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## Enabling Enzyme-Like Cooperativity in Inorganic Electrocatalysis

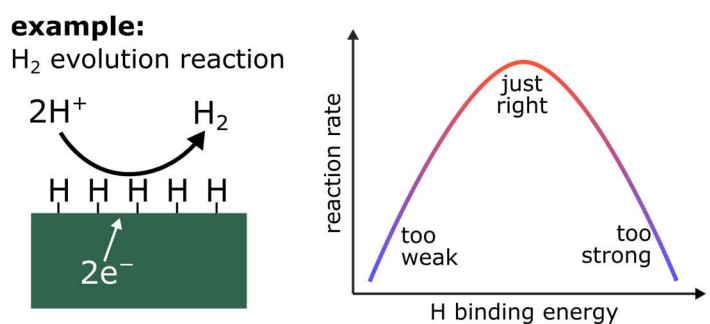
**Aim:** to design a new generation of electrocatalysts for multi-step redox reactions that mimic enzymes by linking together multiple active sites across a proton-electron conducting membrane.

### The Need

The last two decades have seen incredible advances in the performance and economics of renewable energy technologies like solar and wind power.<sup>1</sup> These advances are already driving significant decarbonization of the global electricity supply.<sup>2</sup> However, continued progress toward global sustainability will also require a complete reconceptualization of the chemical industry, which remains deeply entrenched in the use of fossil resources. Electrochemistry can play a key role in this transformation via the development of catalytic reactors that use electric power to recycle carbon dioxide emissions back into useful fuels and chemicals.<sup>3</sup> Nonetheless, after decades of work in this area, the best electrochemical processes that we have today remain uncompetitive with those based on fossil resources. Thus, the overall premise of this proposal is that ***if electrochemical technologies are to have an impact on sustainability, we need to find better ways to catalyze redox reactions.***

### The Opportunity

The dominant paradigm for catalyst design today is based on the Sabatier principle (Figure 1), which states that the most active catalysts are those that interact with reaction intermediates neither too strongly nor too weakly.<sup>4</sup> As a result, the vast majority of work in this field is focused on modifying the composition and structure of individual catalyst active sites to optimize their binding energies toward target intermediates.<sup>5</sup> The problem with this approach is that it is not possible to independently tune the binding energy



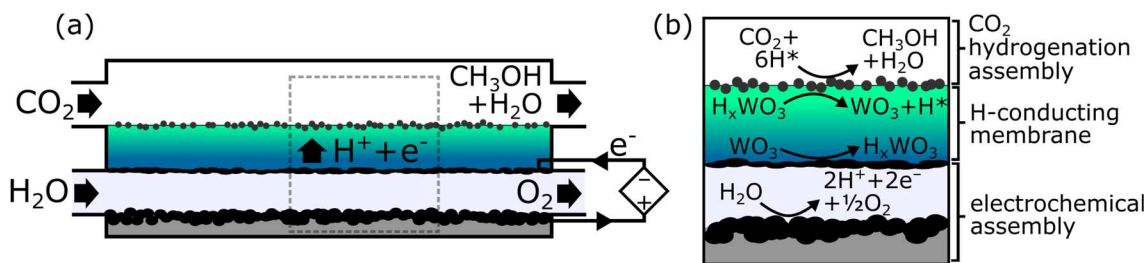
**Figure 1.** Schematic depiction of the Sabatier principle, using the electrochemical hydrogen evolution reaction in acid (left) as an example. The most efficient catalysts for this reaction are those that exhibit moderate binding energies for a single reaction intermediate: surface-bound hydrogen atoms.

of a single active site toward multiple reactive intermediates.<sup>6</sup> This makes it difficult, if not impossible, to design an ideal “single-site” catalyst for most multi-step redox reactions.<sup>7</sup>

Nature has developed elegant ways to overcome this challenge. Unlike inorganic catalysts, many enzymes function like molecular assembly lines, where sequential reaction steps are carried out by a series of distinct active sites that are each optimized for their respective tasks.<sup>8</sup> ***Our research group is building a new generation of inorganic catalysts that directly mimic the multifunctional behavior of enzymes, thereby overcoming the limitations of traditional catalyst design.***

### Research Approach

Figure 2 depicts our vision for a new type of catalytic assembly, which we are calling an electrochemically pumped membrane reactor (EPMR). The key feature is a specialized membrane that transports reactive hydrogen between two independent catalytic units. On one



**Figure 2.** Conceptual schematics of an electrochemically pumped membrane reactor that converts CO<sub>2</sub> into methanol by partitioning reaction steps between two catalytic assemblies separated by a proton-electron conducting membrane. Panel (a) schematizes a plausible reactor design, while the detail in panel (b) illustrates the constituent redox reactions at the catalyst and membrane interfaces.

side is an electrochemical assembly containing catalysts that oxidize water into O<sub>2</sub> and inject H-equivalents (protons and electrons) into the membrane. On the other side are catalysts that accept H-equivalents from the membrane and use them to hydrogenate CO<sub>2</sub> into methanol—a highly versatile fuel and chemical precursor.<sup>9</sup> Thus, the EPMPR directly mimics the catalytic machinery of photosynthesis in which water oxidation, hydrogen transport, and CO<sub>2</sub> fixation are each carried out by different enzymes.<sup>10</sup> This characteristic makes our concept unique from the vast majority of ongoing work in the field and offers numerous opportunities for scientific and practical advances.

The feasibility of this EPMPR approach has been demonstrated, showing that tungsten oxide (WO<sub>3</sub>) can be hydrogenated under electrochemical and gas-phase reaction conditions to create tungsten hydrogen bronze (H<sub>x</sub>WO<sub>3</sub> where  $x \leq 0.5$ ), in which hydrogen diffuses rapidly and retains its ability to act as a chemical reductant.<sup>11</sup> Nonetheless, two scientific limitations stand in the way of being able to develop the EPMPR into a viable technology. First, the basic thermochemistry and transport properties of hydrogen in metal oxide bronzes like H<sub>x</sub>WO<sub>3</sub> are not well understood. Second, we lack the necessary design rules for creating catalytically active interfaces between oxides and catalytic metals like Pt or Cu. In the proposed work, we will develop new experimental capabilities to address each of these challenges.

### **Objective 1: elucidate the basic physics and chemistry of oxide hydrogen conductors**

The prior work on H<sub>x</sub>WO<sub>3</sub> demonstrated the potential to use metal oxides to transport hydrogen between discrete catalytic units, but much remains to be understood about the underlying physics and chemistry of hydrogen bronzes.<sup>12</sup> The key research questions we are interested in include:

1. What are the mechanistic steps of metal oxide hydrogenation/dehydrogenation?
2. Do protons and electrons move independently, or are they tightly bound together?
3. How can we manipulate the reactivity of hydrogen in an oxide host toward a molecular target like CO<sub>2</sub>?

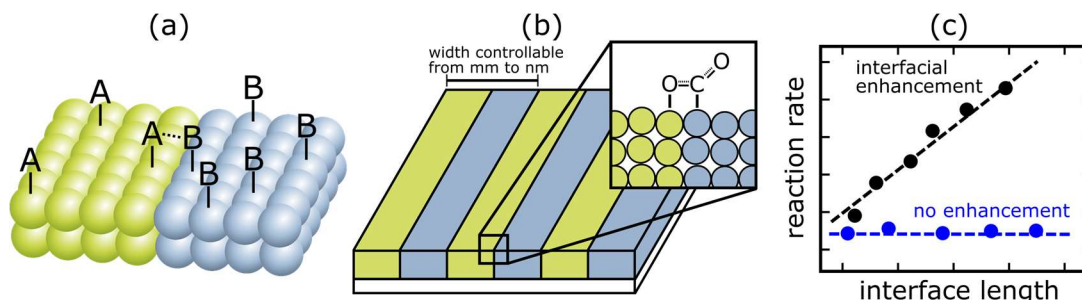
To address these questions, we will deploy a new, purpose-built analytical tool that draws on *in-situ* optical microscopy<sup>11</sup> to study the hydrogenation chemistry of WO<sub>3</sub>. Figure 3 schematizes this tool, which comprises a thin-layer microfluidic flow cell that is configured to provide complete control over the chemical environment of an oxide sample under electrochemical and thermochemical reaction conditions. This cell will be integrated into an optical microscope that is equipped with a suite of spectroscopic capabilities and an online mass-spectrometer for real-time analysis of reaction products.<sup>13</sup> This multimodal, *in-situ* analytical

platform will be the first of its kind, and it will allow us to execute the most detailed studies to date of thermodynamic, kinetic, and transport processes in hydrogen bronzes.

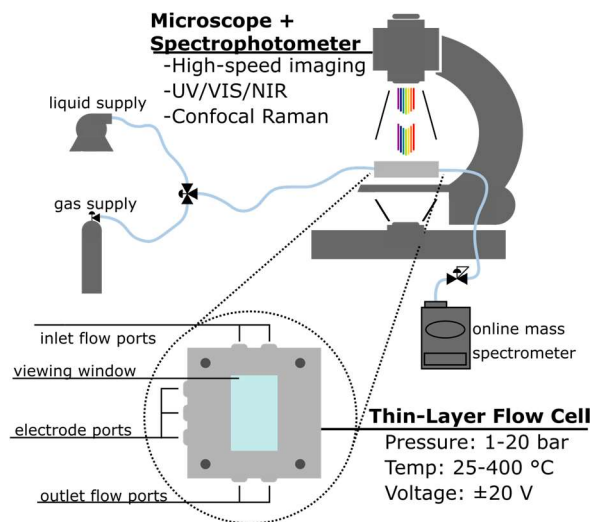
## Objective 2: understand catalytic synergy at metal/oxide interfaces

Synergistic interactions between metals and metal oxides are often invoked in the catalysis literature,<sup>14</sup> but they remain very poorly understood—especially in electrochemical systems. This makes it prohibitively difficult to rationally design metal/oxide interfaces with high catalytic activity, which are integral to the EPMR design. To address this challenge, we propose an innovative approach involving the use of cleanroom nanofabrication techniques to create atomically flat, periodic arrays of metal and oxide films in a simple striped pattern (Figure 4). In this geometry, synergistic catalytic activity can only occur along the one-dimensional interface at the metal/oxide boundary. By progressively decreasing the width of the stripes in these structures, we can systematically increase the proportion of the interfacial edge length over several orders of magnitude. Catalytic activity that scales linearly with edge length can then be directly interpreted as emergent reactivity due to cooperative interactions between metallic and oxidized surface sites.<sup>15</sup> Hence, this method offers a straightforward and highly generalizable strategy for identifying and quantifying synergistic catalysis at metal/oxide interfaces.

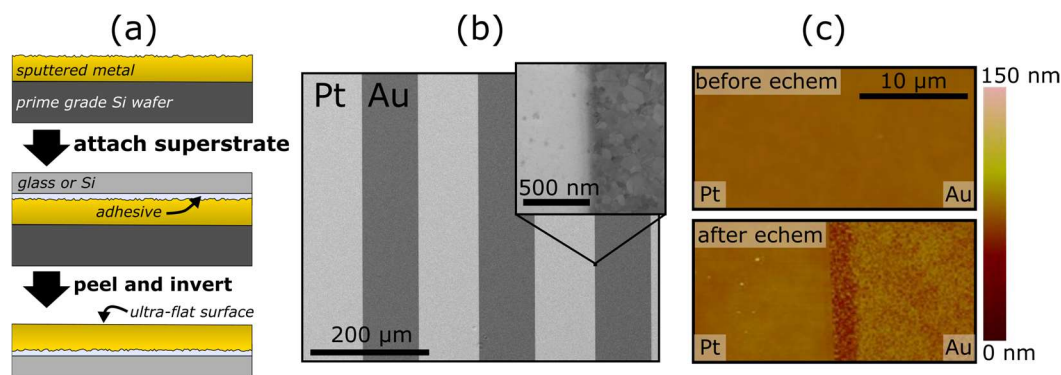
We will take this approach a step further by deploying advanced electrochemical scanning probe microscopy to locate “hot spots” in catalytic activity at the metal/oxide interface with nanometer precision. These active regions will then be re-located and imaged at the atomic scale using transmission electron microscopy and scanning tunneling microscopy to identify the structural motifs that give rise to the highest catalytic activity toward water splitting and CO<sub>2</sub> hydrogenation. Figure 5 compiles proof-of-concept data demonstrating our ability to use nanofabrication techniques<sup>16,17</sup> to observe emergent electrochemical behavior at Pt/Au interfaces.



**Figure 4.** Proposed approach for quantifying emergent catalytic activity at metal/oxide interfaces. (a) Conceptual diagram of a well-defined interface between two catalyst components that preferentially bind two generic reaction intermediates A and B, such that synergistic reactivity between A and B occurs only at the interface. (b) Idealized schematic of nanofabricated stripes containing two catalyst components (e.g., a metal and an oxide) that activate CO<sub>2</sub> across the interfacial boundary. (c) Anticipated relationship between reaction rate and interface length for nanofabricated metal/oxide stripes with and without cooperative catalytic activity.



**Figure 3.** Schematic of the *in-situ* microscopy platform that we will use to elucidate the thermodynamic, kinetic, and transport properties of metal oxide hydrogen bronze compounds.



**Figure 5.** Preliminary results demonstrating our ability to fabricate and characterize linear interfaces between two electrochemically active materials. Periodic stripes of Pt and Au were deposited by integrating photolithography with a technique called template stripping, which is schematized in panel (a).<sup>17</sup> This results in a surface that is nearly atomically flat (sub-nm RMS roughness) even across the Pt/Au boundary. Panel (b) shows representative scanning electron micrographs demonstrating the overall fidelity of the array. Panel (c) depicts AFM topography data before and after extended electrochemical analysis in  $\text{H}_2\text{SO}_4(\text{aq})$  electrolyte, showing the emergence of a shallow trench at the Pt/Au interface that we attribute to an increased rate of oxidative dissolution.

## Impact

Success in this work will open up entirely new ways to design inorganic catalysts for challenging redox reactions. We anticipate direct practical applicability in the development of EPMRs that convert  $\text{CO}_2$  into fuels and chemicals, which addresses an urgent and critical need to close the anthropogenic carbon cycle. Moreover, the same concepts readily translate to a wide range of important chemical processes—including ammonia electrosynthesis and the removal of oxygen impurities from biofuels. Hence, this BYJ project offers the potential to reinvent the global chemical industry as an environmentally sustainable enterprise.

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