A stable molecular water oxidation catalyst for artificial photosynthesis

B. Botar[1], P. Kögerler[1,2]

[1] IFF-9: Electronic Properties
[2] Institute of Inorganic Chemistry, RWTH Aachen University

The oxidation of water represents a key reaction in many proposed artificial photosynthesis systems that aim to convert sunlight energy into the splitting and formation of chemical bonds. However, catalysts are required to eliminate kinetic obstacles inherent to this elementary reaction. While numerous relevant molecular catalysts were tested in the past decades, all systems suffer from oxidative degradation of their organic constituents during the course of the catalyzed reaction. We now identified an all-inorganic that retains its high efficiency at ambient temperature under turnover conditions.

The design of viable and well-defined molecular catalysts for water oxidation, in part inspired by the Mn_4Ca-centered water oxidation-oxygen evolving center (OEC) in photosystem II, is being pursued for three decades and centers on transition metal coordination complexes such as the classic $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ system.[1] Despite ongoing research, however, stable and rapid molecular and homogeneous catalysts for the elementary reaction ($2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$) that exhibit long-term stability have yet to be achieved: Homogenous catalytic oxidation studies suggest that likely intermediates in H_2O oxidation would degrade all organic ligands, a point consistent with the findings in the molecular H_2O oxidation catalysts reported to date.[2] Thus, the need to develop highly active and stable H_2O oxidation catalysts remains of considerable importance. Based on the reported Ru_2 catalysts for H_2O oxidation, documented polyoxometalate complexes with multinuclear d-electron-containing centers capable of accepting several electrons needed for H_2O oxidation, and the report of electrocatalytic O_2 evolution by the complex $[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$,[3] we developed a tetraruthenium(IV) polyoxotungstate complex, isolated as

$$Rb_8K_2[\,\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma{-}Si\,W_{10}O_{36})_2\,]\cdot 25\,H_2O\ , \qquad \textbf{(1)}$$

an oxidatively and hydrolytically stable complex that addresses some of the core challenges – it catalyzes the rapid oxidation of H_2O to O_2, does so in aqueous solution, and is quite stable under turnover conditions.[4]

The X-ray crystal structure of **(1)** reveals the same “out-of-pocket” d-metal coordination polyhedra observed in water-soluble γ-di-iron(III) derivatives; namely, the Ru centers are corner-sharing and not ligated to the central SiO_4 unit. The two “out-of-pocket” $\{\gamma\text{-}SiW_{10}Ru_2\}$ monomeric units are rotated by 90° around the vertical C_2 axis relative to one another defining overall D_{2d} symmetry for the polyanion (Fig. 1). The staggered structure facilitates incorporation of a $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4]^{4+}$ core in which the four Ru centers span a slightly distorted tetrahedron with Ru-Ru distances of 3.47-3.66 Å. The adjacent Ru centers within each $\{\gamma\text{-}SiW_{10}Ru_2\}$ unit are bridged by hydroxo ligands, while oxo ligands bridge the Ru centers of different monomeric units. The presence of μ-oxo Ru-O-Ru bridges is consistent with other structural reports on dimeric Ru-containing polyoxometalates. Several lines of evidence – magnetic properties, bond valence sums, electrochemical properties – indicate that during the synthesis of **(1)**, the Ru(III) reactant is oxidized by O_2 to give a $Ru(IV)_4$ complex.

In preparation for catalytic studies, several techniques were used to further characterize oxidation states and potentials of the ruthenium centers and the protonation states of the $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4]^{4+}$ core. Repeated acid-base titration in both directions monitored both by pH and the UV-visible spectra indicate that **(1)** has 2 pK_a values in the pH range 3.5-4.5 and these titrations are reversible. Cyclic voltammograms (CVs) of aqueous solutions of **(1)** are pH dependent. At pH 1.0, two oxidation peaks at ca. 940 and at 1050 mV are observed in a scan from the rest potential (800 mV) to positive potentials and corresponding reduction peaks at ca. 750 and 965 mV are observed on the reverse scan. The currents at 950-1050 mV are several-fold higher in the presence of less than 1 mM of **(1)**, consistent with electrocatalytic H_2O oxidation at these unusually low potentials, which motivated us to evaluate **(1)** as a catalyst for homogeneous H_2O oxidation in aqueous solution.

The test reaction for H_2O oxidation was the well-studied model reaction: $4\,[Ru(bipy)_3]^{3+} + 2\,H_2O \rightarrow 4\,[Ru(bipy)_3]^{2+} + O_2 + 4\,H^+$ (employing the Ru(III) bipyridine complex as a chemical oxidation agent). A CV of $[Ru(bipy)_3]^{2+}$ at pH 7.0 shows reversible behavior (E_a = 1100, E_c = 940 mV, and $I_a/I_c \sim 1$), and this potential is higher than both the most pos-

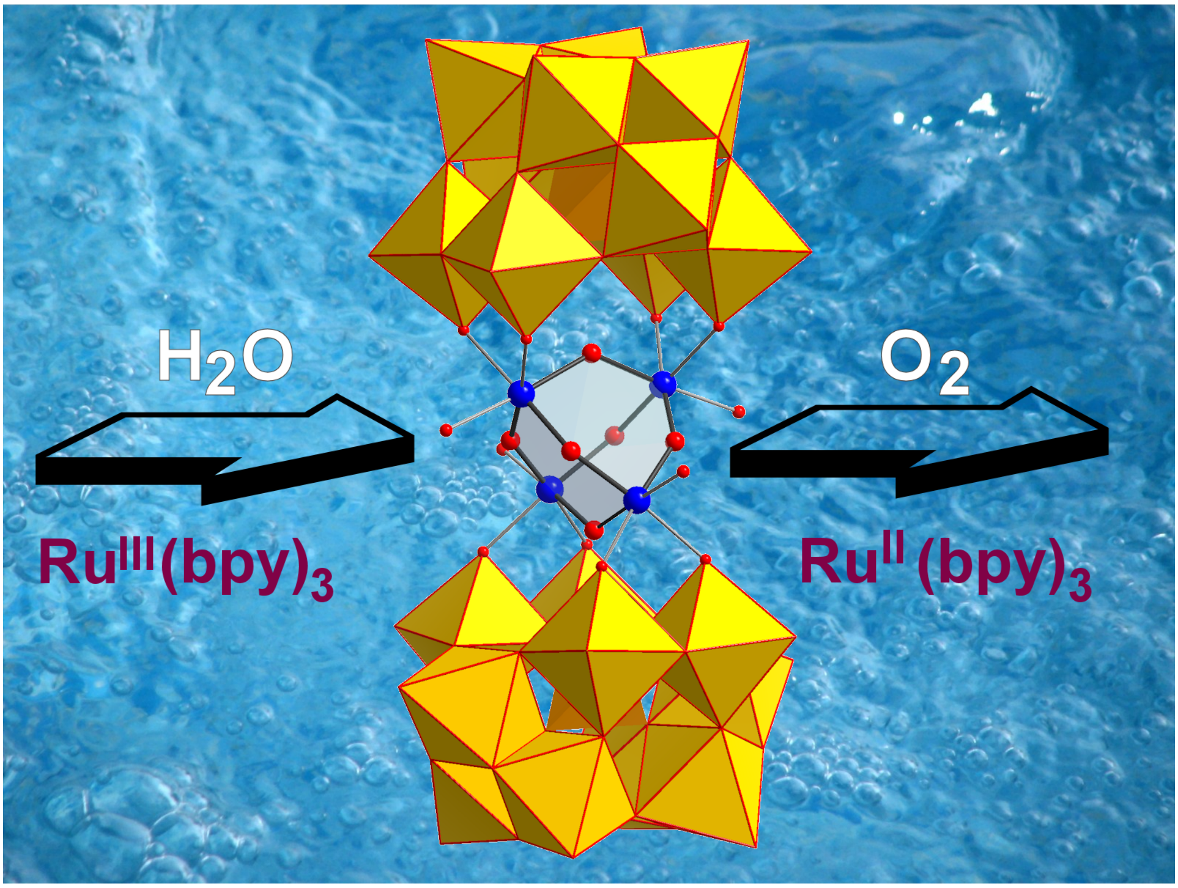

FIG. 1: Scheme of the water oxidation catalyst $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma-SiW_{10}O_{36})_2]^{10-}$*. Ru: blue spheres, O: red spheres, tungstate units: yellow polyhedra.*

itive peak observed for **(1)** (at pH 1.0) and the standard potential for the 4-electron oxidation of H_2O to O_2 (E^0 = 0.82 V at pH 7). At a very low concentrations of **(1)** (several μM), catalytic currents are observed at potentials corresponding to the oxidation of $[Ru(bipy)_3]^{2+}$ to $[Ru(bipy)_3]^{3+}$, where the peak current increases almost linearly with the concentration of **(1)**. An increase in the anodic peak is accompanied by a complete disappearance of a cathodic peak.

These electrochemical findings led us to investigate catalysis of the model reaction by **(1)**, monitored spectrophotometrically (determining the accumulated $[Ru(bpy)_3]^{2+}$) and chromatographically (detecting formed O_2). In the absence of **(1)** the typical reaction time, $\tau_{1/2}$ is $>$ 30 min. Addition of very small amounts of **(1)** (0.5 to 1.5 μM) considerably shortens the reaction time. Furthermore, experiments performed in ^{18}O-labelled water prove that H_2O is not only the solvent but also the source of oxygen atoms in the produced O_2. Although the kinetics of H_2O oxidation catalyzed by **(1)** are complicated, possibly indicating multiple intermediates, several observations (fully reversible acid-base titrations, reproducible CVs, catalytic turnover numbers) suggest that **(1)** remains intact in many oxidation states in neutral aqueous solutions.

In summary, we document an all-inorganic catalyst with long-term stability for rapid H_2O oxidation to O_2 that is operational in H_2O under ambient conditions. Work is ongoing to integrate this system into photochemical cells.

---

[1] S. W. Gersten, G. J. Samuels, T. J. Meyer, *J. Am. Chem. Soc.* **1982**, 104, 4029–4030.

[2] J. K. Hurst, *Coord. Chem. Rev.* **2005**, 249, 313–328.

[3] A. R. Howells, A. Sankarraj, C. Shannon, *J. Am. Chem. Soc.* **2004**, 126, 12258–12259.

[4] Y.V. Geletii, B. Botar, P. Kögerler, D.A. Hillesheim, D.G. Musaev, C.L. Hill, *Angew. Chem. Int. Ed.* **2008**, 47, 3896–3899.