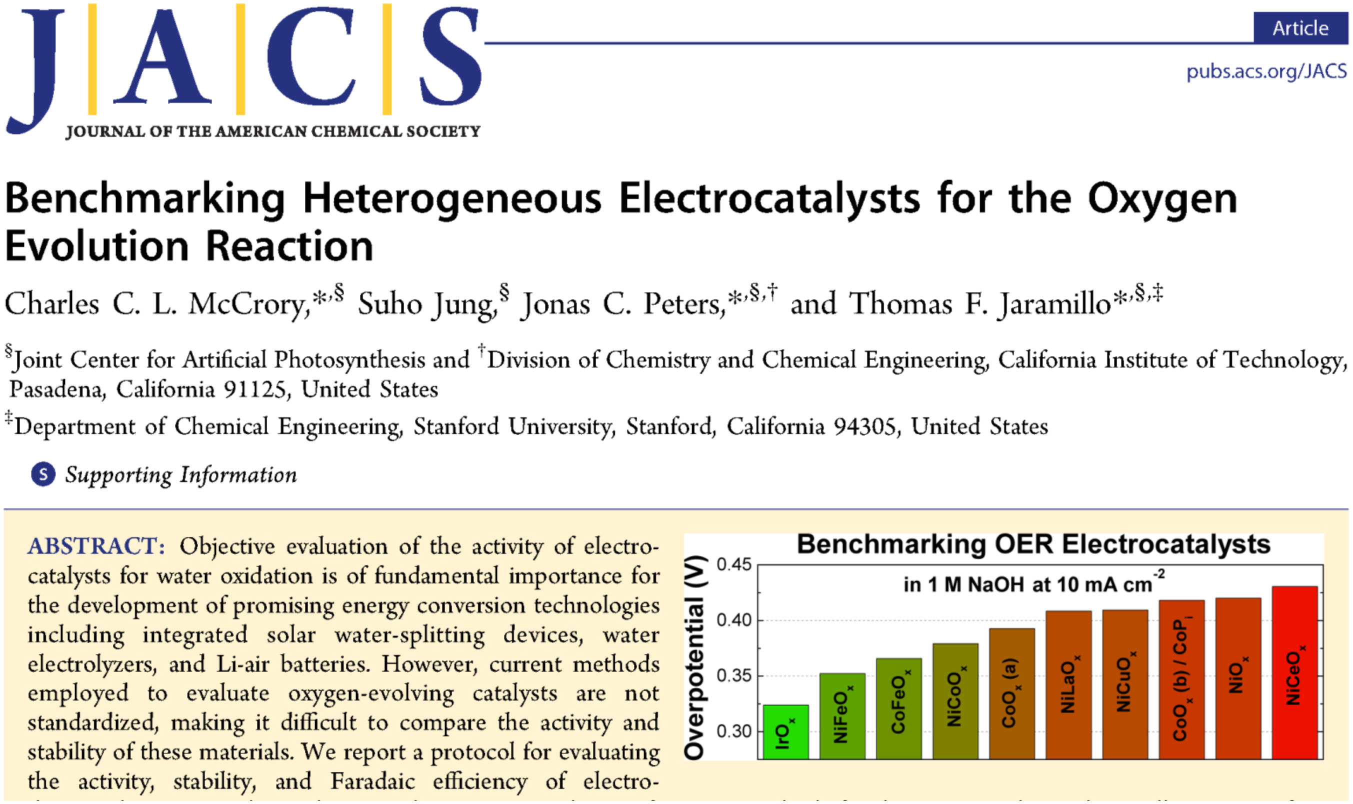
6. How can one monitor the mass change of the catalyst during the catalysis?

a. Electrochemical quartz crystal microbalance (eQCM) has been used.
b. Elemental analysis by inductively coupled plasma mass spectrometry (ICP-MS) is more reliable for detecting the mass change of the catalysts. Electrochemical flow cells connected to an ICP-MS can monitor the dissolution of catalyst during operation.

8. What are some of the important achievements in the studies of OER catalysts?

(ii) the determination of true activity trends across a wide range of metal oxides and establishment of $NiFeO_x$ as a benchmark catalyst,
(iii) the in situ and operando spectroscopic characterization of catalysts, which provides previously elusive information about the catalysts,
(iv) the development of novel nanomaterials which exhibit superior geometric activity

9. What are the three future challenges?
(i) The determination of active sites.
(ii) The development of catalysts with much higher intrinsic activity than the $NiFeO_x$ benchmark
(iii) a successful application of the newly developed OER catalysts in a commercializable energy device.



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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-

Questions:

1. Why do we need a benchmarking methodology?

A: Typical OER catalysts are deposited on a variety of different substrates, and their electrocatalytic activity is measured at a range of pH values, temperatures, and electrolyte compositions and concentrations, making it difficult to compare the performance and stability of different materials.

2. What are the criteria the authors set out to meet?

A: (1) to use standard electrochemical procedures and equipment easily accessible to a typical researcher in the field of electrocatalysis, and (2) to minimize the time and number of experiments necessary to evaluate a catalyst’s activity and short term stability.

3. What catalysts have been measured?

A: electrodeposited Ni- and Co-based metal oxide catalysts, IrO_x, GC background

4. How is electrochemical surface area determined?

A: Measurements of the double-layer capacitance from either CV or Impedance.

5. What are the parameters used for electrocatalytic activity?

Overpotential to reach 10 mA cm^{-2}; Specific activity - current density divided by elctrochemical surface area

6. What are the best catalysts in alkaline solutions?

NiFeOx

7. Suggest a weakness of the proposed method and how this can be improved.

A: The difference in loadings is not taken into account. Comparison by turnover frequency or mass-averated activity should be used as well.

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.

There is intense research on the fundamental characterization and understanding of the catalysts, as well as on new catalyst developments.