

## 6 LOOKING FORWARD: THE FUTURE OF HETEROGENEOUS WATER OXIDATION CATALYSTS

### 6.1. Where are we at?

The current high-performing, earth-abundant materials are generally made from iron, cobalt, and nickel. We have finally reached overpotentials and current densities which justify incorporating these catalysts into electrolysis devices and researching their stability and efficiency. Moving forward with these materials, incremental changes in morphologies and attachment strategies will provide small improvements in overall device efficiency; these efforts will mirror the ongoing efforts to increase the efficiency of silicon-based photovoltaics.

### 6.2. The Future

Major advances in device efficiency that will allow solar-driven water splitting to compete with traditional photovoltaics must come from the development of a new class of heterogeneous water oxidation catalyst. These new materials will have exceptionally low overpotentials, ultrafast kinetics, and be stable both intrinsically and in their attachment to photoanodes. Below, I share my final thoughts on what these materials might look like, based on my experience exploring the [NiFe]-LDH material.

### 6.3. Electronic Considerations

#### 6.3.1. Straddle the “Oxo Wall”

The stabilities of metal-oxo complexes with tetragonal (four-fold) symmetry decrease across the periodic table due to the addition of  $d$  electrons to formally  $\pi^*$  orbitals.<sup>1</sup> Correspondingly, oxo ligands bound to metals with low  $d$ -counts ( $d^1$ ,  $d^2$ ) are strongly acidic, whereas those in  $d^4$  complexes can be strongly basic.<sup>2</sup> Notably, an “oxo wall” separates the Fe-Ru-Os and Co-

Rh-Ir triads in the periodic table.<sup>1</sup> To the left of the wall, multiply-bonded metal oxos are common; to the right of the wall, they are very scarce.

Betley et al. have proposed an acid-base (AB) strategy for O-O bond formation, in which an oxygen nucleophile (*e.g.* water or hydroxide) attacks an electrophilic metal-oxo.<sup>3</sup> Notably, the AB strategy is one proposed mechanism for oxygenic photosynthesis in photosystem II.<sup>4</sup> It is also the microscopic reverse of the O-O bond heterolysis step in cytochrome P450.<sup>5,6</sup> If nucleophilic attack on a metal-oxo is indeed an operative mechanism in water oxidation catalysis, an oxo of moderate stability would be critical for catalysis.

In order to facilitate catalytic O-O bond formation, I propose two criteria for the active metal site: (1) a metal-oxo must be formed, and (2) the oxo must not remain triply-bonded to the metal. In (1), the species may be transient, but must exist long enough for attack (and bond formation) to take place. Condition (2) can be satisfied by either a high *d*-count ( $>d^3$ ) or an elevated reduction potential for a high-valent metal center. Such a complex would be reduced upon attack, allowing for the formation of an O-O bond.

Considering the early transition metals (Sc-V), the *d*-counts are very low in all common oxidation states. Even by tuning the reduction potentials of the complexes, it is unlikely that triply-bonded oxos will be destabilized enough to form active heterogeneous catalysts for water oxidation. This prediction is realized experimentally in the materials developed featuring these metals: the addition of other, more active, metals is critical to their performance.

Materials containing chromium and manganese perform better, though the higher oxidation states are still too stabilizing. The key to improving the performance of these materials is the careful tuning of the 2-electron reduction potentials, *e.g.*  $E_{\text{red}}(\text{Mn(V/III)})$ , which reduce the metal to a  $d^4$  configuration. This can be accomplished readily in a protein environment, but will be more difficult in a heterogeneous catalyst consisting primarily of oxide and hydroxide ligands.

Iron, cobalt, and nickel straddle the “oxo wall,” which is perhaps a good explanation for their high activity for water oxidation. These oxos follow the Goldilocks principle, being neither too strong nor too weak. Based on these considerations, it may be prudent to stay

close to the oxo wall while developing new, highly active catalysts without extensive tuning of reduction potentials.

Finally, Cu and Zn show reduced activity because the  $d^9$  and  $d^{10}$  configuration do not support oxos for long enough to observe catalysis. As such, it is proposed that many of the late first-row transition metals are poor water oxidation catalysts because they cannot reach a  $\sim d^4$  electron count at reasonable potentials.

### 6.3.2. An Exception: Move to Trigonal Ligand Fields

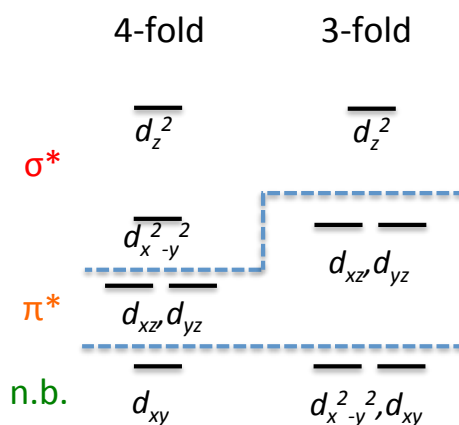


Figure 6.1. Electronic structures for complexes in tetragonal (four-fold) and trigonal (three-fold) ligand fields.

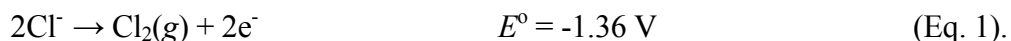
One strategy for activating mid-to-late transition metal-oxos would be to move to trigonal (three-fold) symmetry, as shown in Figure 6.1. In trigonally symmetric point groups, the lowest orbitals of  $d$  parentage are a non-bonding  $e$  set, which can be occupied by four electrons. Thus, a  $d^4$  complex in tetragonal symmetry can be “isoreactive” to a  $d^6$  complex in trigonal symmetry. For some of the late transition metals with high  $d$ -counts, moving to trigonal symmetry may be a considerable advantage; the non-bonding  $e$  set of molecular orbitals can hold twice as many electrons (as compared to tetragonal symmetry) before beginning to weaken the metal-oxo bond.

These electronic considerations have profound experimental ramifications: no terminal metal-oxos have been isolated beyond the “oxo wall” in tetragonal symmetry. In trigonal ligand frameworks, however, one can move past the wall (*e.g.* (Mes)<sub>3</sub>Ir<sup>V</sup>(O)).<sup>8</sup>

## 6.4. Kinetic Considerations

### 6.4.1. Operating at pH 7

Ultimately, a successful water splitting device must operate in *seawater* at pH 7, not in acid or base. Due to the high levels of chloride in seawater (often at concentrations greater than 0.5 M),<sup>9</sup> water oxidation will necessarily compete with the more kinetically facile oxidation of chloride to chlorine:



The chlorine/chloride couple is proton- and pH-independent (Figure 6.2), so operation at higher pH is desirable. A low operating overpotential at pH 7 would be sufficient to exclude chloride oxidation, since  $\Delta E = E(\text{Cl}_2/2\text{Cl}^-) - E(\text{O}_2/2\text{H}_2\text{O}) = 0.54 \text{ V}$ .

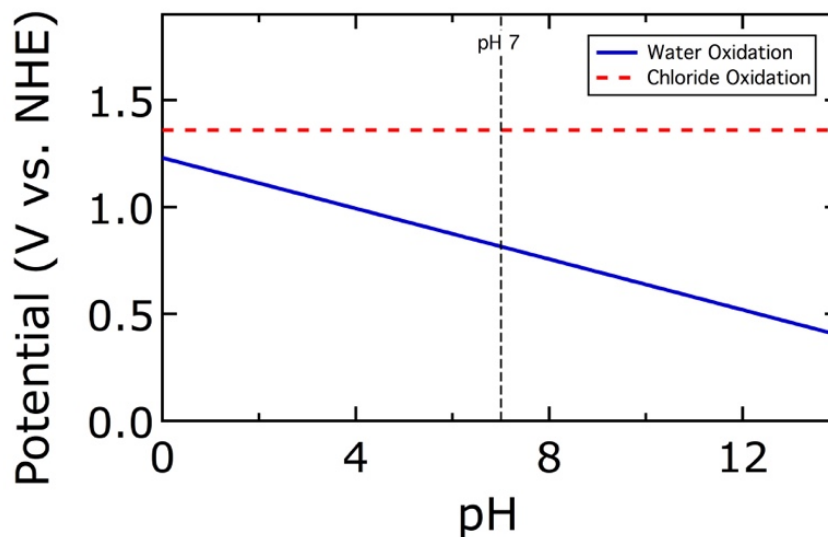


Figure 6.2. Potentials (V vs. NHE) for water oxidation (blue) and chloride oxidation (red) at pH 0-14. Note that water oxidation is pH-dependent while chloride oxidation is pH-independent. The dotted black line indicates pH 7.

### 6.5. A Prediction

My prediction is that the next generation of earth-abundant heterogeneous water oxidation catalysts will be mineralogical (hence, geologically stable) motifs in nanoparticulate form. I believe they will be late transition metals with mild 2-electron reduction potentials, but weakened metal-oxo bonding due to elevated  $d$  counts. These complexes will likely only be stable with trigonal symmetry.

### 6.6. Outlook

We have made considerable progress developing catalysts and beginning to understand how they operate. In the future, water splitting devices will provide electrons and protons to a myriad of “plug-and-play” fuel and material generators which will supply us with value-added chemicals on-the-spot, reducing transportation inefficiencies. Farmers will produce fertilizer, bottlers will produce ethylene, and fuel stations (previously known as gas stations)

will produce hydrogen on-site. It's an exciting time to be doing fundamental research in sustainable energy, and I encourage a dramatic increase in the amount of funding and attention being spent on these basic research projects.