

Macrocyclic cyanocobalamin (vitamin B12) as a homogeneous electrocatalyst for water oxidation under neutral conditions

Summary:

Highly water-soluble cyanocobalamin (also known as vitamin B12) is the most structurally macrocyclic complex comprising cobalt in the center of a corrin ring. Interestingly, it acts as a robust electrocatalyst in water oxidation at ~ 0.58 V overpotential with a faradaic efficiency of 97.50% under neutral buffered conditions. The catalyst is impressively stable even after long-term bulk electrolysis, and homogeneous in nature, as established by a series of experiments and characterization techniques. At a lower pH (5.0–7.0), the onset potentials shift to higher values as the pH is lowered and the slope of onset potential vs. pH indicates that the rate-determining step should be a PCET process by a slope of ca. -55 mV per pH unit, indicating a $1e^-/1H^+$ coupled transition. CV, CPE, UV-Vis, ESI-MS, SEM, and EDX measurements revealed that vitamin B12 displays robust homogeneous electrocatalysis in neutral phosphate buffer rather than forming any active CoOx film or nanoparticles as active species during electrolysis. Because of its cost, commercial availability and robustness, vitamin B12 will be a strong candidate for benchmarking in molecular WO catalysis.

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