The Role of Uranium-Arene Bonding in H₂O reduction Catalysis

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Background:
Storage of unequally produced renewable energies, preferentially by electrocatalytic H₂O reduction to H₂, is required to promote green energy. Due to its high reducing power, depleted (only weakly radioactive) U(IV) is an appealing material to catalyze H₂O reduction, as recently shown by the first uranium-based electrocatalyst [U(IV)(H₂O)₆]₃⁺(U) (1). Despite the rich redox chemistry of uranium complexes, catalysis remains scarce. An often discussed reason is that U complexes tend to undergo step-wise 1e⁻ reactions, whereas transition metal catalysis often proceeds through concerted 2e⁻ pathways. This poster presents a detailed analysis how metal-ligand redox-cooperativity enables catalysis via concerted 2e⁻ reactivity with uranium. Analogous lanthanide complexes were investigated to gain further insight in Felament catalysis.

DFT supports S-bonding: Computational evidence for coordinated S-bonding

Introduction
Low-valent U(III) is a strong reductant activating small molecules. Catalysis is very rare due to prevailing 1 e⁻ reactivity.

- Metal-ligand redox-cooperativity is desired
- Uranium-arene β-bonding facilitates direct electronic communication

The Complex

The Ligand

Lanthanide catalysts

- 7-RNd-H₂O 
- 7-R

Structural parameters: 

<table>
<thead>
<tr>
<th>Parameter</th>
<th>U-O</th>
<th>U-N</th>
<th>M-O</th>
<th>M-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>2.325 Å</td>
<td>2.193 Å</td>
<td>2.003 Å</td>
<td>1.972 Å</td>
</tr>
<tr>
<td>Gd</td>
<td>2.199 Å</td>
<td>2.069 Å</td>
<td>1.898 Å</td>
<td>1.873 Å</td>
</tr>
<tr>
<td>Tm</td>
<td>2.055 Å</td>
<td>2.415 Å</td>
<td>1.978 Å</td>
<td>1.965 Å</td>
</tr>
</tbody>
</table>

Proposed Mechanism: 

1. Active catalyst is formed by metal-ligand redox-cooperativity.
2. Electrocatalytic H₂O reduction to H₂ is enabled.
3. Tafel analysis of the electrocatalytic reaction is shown.

Electrocatalytic parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LNC/H₂O</th>
<th>LNC/H₂O</th>
<th>LNC/H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₀</td>
<td>-0.05 V</td>
<td>-0.02 V</td>
<td>-0.04 V</td>
</tr>
<tr>
<td>kcat</td>
<td>1.2 × 10⁷ M⁻¹ s⁻¹</td>
<td>2.1 × 10⁶ M⁻¹ s⁻¹</td>
<td>1.5 × 10⁶ M⁻¹ s⁻¹</td>
</tr>
</tbody>
</table>

Tafel plot obtained by foot-of-the-wave analysis (FOWA)

Proposed Mechanism

DFT Analysis

SOMOS of TS-1

Redox Activity of Ligand – Organic Radicals?

Catalytic activity of U(III) complex 1 is enabled by metal-ligand redox-cooperativity as evidenced by EPR, DFT, and reactivity studies.

Take–Home Message

- Redox active ligand
- 2 e⁻ concerted fast

- Metal–ligand redox cooperativity through covaent bonding is a new and broadly applicable concept to enable catalysis.
- A plethora of reported Felament mediated reactions could become catalytic by following the concept introduced here.

Summary:

- Complex [U(IV)(H₂O)₆]₃⁺(U) (1) is the first reported uranium electrocatalyst. It facilitates H₂O reduction to H₂ by harnessing metal ligand redox-cooperativity.
- The proposed catalytic cycle and the redox cooperativity are supported by CV, EPR, XRD, and DFT analysis.
- Lanthanide complexes [L₃M(H₂O)₆]³⁺ (7-L₆) also catalyze H₂O reduction, allow overpotential tuning, and provide further mechanistic insight in underdeveloped Felament catalysis.

Literature: