

A Diruthenium-Substituted Polyoxometalate as an Electrocatalyst for Oxygen Generation

Annette R. Howells, Anand Sankarraj, and Curtis Shannon*
Department of Chemistry, Auburn University, Auburn, Alabama 36849
Received January 23, 2004; E-mail: shanncg@auburn.edu

The electrocatalytic generation of O₂ is one of the most important and well-studied reactions in electrochemistry, with applications ranging from regenerative fuel cells to large-scale industrial processes.¹ The first reported O₂ electrocatalysts were nickel and nickel oxide electrodes.² Since then, numerous other materials have been investigated, including RuO₂ and IrO₂, as well as perovskite and mixed oxide systems.³

The chemistry of transition metal heteropolyanions is highly developed, and much of the current interest in these compounds is driven by their prospects as “green” oxidation catalysts and model transition metal oxide surfaces.^{4–7} An attractive feature of these materials is that the wholly inorganic coordination environment is inherently stable toward oxidative decomposition.

Tourné et al. first reported the synthesis of a series of chiral polytungstometalates, including [WZn₃(H₂O)₂(ZnW₉O₃₄)₂]^{12–}, that can be described as consisting of a central “belt” of four transition metals (WZn₃) capped at both axial positions by a polyoxometalate (POM) framework.⁸ Later, Neumann and co-workers synthesized the di-Ru-substituted analogue, [WZnRu₂(OH)(H₂O)(ZnW₉O₃₄)₂]^{11–}, using a DMSO solvate.⁹ This compound has been shown to catalyze a variety of organic oxidation reactions but has not previously been used to catalyze the O₂ generation reaction, despite some structural similarities with the dioxoruthenium catalysts used for this purpose.¹⁰

Here, we describe a previously unreported di-Ru-substituted POM that can be used to catalyze the electrochemical generation of O₂. This compound was synthesized from the corresponding unsubstituted Zn–POM precursor, Na₁₂[WZnZn₂(H₂O)₂(ZnW₉O₃₄)₂], using Neumann’s synthesis.⁹ X-ray diffraction measurements and elemental analysis show that the resulting di-Ru-substituted POM corresponds to Na₁₄[Ru^{III}₂Zn₂(H₂O)₂(ZnW₉O₃₄)₂], with a Ru–Ru distance of 0.318 nm. An ORTEP plot of the crystal structure of the POM is shown in Figure 1.¹¹

Electrochemical generation of O₂ was investigated using pulsed voltammetry. In the first set of experiments, the amount of O₂ produced was measured using a Clark sensor fabricated with a 500 μm diameter Pt disk. The sensor was separated from the test solution with an oxygen-permeable Teflon membrane and held in close proximity to a polycrystalline Au anode. The Clark sensor and Au anode served as dual working electrodes in a four-electrode electrochemical cell in which a Pt wire was the counter electrode and an Ag wire served as a quasireference electrode (QRE). The potentials of the Clark sensor and the Au anode were controlled using a conventional bipotentiostat. The potential of the Ag QRE was calibrated against a standard hydrogen electrode (SHE), and all potentials are referenced to the H⁺/H₂ couple. The supporting electrolyte was a pH 8 phosphate buffer in which the analytical concentration of phosphate was 0.10 M. Solutions were purged with ultrahigh purity N₂ for at least 30 min and maintained under a N₂ atmosphere during all subsequent measurements. The Au anode was stepped from a rest potential of +0.2 V (vs H⁺/H₂) to a series of increasingly positive potentials. The duration of each voltage

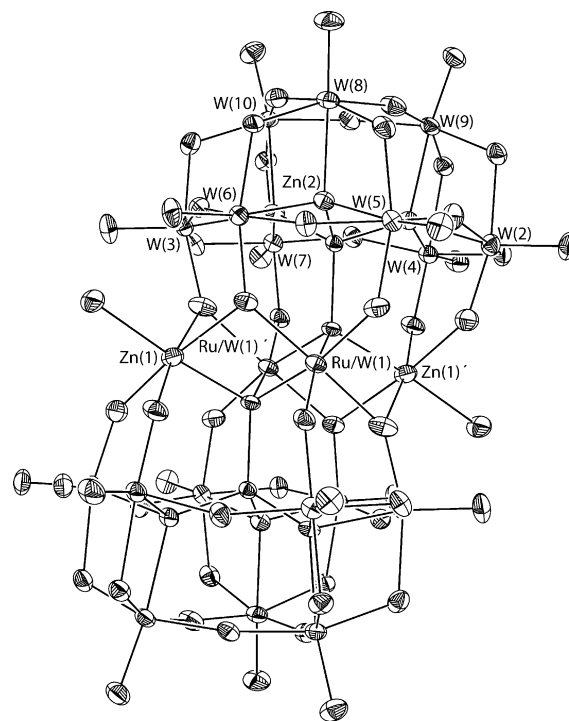


Figure 1. ORTEP plot (ellipsoids at 40% probability) of the X-ray structure of [Ru^{III}₂Zn₂(H₂O)₂(ZnW₉O₃₄)₂]^{14–}.

pulse was 5 s; after each pulse, the potential was stepped back to +0.2 V to re-establish the baseline response of the O₂ sensor. The amperometric response of the Clark electrode was measured continuously as the Au anode was subjected to this potential program and is plotted as a function of time in Figure 2.

Trace A shows the response of the Au anode (no catalyst) to a series of voltage pulses. No measurable O₂ generation is observed from naked Au until a potential of greater than +1.05 V is applied (not shown), consistent with the known behavior of Au anodes.¹² The narrow current spikes that are observed in this data set are due to capacitive charging that occurs when the working electrode is subjected to a voltage step and are not faradaic. Trace B shows the response of the system to an identical potential program after the addition of the di-ZnPOM (formal concentration 2 μM) to the electrochemical cell. The behavior of this system is identical to the behavior of the Au anode alone, indicating that the di-ZnPOM is not catalytically active for O₂ generation. Trace C shows the response of the Clark sensor after the addition of the di-RuPOM (2 μM concentration) to pure electrolyte. Electrochemically driven generation of O₂ by this system is clearly observed as negative-going current spikes in phase with the applied potential pulses. Negative changes in current correspond to O₂ generation, and positive-going currents correspond to a decrease in the amount of O₂ at the sensor. It is clear that O₂ generation is only observed when the working electrode potential is stepped positive from the

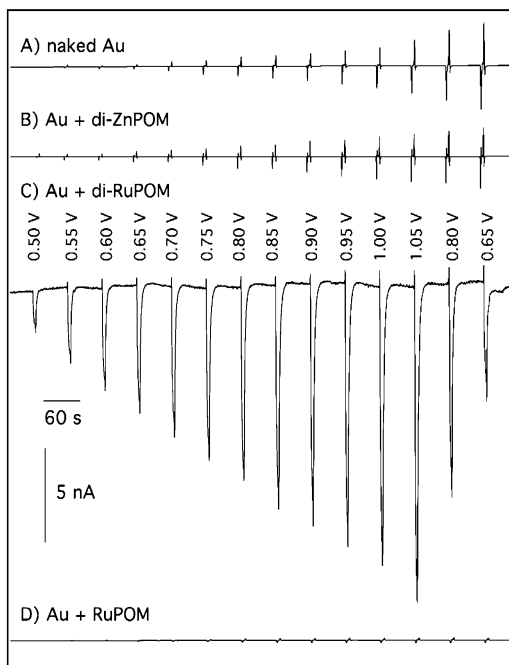


Figure 2. Electrochemical generation of O₂ from (A) naked Au, (B) Au + 2 μM di-ZnPOM, (C) Au + di-RuPOM, and (D) Au and mono-RuPOM. Note: the traces have been offset for clarity of presentation.

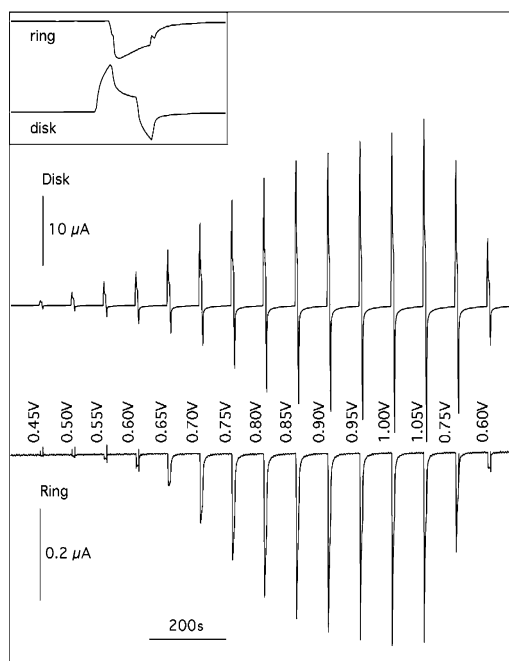


Figure 3. Rotating ring-disk measurements. Disk current (upper trace) and ring current (lower trace) were acquired simultaneously. Conditions: rotation rate, 1600 rpm; disk geometrical area, 0.27 cm².

rest potential; when the potential is stepped back to +0.2 V, the response of the Clark sensor returns to its baseline value. Finally, trace D shows the response of the Clark sensor in a solution containing a monosubstituted RuPOM catalyst, [PW₁₁O₃₉Ru^{III}(H₂O)]⁴⁻ a compound first synthesized by Pope et al. that exhibits a Keggin-type structure.¹³ Interestingly, no catalytic activity for O₂ generation is observed for this compound.

Further characterization was undertaken using a rotating ring disk assembly, Figure 3. The Pt ring was maintained at a constant potential of -0.20 V, while the potential of the Au disk was stepped

to increasingly positive voltages (pulse duration, 5 s). O₂ generated at the Au disk was collected at the Pt ring. Mass transport from the disk to the ring was controlled by the electrode rotation rate. The disk response consists of an initial rapid positive (i.e., anodic) increase in current, followed by a slower, quasi-Cottrell (i.e., $i \propto t^{-1/2}$) decrease (inset). The current-time response is similar to that of a stationary electrode because the voltage pulses were kept shorter than the time required to establish a steady-state current in order to prevent the accumulation of excess O₂. When the potential is stepped back to its base value, a negative-going current is observed due to reduction of O₂ in the double layer. The response of the Pt ring to this voltage program is shown in the lower trace; the pulse shapes are qualitatively similar to those seen for the disk. A small but noticeable dip in the ring response occurs at the same time point that the cathodic disk current reaches its maximum value and is due to the disk shielding the ring. An approximate $E_{1/2}$ for the electrocatalytic generation of O₂ of +0.750 V was calculated from the disk $i - E$ data and is consistent with the thermodynamics of oxygen generation ($E^\circ = +0.760$ V vs SHE at pH 8) and with the redox properties of the di-RuPOM electrocatalyst. Cyclic voltammetry shows three waves at ca. -0.15, +0.28, and +0.76 V for this compound, which we tentatively assign as corresponding to the Ru^{III/II}, Ru^{III/IV}, and Ru^{IV/V} couples. These assignments are consistent with the values of -0.10, +0.20, and +0.85 V, respectively, reported by Pope for [PW₁₁O₃₉Ru^{III}(H₂O)]⁴⁻. We sampled the disk current at a constant delay time after each voltage pulse and performed a Tafel analysis (i.e., a plot of $\ln i$ vs E). A Tafel slope of ca. 120 mV was found, about twice the value typically observed for RuO₂, but typical of values measured for perovskite anodes.¹⁴ In conclusion, the di-Ru-substituted POM Na₁₀[Ru₂Zn₂(H₂O)₂(ZnW₉O₃₄)₂] catalyzes the electrochemical generation of oxygen. The proximity of the two Ru atoms appears to be a key factor in the electrocatalyst's ability to generate O₂.¹⁵

Acknowledgment. We acknowledge Solutia, Inc., for their financial support. We are grateful to Dorit Sloboda-Rozner (Weizmann Institute) for advice concerning POM synthesis.

Supporting Information Available: CIF file and electrochemical data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Chen, G.; Delafuente, D. A.; Sarangapani, S.; Mallouk T. E. *Catal. Today* **2001**, *67*, 341.
- (2) Justi, E. W.; Winsel, E. A. *Kalte Verbrennung-Fuel Cells*; Franz Steiner Verlag: Wiesbaden, 1962; p 248.
- (3) Damjanovic, A. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M., Conway, B. E., Eds.; Plenum Press: New York, 1969; Vol. 5, p 369.
- (4) Baker, L. C. W.; Glick, D. C. *Chem. Rev.* **1998**, *98*, 3.
- (5) Hill, C. L.; Prosser-McCarthy, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407.
- (6) Sadakene, M.; Steckhan, E. *Chem. Rev.* **1998**, *98*, 219.
- (7) Kim, J.; Gewirth, A. A. *Langmuir* **2003**, *19*, 8934.
- (8) Tourné, C. M.; Tourné, G. F.; Zonnjeville, F. *J. Chem. Soc., Dalton Trans.* **1991**, 143.
- (9) Neumann, R.; Khenkin, A. M. *Inorg. Chem.* **1995**, *34*, 5753.
- (10) Rüttinger, W.; Dismukes, G. C. *Chem. Rev.* **1997**, *97*, 1.
- (11) Single-crystal X-ray diffraction studies of the substituted POM reveal two α -B-[ZnW₉O₃₄]¹²⁻ units related through a center of inversion and linked by a four-metal atom belt. The belt consists of two zinc centers bound in five positions by the two α -B-[ZnW₉O₃₄]¹²⁻ fragments and in their sixth site by a coordinating water molecule. W and Ru atoms that are disordered by the inversion center occupy the remaining two positions. Refinement on the occupancy of this site reveals an excess of Ru in the belt consistent with the formulation [W_{0.76}Ru_{1.24}Zn₂(H₂O)₂(ZnW₉O₃₄)₂]¹⁴⁻. This indicates that there is some compositional variation in the clusters and that diruthenium clusters exist in the product mixture. Analogous compositional variations were observed by Tourné (ref 8). On the basis of elemental analysis, the di-RuPOM is formulated as Na₁₄[Ru^{III}₂Zn₂(H₂O)₂(ZnW₉O₃₄)₂].
- (12) Conway, B. E. *Prog. Surf. Sci.* **1995**, *49*, 331.
- (13) Cong, C.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932.
- (14) Bockris, J. O'M.; Otagawa, T. *J. Phys. Chem.* **1983**, *87*, 2960.
- (15) Sens, C.; et al. *J. Am. Chem. Soc.* **2004**, *126*, 7798.

JA0495821