

Design Principle of Multi-electron Water Oxidation Catalysts Composed of Mn Oxides

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The water oxidation reaction is often referred to as the bottleneck in artificial photosynthetic systems that aim to produce hydrogen by proton reduction or convert carbon dioxide to liquid fuel, because of the inherent difficulty of catalyzing the overall four-electron/four-proton process ($2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2$). However, the water oxidation reaction occurs at the extraordinary high catalytic activity in the naturally occurring photosystem II (PSII), where the μ -oxo bridged tetrameric Mn cluster, (Mn_4CaO_5), embedded in a complex protein environment serves as a multi-electron oxidation catalyst. Thus, the Mn cluster within photosynthetic organisms has triggered extensive research efforts to explore the water oxidation catalyst composed of inexpensive and abundant Mn. There have been notable developments in relation to bioinspired water oxidation catalysts, in particular Mn-oxide such as simple oxides and mixed metal oxides have been demonstrated to function as effective electrocatalysts under strongly alkaline conditions. However, O_2 evolving activity of these Mn catalysts was markedly suppressed in neutral conditions. For the successful application of Mn catalysts as components for artificial photosynthesis, improvement of the water oxidation activity, particularly under neutral conditions, is essential. Nevertheless, few studies have investigated the mechanisms of water oxidation at the surface of Mn-oxide electrodes. Thus, the reasons for the sharp decline of the catalytic activity of Mn oxides under neutral conditions have remained enigmatic and have been still the subject of debate.

Recently, we identified that an optical absorption band peak at 510 nm was generated for a Mn-oxide electrocatalyst during the catalytic cycle of water oxidation. Measurement of *in-situ* water oxidation current and optical absorption, and the results of a probe experiment using pyrophosphate (PP), have shown that the 510-nm absorption is assignable to d-d transition of surface-associated Mn^{3+} ions, which is formed by the electron injection from H_2O to anodically poised MnO_2 and acts as a precursor of the O_2 evolution reaction. Notably, Mn^{3+} is unstable at $\text{pH} < 9$ due to charge disproportionation (CD) that results in the formation of Mn^{2+} and Mn^{4+} ($2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$), but is effectively stabilized by comproportionation at high alkalinity. Thus, the low water oxidation activity of Mn oxides under neutral conditions is attributable to the inherent instability of Mn^{3+} , whose accumulation at catalytic surfaces requires the electrochemical oxidation of Mn^{2+} at a potential of approx. 1.4 V. Based on this proposed model, we hypothesize that the stabilization of Mn^{3+} relative to CD is essential for the development of Mn catalysts that afford water oxidation with small overpotential at neutral pH.

In the present work, we report that the surface modification of a Mn-oxide electrocatalyst with amine-containing polymers, poly(allylamine hydrochloride) is an effective strategy to suppress the CD of Mn^{3+} . Stabilization of Mn^{3+} relative to CD was found to markedly decrease the overpotential for electrochemical

water oxidation by MnO_2 at neutral pH, resulting in the initiation of O_2 evolution at a potential near the thermodynamic reversible potential of the four-electron oxidation of H_2O .

Concerning the mechanisms of Mn^{3+} stabilization, we noticed that CD is a competing process to Jahn-Teller (JT) distortion for eliminating orbital degeneracy. As the trivalent state of Mn in MnO_2 adopts a high-spin d^4 configuration ($t_{2g}^3 e_g^1$), Mn^{3+}O_6 octahedra are typically subjected to JT distortion. On one hand, the Mn^{2+} and Mn^{4+} produced by the CD of Mn^{3+} adopt non-degenerate $t_{2g}^3 e_g^2$ and $t_{2g}^3 e_g^0$ configurations, respectively. Therefore, the Mn^{3+} in MnO_2 is able to eliminate orbital degeneracy by CD. Therefore, we consider that asymmetrization of the Mn-centered crystal field via N–Mn bond formation favors JT distortion over CD as the mechanism to eliminate the orbital degeneracy of Mn^{3+} (Figure 1) and represents a new design principle for efficient multi-electron water oxidation catalysts composed of inexpensive and abundant MnO_2 for artificial photosynthesis.

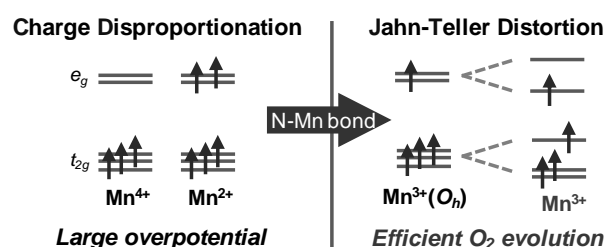


Figure 1. Stabilization of Mn^{3+} relative to charge disproportionation by asymmetrization of the Mn-centered crystal field via N–Mn bond formation.

References:

- (1) T. Takashima, K. Hashimoto, R. Nakamura, *J. Am. Chem. Soc.* **2012**, *134*, 1519–1527.
- (2) T. Takashima, K. Hashimoto, R. Nakamura, *J. Am. Chem. Soc.*, **2012**, *134*, 18153–18156.