



#### Ab-initio modeling of Ru-based homogeneous catalysts for water oxidation



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### Artificial photosynthesis: using light to make fuels



Overall reaction: $2H_2O$  $\rightarrow O_2 + 2H_2$  $(\Delta G^0 = 4.92 \text{ eV}, E^0 = -1.23 \text{ V})$ Oxidation: $2H_2O$  $\rightarrow O_2 + 4H^+ + 4e^ (E^0 = 1.23 \text{ V})$ Reduction: $2H^+ + 2e^ \rightarrow H_2$  $(E^0 = 0.00 \text{ V})$ 

Figure from: Lewis and Nocera, PNAS 103, 15729 (2006)

### Artificial photosynthesis: using light to make fuels



 $2H^+ + 2e^- \rightarrow H_2$ **Reduction:** 

*Figure from:* Lewis and Nocera, PNAS **103**, 15729 (2006)

### **Natural photosynthesis: PSII**



### **Requirements for water oxidation catalysts**

The ideal water oxidation catalyst should be:

(1) <u>Efficient</u>: minimize the overpotential ( $\eta$ ) avoiding the formation of high energy intermediates such OH or  $H_2O_2$ 



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(2) **<u>Stable</u>**: organic ligands of organometallic catalysts are typically easily oxidized, reducing the lifetime of the catalyst

(3) **Cheap:** we should minimize the use of precious metals such as Pt, Ru, Ir, ...



Synthesized by two research groups: Sartorel *et al.* JACS **130**, 5006 (2008) Geletii *et al.* Angew. Chem. **47**, 3896 (2008)





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S,

#### WHY Ru<sub>4</sub>-POM?

OX:

- Small overpotential ~ 0.35 V
- No deactivation over days
- High turnover rate (~ 450 cycles/h)



# Ru<sub>4</sub>-POM



- Ru<sub>4</sub>-POM has been adsorbed on functionalized nanotubes, on top of a conducting electrode, thus creating an anodic material for WAT-OX.
- The catalytic performance seen in the homogeneous phase is preserved also in the heterogeneous one

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# Ru<sub>4</sub>-POM

- 5 reaction intermediates  $(S_0 S_4)$  have been identified and characterized through Raman spectroscopy
- The energetics of 3 steps  $(S_0 S_3)$  has been determined

through cyclic voltammetry (also pH dependency)

• 4 PCET steps:  $Ru(IV)-H_2O \rightarrow Ru(V)-OH$ 



Sartorel et al. J.AM. CHEM. SOC., 131, 16051 (2009)

### **Proposed reaction clycle: PCET**



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## **Computational approach**

#### **Electronic structure**

• GGA (PBE) / Hybrid (HSE06, B3LYP) exchange-correlation functionals (CP2K)

#### Nørskov's approach for the energetics of PCET

- $\frac{1}{2} \mu(H_2) = \mu(H^+) + \mu(e^-)$
- $\bullet \, \Delta \, G \simeq \Delta \, E^{\text{DFT}} + \Delta \, Z P E^{\text{DFT}} \text{ } T \Delta \, S$



## **Computational approach**

#### Solvent effects?

• Energetics computed in vacuum. For PCET reactions implicit solvent calculations show very small solvent effects on the energetics (~0.01 eV per PCET step)



**QM/MM** calculations in 1800 TIP3P water molecules to study the effect of the solvent on the structural and electronic properties of  $Ru_4$ -POM

## Molecule in solution: QM/MM (PBE)

#### Ru-Ru distances





The distortion of the Ru tetrahedron is correctly captured only when solvent effects are included

Distance	Vacuum	QM/MM	Ехр
μ -ΟΗ	3.55	3.67	3.66
μ-Ο	3.53	3.49	3.47

## **Simplified cluster for hybrids**

To reduce the computational cost associated with the use of **hybrid functionals** we replace the POM ligands with CI atoms:



## Simplified cluster for hybrids

- All calculations predict a singlet ground state Diamagnetic EPR silent
- Ru spin polarization 1.5: Ru(IV) with 2 unpaired spins per Ru atom
- Antiferromagnetic coupling of Ru centers across  $\mu$  -OH bridges
- HOMO-LUMO 1.92/1.68 eV (B3LYP/HSE06)
- Frontiers orbitals always localized on the Ru<sub>4</sub>O<sub>6</sub> core
- Four highest occupied states in 0.37 eV energy window



### **Analysis of spin density**





## **Energetics of the simplified cluster**

To reduce the computational cost associated with the use of hybrid functionals we replace the POM ligands with CI atoms:



Error of structural simplification: ~ 0.1 eV per PCET event.

 $\Delta E^{\text{hybrid}}(\text{Ru}_{4}\text{-POM}) \sim \Delta E^{\text{PBE}}(\text{Ru}_{4}\text{-POM}) + [\Delta E^{\text{hybrid}}(\text{Ru}_{4}\text{-CI}) - \Delta E^{\text{PBE}}(\text{Ru}_{4}\text{-CI})]$ "core" correction









#### **Oxygen evolving complex in PSII**



*Figure from:* JP McEvoy and GW Brudvige, Chemical Reviews **106**, 4455 (2006)



 $\Delta G(S0 \rightarrow S4)$  is not sufficient to oxidize water: Higher oxidation states?



 $\Delta G(S0 \rightarrow S4)$  is not sufficient to oxidize water: Higher oxidation states?





 $\Delta G(S2 \rightarrow S6)$  is sufficient to oxidize water.

 In this scheme the O-O bond making step takes place after the catalyst has been oxidized 4 times





### **DFT simulations of the O-O bond formation**

#### Solvated Ru<sub>4</sub>-CI: PBE simulations



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#### Solvated Ru<sub>4</sub>-CI: PBE simulations





### **Possible mechanisms of O-O bond formation**

#### Intramolecular paths (direct mechanism)



• oxo ligand - oxo  $Ru_4O_4$  cluster (as in PSII)

#### Nucleophilic attack (acid-base mechanism)



• This is the mechanism found in "Blue dimer"

### **Possible mechanisms of O-O bond formation**



Figure from: LP. Wang and T. van Voohris, J. Phys. Chem. Lett., 2011, 2 (17), pp 2200–2204

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CV1: O-O coordination number



Nucleophilic attack (Acid-base) is favored



- CV1: O-O coordination number
- CV2: O-H coordination number



CV1: O-O coordination number

CV2: O-H coordination number

<u>B3LYP correction</u> to PBE activation energy evaluated through single point calculations





Metadynamics predicts a nucleophilic attack rather than an intramolecular mechanism

<u>PBE/B3LYP</u> estimate: 0.79 - 0.96 eV <u>Experimental</u> estimate: 0.83 - 1.01 eV (Blue dimer: 1.12 eV)

The intramolecular mechanism has a prohibitively high activation energy (2.2 eV)









• In this path a single Ru atom is involved in the catalytic process



- Thermodynamically the two paths are equivalent
- Activation energies of the PCET steps might favor one of the two paths

## **Intermediates of the catalytic cycle**

#### Mechanism on Ru₄-POM



### Intermediates of the catalytic cycle

#### Mechanism on Ru₄-POM







- Overpotential  $\eta$  = 1.53-1.23 = 0.30 eV (exp: 0.35 eV)
- $\eta$  is determined by the Ru(V)-OH  $\rightarrow$  Ru(VI)=O step

#### **Electrolysis of water on oxide surfaces**



Why do we have a finite overpotential?

Figures from: Rossmeisl et al. J. Electr. Chem 607, 83-89 (2007)

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Ru<sub>4</sub>-POM ΔG<sub>2</sub> + ΔG<sub>3</sub> = 3.00 eV η = 0.30 eV 

 Metal oxides

  $\Delta G_2 + \Delta G_3 = 3.2 \text{ eV}$   $\pm 0.2 \text{ eV} (68\%)$ 
 $\pm 0.4 \text{ eV} (95\%)$  

 "Ideal" catalyst  $\Delta G_2 = \Delta G_3 = 1.6 \text{ eV} (\eta = 0.37 \pm 0.1 \text{ eV})$ 



 $\label{eq:relation} \begin{array}{l} \textbf{Ru}_{4}\textbf{-POM} \\ \textbf{\Delta G}_{2} + \textbf{\Delta G}_{3} = 3.00 \text{ eV} \\ \eta = 0.30 \text{ eV} \end{array}$ 

Ru<sub>4</sub>-POM complies with the "universal" constraint on  $\Delta G_2 + \Delta G_3$ 

- Ru<sub>4</sub>-POM is an almost "ideal" catalyst
- All atoms in Ru<sub>4</sub>-POM are active sites

## **Summary**

- The O-O bond formation takes place through a nucleophilic attack of water molecule on an oxo intermediate
- The overpotential is determined by the formation of the oxo intermediate
- The activation energy of the O-O bond formation is compatible with the observed kinetics

• Paths involving a single Ru center are also possible, suggesting that the efficiency of this catalyst is not linked to cooperative effects of the four Ru centers, but to the favorable spread of the thermodynamic cost among the key intermediates

• The thermodynamics of the reaction cycle promoted by Ru₄-POM can be understood on the basis of the energetics of metal oxides

•  $Ru_4$ -POM is an "optimal  $RuO_2$  cluster" where every single atom is a surface atom and hence an active site.

### **Summary**

#### THANKS TO:

- Stefano Fabris
- Andrea Sartorel and Marcella Bonchio
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(1) S. Piccinin and S. Fabris, *Phys. Chem. Chem. Phys.* 13, 7666-7674 (2011)
(2) S. Piccinin. A. Sartorel, M. Bonchio and S. Fabris, *submitted*