Ab-initio modeling of water oxidation catalysts: Co-Pi and Ru4-POM

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Artificial photosynthesis: “solar to fuel”

\[ 2H_2O \rightarrow O_2 + 2H_2 \quad \Delta G^0 = 4.92 \text{ eV}, \quad E^0_{\text{NHE}} = -1.23 \text{ V} \]

**Ox:** \[ 2H_2O \quad \rightarrow \quad O_2 + 4H^+ + 4e^- \quad E^0_{\text{NHE}} = 1.23 \text{ V} \]

**Red:** \[ 2H^+ + 2e^- \rightarrow H_2 \quad E^0_{\text{NHE}} = 0.00 \text{ V} \]

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

Heterogeneous catalysts
RuO$_2$, IrO$_2$, Co$_3$O$_4$

Homogeneous catalysts
Single- and multi-center TM-based catalysts (Ru, Ir, Co, Mn)

- The surface of the catalyst under reaction conditions is difficult to characterize
- Stable under suitable pH conditions

- Well characterized, the mechanism of reaction can be investigated with a variety of techniques
- Often short-lived, due to ligand oxidation

Requirements
- Low overpotential
- No degradation
- Based on earth-abundant elements
Outline of the talk

Heterogeneous catalysts

Co-Pi: What is the structure?

Homogeneous catalysts

Ru4-POM: What is the reaction mechanism?
**Co-Pi: experimental determination of the structure**

**SEM**

of electrodeposited film

• Amorphous

• Electrodeposited (1.10-1.25 V, NHE) on ITO

• Co(II) ions and KPi buffer at pH=7

• Co:P:K ~ 2:1:1 ratio

• Evidence of Co(III) and Co(IV) ions in the film

Co-Pi: experimental determination of the structure

SEM
of electrodeposited film

EXAFS
Ext. X-ray absorption fine structure

Co-Pi clusters
Complete/incomplete cubanes

• Amorphous
• Electrodeposited (1.10-1.25 V, NHE) on ITO
• Co(II) ions and KPi buffer at pH=7
• Co:P:K ~ 2:1:1 ratio
• Evidence of Co(III) and Co(IV) ions in the film

M.W. Kanan et al., JACS 132, 13692 (2010)
Computational approach

- Metadynamics (Shell Model)
- DFT optimizations
- EXAFS simulations

\[ \left( -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \]
Co-Pi: metadynamics simulations (Shell Model)

To drive the formation of Co-O and O-Co-O bonds:

$\textbf{CV1:}$ # Co$_i$-O bonds \[ \Sigma_{ik} \text{CN} (\text{Co}_k-\text{O}_i) \]

$\textbf{CV2:}$ # Co bridging 2 O atoms \[ \Sigma_{ikj} \text{CN} (\text{Co}_k-\text{O}_i) \times \text{CN} (\text{Co}_k-\text{O}_j) \]
Co-Pi: free energy landscape
Co-Pi: formation of cubanes

To drive the formation of $\text{Co}_4\text{O}_4$ cubanes:

CV3: $\sum \text{CN}_1 (\text{Co-Co}) \times \cdots \times \text{CN}_6 (\text{Co-Co})$

Cubanes are terminated with phosphates.
Co-Pi: formation of cubanes

To drive the formation of $\text{Co}_4\text{O}_4$ cubanes:

CV3: $\Sigma \text{CN}_1 (\text{Co-Co}) \times \ldots \times \text{CN}_6 (\text{Co-Co})$

Cubane units are stable even at high temperature
Co-Pi: simulated EXAFS

Grain 6

\[ \chi(k) \propto k^3 \]

\( k [\text{Å}^{-1}] \)

EXAFS

Grain 1

\[ \exp \quad \text{grain 1} \]

\[ \text{cubane motifs} \]

\( k [\text{Å}^{-1}] \)

EXAFS

\( r [\text{Å}] \)

\[ g(r) \]

\[ |\chi(R)| [,\text{Å}^{-1}] \]

Apparent distance \( R [\text{Å}] \)

FT–EXAFS

\( r [\text{Å}] \)

\[ g(r) \]

\[ |\chi(R)| [,\text{Å}^{-1}] \]

Apparent distance \( R [\text{Å}] \)

FT–EXAFS
Co-Pi: summary

- Cubanes are present in Co-Pi and stable even at high T
- Cubanes are always connected to phosphates
- The cubane-rich portion of the simulated particles reproduce well the experimental EXAFS
- The cubane-rich portion of our amorphous nanoparticles are reliable structural models of the Co-Pi catalyst surface.
Water oxidation catalysts

Heterogeneous catalysts

Co-Pi: What is the structure?

Homogeneous catalysts

Ru4-POM: What is the reaction mechanism?
Ru4-POM

Synthesized by two research groups:
Sartorel et al. JACS 130, 5006 (2008)

**OX:** 2H₂O → O₂ + 4H⁺ + 4e⁻

**RED:** 4Ce⁴⁺ + 4e⁻ → 4Ce³⁺ (pH 1.8)

WHY Ru4-POM?
- Small overpotential ~ 0.35 V
- No deactivation over days
- High turnover rate (~ 450 cycles/h)
Ru4-POM @ CNT

Toma et al., Nature Chemistry 2, 826 (2010)
Computational approach

Electronic structure

• DFT calculations with GGA (PBE) / Hybrid (HSE06, B3LYP) functionals (CP2K)

Nørskov’s approach for the energetics of PCET

• $\frac{1}{2} \mu(H_2) = \mu(H^+) + \mu(e^-)$
• $\Delta G \approx \Delta E_{\text{DFT}} + \Delta ZPE_{\text{DFT}} - T\Delta S$

\[
\Delta G(V) = G(M-OH) + \mu(H^+) + \mu(e^-) - G(M-OH_2) \\
= G(M-OH) + \frac{1}{2} \mu(H_2) - eV - G(M-OH_2) \\
= \Delta G(V=0) - eV
\]

Proposed reaction cycle: 4 PCET

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]

1) Raman spectra

Sartorel et al. JACS 131, 16051 (2009)

2) pH variation of CV peaks

Geletii et al. JACS 131, 17360 (2009)
Energetics of the catalytic cycle

\[
\Delta G \text{ [eV]}
\]

Reaction Intermediates

S_0 \quad S_1 \quad S_2 \quad S_3 \quad S_4
Energetics of the catalytic cycle

\[ \Delta G(S_0 \rightarrow S_4) = 3.38 \ll 4.92 \ (4.56) \text{ eV} \]
Energetics of the catalytic cycle

\[ \Delta G = 3.38 \text{ eV} \]
Energetics of the catalytic cycle

\[ \Delta G = 3.38 \text{ eV} \]

Higher oxidation states?
Energetics of the catalytic cycle

S2

S6

OH – Ru^V

Ru^V

Ru^vi

Ru^vi – O

H_2O

OH – Ru^V

Ru^V

Ru^iv – H_2O

OH
Mechanism for O-O bond formation
Possible mechanisms of O-O bond formation

Intramolecular paths (direct mechanism)

- oxo ligand - oxo in Ru₄O₄ cluster
  (as proposed for OEC in PSII)

Nucleophilic attack (acid-base mechanism)

- oxo ligand – oxygen in water
  (as proposed for the “Blue dimer”)
Metadynamics

~ 2ps x 8 replicas, biasing 2 CVs to drive the O-O bond formation
Metadynamics simulations of the O-O bond formation

**CV1**: O-O coordination number

**CV2**: O-H coordination number
Metadynamics simulations of the O-O bond formation

**CV1**: O-O coordination number

**CV2**: O-H coordination number

PBE/B3LYP estimate: 0.79 - 0.96 eV
Experimental estimate: 0.83 - 1.01 eV

The intramolecular mechanism has a prohibitively high activation energy (2.2 eV)
Energetics of the catalytic cycle
Energetics of the catalytic cycle
Energetics of the catalytic cycle
Energetics of the catalytic cycle

- In this path a single Ru atom is involved in the catalytic process
Energetics of the catalytic cycle

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

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

Overpotential: 1.53 - 1.23 = 0.30 V
Exp: = 0.35 V
Intermediates of the catalytic cycle

Mechanism on Ru4-POM

a) Ru-$\text{H}_2\text{O}$    b) Ru-$\text{OH}$    c) Ru=$\text{O}$    d) Ru-$\text{OOH}$    e) Ru-$\text{OO}$
Intermediates of the catalytic cycle

Mechanism on Ru4-POM

- **a)** Ru-H_2O
- **b)** Ru-OH
- **c)** Ru=O
- **d)** Ru-OOH
- **e)** Ru-OO

Mechanism on metal oxides

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{OH}^- \rightarrow \text{O}^2- \rightarrow \text{O}^2- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}
\end{align*}
\]
Intermediates of the catalytic cycle

Mechanism on Ru4-POM
a) Ru-H₂O  b) Ru-OH  c) Ru=O  d) Ru-OOH  e) Ru-OO

Ru4-POM vs RuO₂
- same key intermediates as RuO₂
- same reaction mechanism
- same overpotential (~ 0.3 V)
- can the core of Ru4-POM be thought of as minimal RuO₂ unit embedded in inorganic ligands?
Intermediates of the catalytic cycle

Mechanism on metal oxides

\[ \Delta G_2 = \Delta E(O) - \Delta E(OH) + \Delta ZPE - T\Delta S \]
\[ \Delta G_3 = \Delta E(OOH) - \Delta E(O) + \Delta ZPE - T\Delta S \]

\[ \Delta G_2 + \Delta G_3 = \text{const } (3.2 \pm 0.2 \text{ eV}) \]

J. Rossmeisl, J.K. Nørskov et al.
Ru4-POM vs. RuO$_2$

(b)

- $\Delta G_2$
- $\Delta G_3$

$\Delta G$ [eV] vs. $\Delta E_0$ [eV]

-1.23

(b)
Ru4-POM vs. RuO₂

![Graph showing the energetics of water oxidation reactions for Ru4-POM and RuO₂.](image)

(b) 

- ΔG₂
- ΔG₃

overpotential

ΔG [eV] vs. ΔEₕ [eV] plot with highlighted regions and overpotential notation.
Ru4-POM vs. RuO$_2$
Ru4-POM vs. RuO$_2$

(b)

$\Delta G$ [eV] vs. $\Delta E_O$ [eV]

- $-\Delta G_2$
- $-\Delta G_3$

overpotential
Ru4-POM vs. RuO$_2$

Δ$G_2$ = +1.53 eV

Δ$G_3$ = +1.47 eV

Δ$E_O$ [eV]
Ru4-POM vs. RuO$_2$

(a) $\Delta G$ [eV]

(b) $\Delta E_o$ [eV]
Ru4-POM: Summary

- **Mechanism:** nucleophilic attack of water molecule on an oxo intermediate

- **Activation energies ~ 0.8 eV**

- 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

- Ru4-POM is an “optimal RuO$_2$ cluster” where every single atom is a surface atom and hence an active site.
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REFERENCES
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Co-Pi: fitting the empirical potential

Shell Model potential

$$V_{cs} = \frac{1}{2kr_{cs}}$$

$$V_{ij} = A \exp(-r_{ij}/B) + z_i z_j / r_{ij}$$

Fit against DFT-PBE total energy differences for Co$_3$O$_4$ and K$_3$PO$_4$