Supplementary Information (SI) for Chemical Society Reviews.

# Supplementary Materials

**Title: Designing physically separated bimetallic catalysts through Cooperative Redox Enhancement (CORE)**

**Authors:** Bohyeon Kim[1†], Isaac T. Daniel[2†], Mark Douthwaite[2], Samuel Pattisson[2], Richard J. Lewis[2*], Steven McIntosh[1*], Graham J. Hutchings[2*]

**ADDRESS:** [1]Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA, USA.

[2]Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Translational Research Hub, Cardiff, CF24 4HQ, UK.

**Corresponding Authors:** hutch@cardiff.ac.uk, mcintosh@lehigh.edu

†Authors contributed equally.

## General Considerations

All electrochemical methods here utilize a standard three-electrode setup, **Figure S1**. It is recommended to utilize a cell design that enables control of the temperature, pressure, and gas atmosphere, and such cells are readily available from several suppliers. An analytical electrochemical cell uses three main components: the working electrode (WE), the reference electrode (RE), and the counter electrode (CE). The WE provides a conductive surface on which the catalyst can be coated. The RE provides a stable reference potential, ensuring accurate measurement of the potential of WE. The CE completes the circuit, allowing current flow without interfering with the reaction. This setup enables precise analysis of half-reaction activity of half reaction activity on a catalyst.

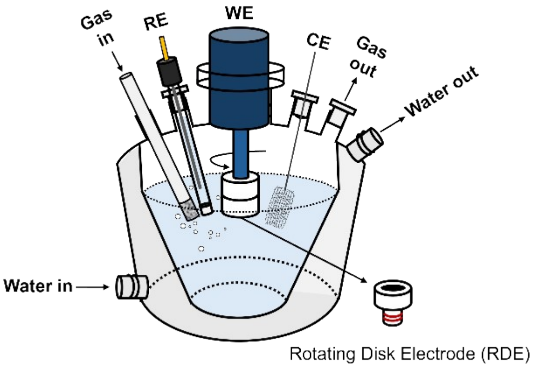

**Figure S1.** a typical three-electrode cell with RDE. It has water jackets that allow temperature control. When using gas, porous gas bubbler can be applied to saturate the solution.

As in any electrochemical measurement, the selection of the electrode is critical. The selection criteria and associated limitations are well-discussed in textbook[1] and here we limit the discussion to an overview of key considerations. The electrode must be highly conductive but non-reactive to prevent any background noise, potential, or current generated by the electrode with conductive layer coated glass electrodes, carbon papers, carbon clothes, and glassy carbon electrodes common choices. Limited mass transfer can influence kinetic measurements, particularly when the half reaction activities are high. Electrodes with a gas diffusion layer (GDL) can be applied, considering oxygen or hydrogen as mass transfer inhibitors for the half reaction because of their low solubility in water. By placing the GDL electrode halfway submerged, the gas can diffuse through the GDL and react with the catalyst, reducing the mass transfer resistance.[2] The use of a rotating disk electrode (RDE) is recommended when kinetic analysis is critical in order to minimize mass transfer limitations by creating a flow of electrolyte towards the catalytic layer[1]. While simpler electrochemical cell designs can be applied for many measurements, including open circuit potential measurements, it is generally better practice to implement these more complex designs to enable the collection of comprehensive data in one set of experiments.

When analyzing kinetic data, it is necessary to carefully consider how the current density from an electrode surface will be converted to, and compare with, any measurements from a purely thermocatalytic system. A common method to normalize current density is to divide the current by the macroscopic geometric surface area of the electrode. This provides a ‘reaction rate’ of electrons per second per bulk electrode area. In contrast, the accepted method to normalize activity in a thermocatalytic reaction is the turnover frequency (TOF) that provides the number of catalytic cycles per atomic scale active site on the catalyst surface. This discrepancy is not easily or completely resolved, as verifying the number of active sites for the targeted reaction in an electrode is challenging. The probe reactions may not be relevant, and not all nanoparticles may be electrochemically accessible in the completed cell due to the necessary addition of binding agents and lack of electrochemical connection to isolated particles.

We can try to overcome the limitation on the geometric area by calculating the electrochemically active surface area (ECSA). ECSA is obtained by scanning the potential in a region where no faradaic processes occur. As many catalysts are synthesized with porous support such as carbon powder, careful consideration for the capacitance is required for accurate measurement.[1] Alternatively, redox curves from CV can be an effective tool to calculate the surface area of the metal catalyst by oxidizing and reducing the metallic layer and calculating the total charge required for oxidation or reduction. However, applying overpotential often induces oxidation of more than monolayer, possibly making this measurement inaccurate.[3]

Given these limitations and challenges, we typically normalize the rates based on moles of catalysts used and by employing the same catalyst preparations for both electrocatalytic and thermocatalytic measurements. While imperfect, it does enable quite strong correlations between the two measurements, even if per site comparisons cannot be made.

$$j\ (mA\ cm^{-2}) = \frac{I}{A}$$

$where\ j = current\ density,\ I = current,\ A = geometric\ surface\ area.$

$$TOF(s^{-1}) = \frac{N_{product}}{N_{active\ catalyst} \cdot t}$$

$$where\ N_{product} = moles\ of\ product, N_{active\ catalyst} = moles\ of\ the\ catalyst\ (active\ sites\ if\ possibl$$

By the first Faraday’s law, TOF from electrochemical units can be calculated assuming 100% faradaic efficiency.

$$TOF(s^{-1}) = \frac{N_{product}}{N_{active\ catalyst} \cdot t} = \frac{I \cdot t}{z \cdot F \cdot N_{active\ catalyst}},$$

$$where\ z = number\ of\ electrons\ involved\ in\ the\ reaction, F = Faraday's\ constant.$$

## Supplementary References

(1) Brett, C. M.; Brett, O. *Electrochemistry Principles, Methods, and Applications*; OXFORD UNIVERSITY PRESS, 1993. https://doi.org/10.2307/jj.8500920.7.

(2) Ryu, J.; Bregante, D. T.; Howland, W. C.; Bisbey, R. P.; Kaminsky, C. J.; Surendranath, Y. Thermochemical Aerobic Oxidation Catalysis in Water Can Be Analysed as Two Coupled Electrochemical Half-Reactions. *Nat. Catal.* **2021**, *4* (9), 742–752.

(3) Giron, R. G. P.; Ferguson, G. S. Development of Cathodic Silence in an Oxide Film on a Gold Electrode. *Electrochim. Acta* **2015**, *180*, 560–563. https://doi.org/10.1016/j.electacta.2015.08.152.