Improving Oxygen Electrochemistry Through Nanoscopic Confinement

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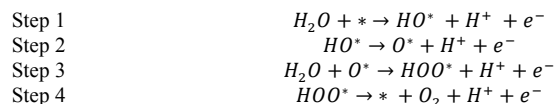*SLAC National Accelerator Laboratory, Menlo Park CA (USA)*
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Introduction

Water splitting is composed of two primary half-reactions: hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Almost all inefficiency in water splitting is due to inefficient OER catalysis at the anode. Previous theoretical work has shown that oxygen electrocatalysts are fundamentally limited by energetic scaling relationships between reaction intermediates [1,2]. Physically this translates to similar bonds formed between surface-bound HO* and surface-bound HOO*.

Our study focuses on the model OER mechanism that progresses through surface-bound HOO* ("nucleophilic attack"). This mechanism can be summarized in the following elementary steps:

Step 1 $\qquad H_2O + * \rightarrow HO^* + H^+ + e^-$
Step 2 $\qquad HO^* \rightarrow O^* + H^+ + e^-$
Step 3 $\qquad H_2O + O^* \rightarrow HOO^* + H^+ + e^-$
Step 4 $\qquad HOO^* \rightarrow * + O_2 + H^+ + e^-$

The symmetry between reaction intermediates is problematic because it fixes the potential required to drive the second and third steps to a minimum of 1.6 V (overpotential of ~0.4 V), or a catalytic efficiency of approximately 75%. Notably these limits seem to be realized in experimental studies, most notably in recent benchmarking efforts [3]. Experimental studies have also shown that well-defined 3D reaction geometries can substantially improve performance for oxygen reduction [4].

Materials and Methods

Our study focuses on the (110) facet of rutile oxides, namely RuO_2 and IrO_2. We used Density Functional Theory as implemented in the Quantum Espresso calculator. In parallel previous successful theoretical investigations [1] we used the RPBE exchange-correlation functional and a plane wave basis set with an energetic cutoff of 550 eV and a density cutoff of 5500 eV. Surface calculations were performed on a (1x1x2) supercell using the optimized bulk lattice constant and 6x6 sampling of the 2D Brillouin Zone. Ionic cores were modeled by ultrasoft pseudopotentials whose positions were relaxed until the sum of all forces was less than 0.05 eV A^{-1}.

Results and Discussion

We find that channel effects substantially change the reaction dynamics for rutile oxides, and have largely the same effects for RuO_2 and IrO_2. While there is no visible change in the adsorption energy for either O* or HO*, there is a pronounced stabilization effect for HOO* as shown in Figure 1. Our results indicate that this is due to hydrogen bond formation with oxygen on the opposite side of the channel. Hydrogen bonds developed for HOO* and not for HO* primarily due to the difference in spatial extent. Our results also suggest that surface termination was largely unimportant so long as opposite oxygen sites remained exposed.

While confinement affected adsorption energies for both RuO_2 and IrO_2 similarly, there were pronounced differences in overpotential. Stabilizing HOO* translates to a lower overpotential for RuO_2, which was initially limited by step three. However IrO_2 was potential-limited by step two, which would suggest that overpotential would be independent of HOO* stability. However we find that as channels grow more narrow that the potential-limiting step actually changes and eventually confinement effects would actually hinder activity.

Significance

We present a general scheme for circumventing electrochemical scaling relations in the oxygen evolution reaction. Because confinement effects impact surface bound HO* differently than surface-bound HOO* we are able to substantially reduce overpotential and increase reaction efficiency. This should be seen as a general method to engineer reaction environment for other OER catalysts or for other scaling-limited reactions.
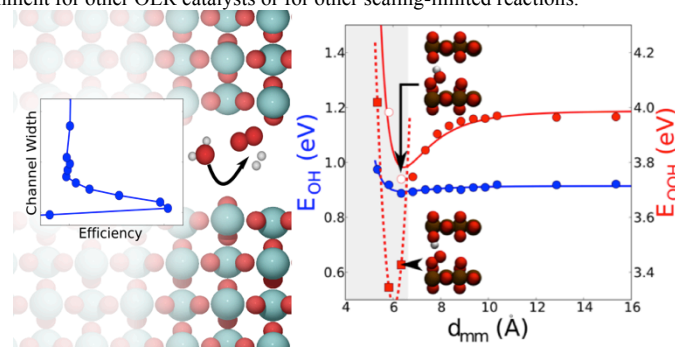

Figure 1. (Left) Schematic representation of the water splitting reaction in a RuO_2 channel and the effect of channel width on oxygen evolution efficiency. (Right) Differences in adsorption energy for HO* (E_{OH}) and HOO* (E_{OOH}) for various channel diameters. Solid lines represent Lennard-Jones fits to the data. Shaded region corresponds to an area for which hydrogen "hops" to opposite side, and dotted parabola represents the corresponding potential well.

References
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