First-principles thermochemistry of water oxidation catalyzed by a tetraruthenium-oxo core $[\text{Ru}_4\text{O}_6]^{4+}$

Simone Piccinin and Stefano Fabris
CNR-IOM Democritos Simulation Center and SISSA
Trieste - ITALY
Artificial photosynthesis

Overall reaction: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2 \quad (\Delta G^0 = 4.92 \text{ eV})$

Oxidation: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (\Delta G^0 = 4.92 \text{ eV, NHE})$

Reduction: $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 \quad (\Delta G^0 = 0.00 \text{ eV, NHE})$

*Picture from:* Lewis and Nocera, PNAS 103, 15729 (2006)
Requirements for wat-ox catalyst

(1) To be **efficient**, the reduction potential ($E^0$) of the catalyst (for each oxidation step!) needs to be fine tuned:

- $E^0$ has to be high enough to oxidize water (>1.23 V, pH=0, NHE)
- $E^0$ has to be low enough to avoid the formation of high energy intermediates like $\text{OH}^-$ or $\text{H}_2\text{O}_2$ (< 1.50 V, pH=0, NHE)

(2) The catalyst needs to be **stable**: organic ligands of all the proposed organometallic catalysts to date are easily oxidized, reducing the lifetime of the catalyst
Synthesized by two research groups:
Sartorel et al. JACS 130, 5006 (2008)
Ru₄-POM

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RED: 4Ce⁴⁺ + 4e⁻ → 4Ce³⁺ (pH 1.8)
OX: 2H₂O → O₂ + 4H⁺ + 4e⁻

WHY Ru₄-POM?
• Small overpotential ~ 0.2 V
• No deactivation over days
• High turnover rate (~ 450 cycles/h)
Proposed reaction cycle: PCET

Raman measurements and pH-dependence of cyclic voltammetry support the PCET model.
Computational approach

**Electronic structure**
- GGA (PBE) / Hybrid (HSE06, B3LYP) exchange-correlation functionals
- Mixed local basis set/plane waves (CP2K/QUICKSTEP)

**Structural optimization**
- All structures are relaxed to the (local) minimum energy configuration

**Solvent effects?**
- Modeling done in vacuum. For PCET reactions implicit solvent calculations show very small solvent effects on the energetics (~0.01 eV per PCET step)

**Nørskov’s approach for the energetics of PCET**
- $\frac{1}{2} \mu(H_2) = \mu(H^+) + \mu(e^-)$
- $\Delta G = \Delta E + \Delta ZPE - T\Delta S$
Simplified cluster for hybrids

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

$$\Delta E = E(S_n) + n/2E(H_2) - E(S0)$$

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta E$ (eV) $\text{Ru}_4\text{-POM}$</th>
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<tbody>
<tr>
<td>S0</td>
<td>0.00</td>
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</tr>
<tr>
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<td>1.03</td>
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<td>S4</td>
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Error of structural simplification: ~ 0.1 eV per PCET event.
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To reduce the computational cost associated with the use of hybrid functionals we replace the POM ligands with Cl atoms:

\[
\begin{align*}
\text{Ru}_4\text{-POM} & \rightarrow \text{Ru}_4\text{-Cl} \\
\end{align*}
\]

Error of structural simplification: \(\sim 0.1\) eV per PCET event.

\[
\Delta E = E(Sn) + n/2E(H_2) - E(S0)
\]

\[
\Delta E_{\text{hybrid}}(\text{Ru}_4\text{-POM}) \sim \Delta E_{\text{PBE}}(\text{Ru}_4\text{-POM}) + [\Delta E_{\text{hybrid}}(\text{Ru}_4\text{-Cl}) - \Delta E_{\text{PBE}}(\text{Ru}_4\text{-Cl})]
\]

"core" correction

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Energetics of the catalytic cycle

![Graph showing energetics of reaction intermediates](image-url)
Energetics of the catalytic cycle

![Graph showing energy changes in reaction intermediates.](image)
Energetics of the catalytic cycle

Spin density for S2

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

Reaction Intermediates

- \( S_0 \)
- \( S_1 \)
- \( S_2 \)
- \( S_3 \)
- \( S_4 \)

Exp Sartorel
B3LYP
HSE06

1.97
1.93
-1.38
-1.36
Energetics of the catalytic cycle

Spin density for S2

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

Reaction Intermediates

- Exp Sartorel
- B3LYP
- HSE06

1.97
1.93
-1.38
-1.36

\[ \text{e}_g \]

\[ \text{t}_{2g} \]

\[ \text{Ru}^{IV} (d^4) \]

\[ \text{Ru}^{V} (d^3) \]
Energetics of the catalytic cycle

- The computed $\Delta G(S_0 \rightarrow S_4)$ is considerably lower than the thermodynamic requirement to oxidize water (4.92 eV).

- Hybrid functionals give a considerably better agreement compared to PBE.
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$\Delta G(S_0 \rightarrow S_4)$ is not sufficient: Higher oxidation states?

$\text{Ru}^{VI}=\text{O}$
Energetics of the catalytic cycle

![Diagram showing energetic changes across reaction intermediates](image-url)
Energetics of the catalytic cycle

- $3.97 \text{ eV}$
- $4.73 \text{ eV}$
Energetics of the catalytic cycle

\[ 5.04 \text{ eV} \]

\[ 5.97 \text{ eV} \]
Energetics of the catalytic cycle

\[ \Delta G(S_1 \rightarrow S_5) = 3.97, 4.73 \text{ eV} \]
\[ \Delta G(S_2 \rightarrow S_6) = 5.04, 5.97 \text{ eV} \]

- Ru\textsuperscript{VI}=O intermediates are likely involved in the catalytic cycle;
- This has been shown to be the case also for OEC of PSII and for the “blue dimer”.

● Ru\textsuperscript{VI}=O intermediates are likely involved in the catalytic cycle;
Summary

• We modeled the structural and electronic properties of the intermediates of the water oxidation catalytic cycle under the assumption of PCET steps;

• The proposed S0/S4 couple does not provide a sufficient driving force to oxidize water \( \Delta G (S0/S4) < 4.92 \text{ eV} \); 

• Ru\textsuperscript{VI}=O (oxo or oxyl) intermediates are likely involved, in line with the proposed mechanism for OEC of PSII and the “blue dimer”.
Summary

• We modeled the structural and electronic properties of the intermediates of the water oxidation catalytic cycle under the assumption of PCET steps;

• The proposed S0/S4 couple does not provide a sufficient driving force to oxidize water [$\Delta G (S0/S4) < 4.92 \text{ eV}$];

• Ru$^{VI}$=O (oxo or oxyl) intermediates are likely involved, in line with the proposed mechanism for OEC of PSII and the “blue dimer”.

OUTLOOK

• Modeling the O-O bond formation in solution starting from Ru$^{VI}$=O

THANKS TO:

• Stefano Fabris
• Andrea Sartorel and Marcella Bonchio
• EU-FP7 Marie Curie, CINECA
PBE vs. HYBRIDS

Ru-OH$_2$ vs. Ru-OH

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<th>System</th>
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<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td>Ru-OH</td>
<td>3.02</td>
<td>2.41</td>
<td>2.36</td>
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PBE vs. B3LYP vs. HSE06

$\mu$ = 0.34

$\mu$ = 1.90

$\mu$ = 1.94
Molecule in solution: QM/MM (PBE)

Ru-Ru distances

<table>
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<tr>
<th>Distance</th>
<th>Vacuum</th>
<th>QM/MM</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu)-OH</td>
<td>3.55</td>
<td>3.67</td>
<td>3.66</td>
</tr>
<tr>
<td>(\mu)-O</td>
<td>3.53</td>
<td>3.49</td>
<td>3.47</td>
</tr>
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\(\mu\)-OH bridged Ru atoms are AF coupled
• E0 as function of the oxidation step is constant in PBE $\rightarrow \Delta G$ to remove a e-/H+ pair is the same for S0, S1, S2, S3
• E0 as function of the oxidation step an oscillating with hybrid functionals
• No functional reproduces the linear increase of E0 fith the oxidation steps;
• PBE and hybrid functionals give quantitatively different results, mostly due to the different description of the Ru-OH bond;
• Solvent effects enhance the distortion of the Ru cage (almost perfect agreement with experimental measurements);
• Our calculations suggest that the PCET model is, not compatible with the cyclic voltammetry measurements.

Acknowledgments

• A. Sartorel and M. Bonchio
• Marie Curie Fellowship
Sartorel et al.

Raman spectra: experimental+theoretical analysis suggests the formation of OH ligands in place of H\textsubscript{2}O ligands → PCET
Method: Nørskov's protocol*

- **Set the reference potential to NHE:**
  
  \[
  \text{NHE: } \quad H^+ + e^- \leftrightarrow \frac{1}{2} \mu(H_2) \\
  \frac{1}{2} \mu(H_2) = \mu(H^+) + \mu(e^-)
  \]

- **Compute total energies via DFT and correct for:**
  
  ΔZPE (zero point energy)
  
  TΔS (entropic contributions)
  
  neglect solvent effects (vacuum)
  
  \[
  \Delta G = \Delta E + \Delta ZPE + T\Delta S
  \]

  → Overpotential for O₂ reduction with ~0.1 eV

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