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## Oxygen Evolution on Doped Metal Oxides, a DFT Study.

G. Ramos-Sanchez<sup>1</sup>, R.G. González-Huerta<sup>2</sup>, P. Balbuena<sup>1\*</sup>

<sup>1</sup>Artie & McFerrin Chemical Engineering Department, Texas A&M University. College Station, Tx 77845. USA.

<sup>2</sup>Instituto Politécnico Nacional, Unidad Prof. ALM, México, D. F., 07738, México

\* tel: +1-979-845-3375, fax: +1-979-845-6446, balbuena@tamu.edu

### ABSTRACT

The Hydrogen economy scheme present big advantages over traditional fossil fuel based systems; hydrogen production by water electrolysis complete perfectly the renewable hydrogen cycle, by using this hydrogen in fuel cells to produce electricity. The oxygen evolution reaction is the limiting step reaction of the overall electrolysis process. High over-voltage is needed to reach an appreciable hydrogen production, even using the best materials available; moreover, it has not been found a route to obtain (design) new materials that promote the diminishment of the over-voltage needed for this reaction. Using an experimental approach it was found that the addition of small quantities during the synthesis of  $\text{RuO}_2$  and  $\text{IrO}_2$  lead to a considerable lower over-voltage; however, neither the structure of the compounds nor the reason by which the overvoltage was reducing has been established. In this paper, using a computing simulation, the adsorption of water is analyzed on pure and Co doped oxides. It was found that water adsorption is weaker in  $\text{RuO}_2$  than on  $\text{IrO}_2$ , the addition of Co as substitutional dopant diminish by the half the adsorption energy; however it was also found that the substitutional doping process is an endergonic process, but the adsorption of doping atoms on the surface is exergonic.

Keywords: Water Electrolysis, DFT, doped oxides, oxygen evolution.

## 1. Introduction



Water electrolysis is the ideal process for hydrogen generation; it produces 100% pure hydrogen and, if renewable sources are used, the process is perfect suitable for an environmentally friendly Hydrogen economy [1]. A major source of irreversibility in the solid polymer electrolyte cell is the overvoltage at the oxygen evolution electrode (OER), platinum, on the other hand, in small quantities at the cathode is sufficient to catalyze the hydrogen evolution nearly reversibly[2]. For the anodic side, when in contact with the acidic Nafion® membrane, non-noble catalytic metals like Ni and Co will corrode and Pt will be covered by a low conducting oxide film [3]. Therefore, different materials have been used to catalyze the OER, being the Ru and Ir the most suitable candidates but in an oxidic form, since both metallic Ir and Ru have been observed to be unstable. Experimentally it has been found that modifications on the composition, stoichiometry and geometry of the electro-catalyst will affect the overall overvoltage for oxygen evolution [4, 5]. Computer based simulations have reach a mature stage in which by choosing an adequate model according to objective, the simulation can not only represent correctly experimental results; but to propose materials that lead to a higher either catalytic activity or durability. In this work we present a Density Functional Theory (DFT) approach linked to experimental set ups to study the evolution reaction on metallic oxides.

## **2. Computational details and experimental setup**

All calculations were performed using the Vienna ab Initio Simulation Package (VASP)[6], employing the projector augmented wave (PAW) pseudopotentials[7, 8]. The electron-exchange correlation was treated within the spin polarized general gradient approximation and the Revised Perdew-Becke-Ernzerhoff (RPBE) exchange-correlation functional [9]. . The cutoff energy for the plane-wave basis expansion was chosen to be 400 eV. A quasi-Newton algorithm is used to relax ions into their instantaneous ground state, during the bulk optimization the ions were allowed to relax but the cell and its shape were kept constant. The first order method of Methfessel-Paxton was used to represent partial occupancies, and a conjugate gradient algorithm for electronic minimization. The convergence criteria for ionic and electronic convergence were set to  $10^{-4}$  and  $10^{-5}$  eV respectively. The  $\text{IrO}_2$  and  $\text{RuO}_2$  bulk experimental structures were obtained from the x-ray Cambridge database, but re-optimized allowing atom position and cell size and shape to change. After bulk optimization the (100) surface was modeled by (1x2) supercell slabs that are separated by 12 Å of vacuum, each oxide slab contains 16 oxide units, two bottom layers were kept fixed while the adsorbate and top layers were allowed to relax. For slab calculations a 11x11x1 Monkhorst-Pack k-point sampling was used. The detailed synthesis and preliminary results of  $\text{RuO}_2$  and  $\text{IrO}_2$  Co doped can be check on the reference in press [Corona-Guinto JL, et al., Performance of a PEM electrolyzer using  $\text{RuIrCoO}_x$  electrocatalysts for the oxygen evolution electrode, International Journal of Hydrogen Energy (2012), <http://dx.doi.org/10.1016/j.ijhydene.2012.12.071>].

## **3. Resultados y discusión**

The synthesized material present diffraction peaks corresponding to both iridium and ruthenium oxides, the inclusion of Co during the synthesis did not show the formation of a new phase, however new peaks (not identified)

are observed. However during the identification of elements present in the sample, the Co shows a uniform distribution on the sample. On figure 1 the polarization curves in stationary state for the oxygen evolution is shown. In this figure the current obtained with a commercial  $\text{RuIrO}_x$  catalyst is compared with the one obtained with the synthesized catalyst. From the open circuit potential to around 1.55 V the current remains equal to zero, implicating 0.4 V of overvoltage needed to reach a measurable current, however around 1.65 V the current using the  $\text{RuIrCoO}_x$  is the double than using the commercial RuIr oxide. Therefore the Co indeed affects the electrocatalytic intrinsic properties of the oxide and provides a way to diminish the overvoltage for the OER.

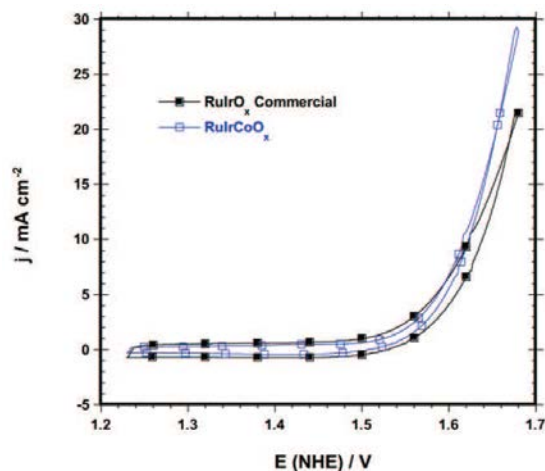
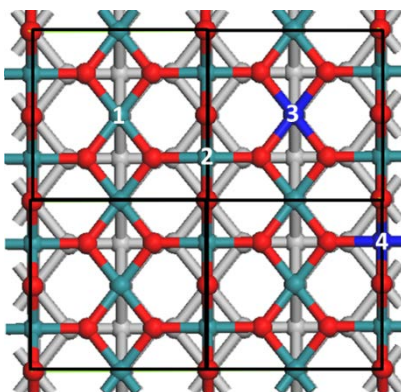


Figure 1. Polarization curves in acid media in oxidation direction, using a commercial  $\text{RuIrO}_x$  and the synthesized  $\text{RuIrCo}_x$  with relatively low amount of Co.

The optimization of the bulk oxide leads to a difference in lattice constant less than 1%. The (100) surface represents different sites for adsorption, the complete mechanism of oxygen evolution includes the adsorption of different species, co-adsorption and desorption of species. In this part of the project we report the adsorption energy of water on different sites and the influence of Co as a doping element. In figure 2, is presented a top view of the surface and the nomenclature used for the identification of the sites for adsorption.



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Figure 2. Top view of the surface of either Ru or Ir oxides, black line squares denote the unit cell. Only first layer is in color; green, blue and red atoms represent Ru (or Ir), Cobalt and oxygen respectively. 1) 5-coordinated metal site (5C), 2) 6-coordinated metal (6C), 3) 5-coordinated doped metal (5D-MO<sub>2</sub>), and 4) 6-coordinated doped metal (6D-MO<sub>2</sub>).

In this work we report water adsorption on top sites, i. e. the initial step of the oxygen evolution. Adsorption energy is calculated according to equation 1:

$$E_{ads} = E_{Ox-H_2O} - (E_{Ox} + E_{H_2O}) \quad (1)$$

Water adsorption on pure and doped structures is reported in Table 1. The results indicate that adsorption energy is function of the adsorption site, as well as dependent of the presence of dopants on the surface.

Table 1. Water adsorption energy on the metallic oxides (eV).

Surface	5C-site	5C-Co	6C-site	6C-Co
<b>RuO<sub>2</sub></b>	-0.61		0.04	
<b>6D-RuO<sub>2</sub></b>	-0.69		-0.12	-0.02
<b>5D-RuO<sub>2</sub></b>	-0.56	-0.29	+0.07	
<b>IrO<sub>2</sub></b>	-1.02		-0.11	
<b>6D-IrO<sub>2</sub></b>	-1.06		-0.14	+
<b>5D-IrO<sub>2</sub></b>	-1.01	-0.38	+0.22	

Some trends can be obtained by analyzing Table 1. 1) the adsorption energy is higher on the Ir oxide in comparison to the Ru oxide independently of the adsorption site; 2) the adsorption energy on the 6 coordinate is lower than in the 5 coordinated site. Therefore, whenever two adsorption sites Ru or Ir, water molecules will prefer to adsorb on Ir and in the 5coordinated sites. These differences in adsorption energy are those that make this system special, some of the reaction intermediates will be more stable in either one or another surface facilitating the subsequent evolution cycles. The addition of Co causes an even weaker adsorption, when water molecules are on top of the Co atom the adsorption is the weakest, but the distance Co-OH<sub>2</sub> (2.135 Å) is shorter than the distance in the pure oxides Ir-OH<sub>2</sub> (2.155Å) and Ru-OH<sub>2</sub> (2.69Å), therefore the Co site makes the adsorption even weaker but keeps the water molecule closer to the surface which also makes easier the electron transference. Now that we have checked the influence of the dopant and the nature of the reaction on the adsorption next we want to analyze the correctness of these assumptions by focusing on the next step of the evolution, given by reaction 2:



where M stands for the adsorption on a metal site, the adsorption site for the adsorption of hydrogen was named “S” because could be either a metal or an oxygen. We simulate the adsorption of hydrogen in every top site in a metal and oxygen finding that the adsorption is more stable on both oxygen sites. Therefore we propose the scheme depicted in Figure 3 for the 1<sup>st</sup> step of the OER.

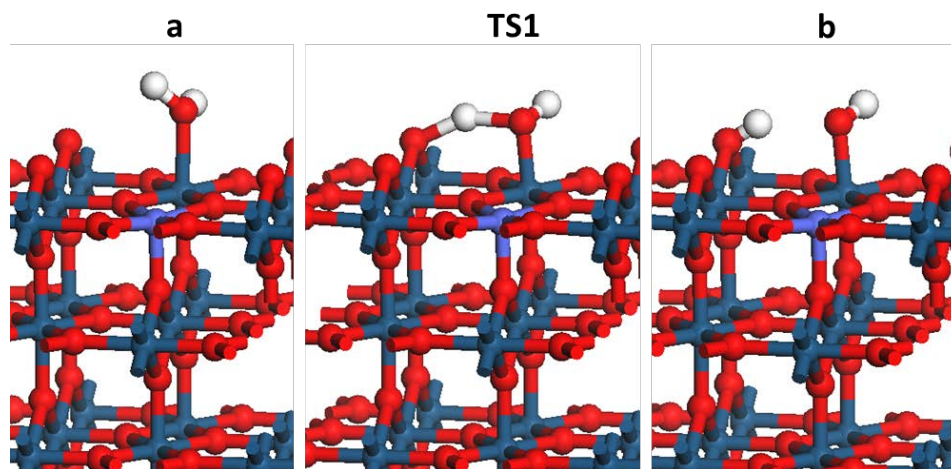
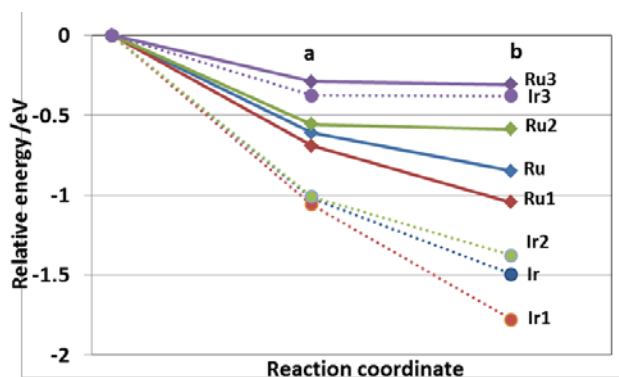


Figure3. First stage of OER; a) water adsorption, b) TS1; c) OH on metal and H on oxygen. Blue, purple, red and white spheres represent: Iridium (or ruthenium), Co, oxygen and hydrogen respectively.

On figure 3, the transition from state a to b implies a TS1 which determine the kinetic barrier for the pass from a to b. In this part of the work we present the energetic difference between b and a, which determines the thermodynamic driving force for the transition from state “a” to state “b”. In Figure 4, the values are graphed as relative energy from “a” to “b”.



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Figure 4. Relative energy change from 0-a (water adsorption energy) and a-b (thermodynamic driving force for the formation of OH-H eq.2). Ru and Ir stand for pure oxides, M1 stands for 6D-MO<sub>2</sub> with H<sub>2</sub>O adsorbed on M on a 5C site, M2 stands for 5D-MO<sub>2</sub> with H<sub>2</sub>O on M on a 5C site and M3 stands for 5D-MO<sub>2</sub> with H<sub>2</sub>O on Co on a 5C site.

The thermodynamic driving force for reaction on eq.2 to occur is higher on Ir compounds, on pure IrO<sub>2</sub> the change in electronic energy is ~0.5 eV while the same process on pure Ru is ~0.25 eV. When a Co dopant is added in a 6 coordinated position and the water is adsorbed on a 5 Ir (or Ru) position the change from “a” to “b” is energetically higher favored; however the process is more favorable in Ir doped compounds (~0.72 eV) than in Ru doped (~0.35 eV), despite of having roughly the same adsorption energy than in the pure oxide case. On the contrary when the dopant is added on the 5 coordinated position and the water molecule is adsorbed on Ir (or Ru) the thermodynamic driving force is lower than in the undoped metal, in the same situation but when the water molecule is adsorbed on the Co atom the driving force is almost zero.

More information on the effect of the dopant will be presented during the congress and specifically the kinetic barriers for the transformation will be reported.

### 4. Conclusions

The adsorption of water on IrO<sub>2</sub> and RuO<sub>2</sub> pure and doped with Co has been analyzed by DFT. It has been found the addition of Co greatly modifies the electronic structure of the oxide leading to very different adsorption energies and to differences on the formation energy of M-HO + S-H which is the first stage for the OER. The Co dopant on a hexa-coordinated site leads to a slightly higher adsorption energy and to a higher thermodynamic driving energy for water splitting. Activation energies will be provided during the meeting.

### 5. Acknowledgements

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