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Oxygen-evolution Reaction by Silicate Stabilized Manganese Oxide.

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Oxygen-evolution reaction (OER) through water oxidation under acidic conditions mediated by efficient and stable first-row transition metal compounds remains a challenge in artificial photosynthesis [1, 2]. A critical issue in the field is the solubility of first-row transition metal compounds during OER and under acidic conditions. In this study, the silicate-stabilized Mn oxide was investigated for OER under acidic conditions (pH < 1). Compared to Mn oxide, the silicate-stabilized Mn oxide is significantly more stable than Mn oxide under acidic conditions (pH < 1), with the overpotential of 457 mV for the onset of OER. The Mn oxides forming in the absence and presence of silicate groups are α-Mn_2O_3 and α-MnO_2, respectively. For the Mn oxides forming in the presence of silicate groups, the corresponding current densities of 1 and 10 mA/cm^2 are recorded at 527 and 640 mV, respectively. Silicate-stabilized Mn oxide was characterized by a number of methods before and after OER. The 29Si NMR spectrum for silicate-stabilized Mn oxide shows that the Si-O groups chemically bonded to Mn ions. The scanning transmission electron microscopy shows small 2 – 10 nm particles of Si-O compound in silicate-stabilized Mn oxide. Especially, Si-O to stabilize the higher indices facets of the Mn oxide crystallites. X-ray absorption spectroscopy confirms that the predominant structure for silicate-stabilized manganese oxide is α-MnO_2, with di- and mono-μ-oxo-bridged Mn atoms. After prolonged oxygen evolution, a certain fraction of the mono-μ-oxo bridges disappear for silicate-stabilized manganese oxide. Adding silicate to Mn oxide is a low-cost and environmentally friendly procedure to increase the stability of Mn oxide toward OER under acidic conditions, thus our procedure is a clear improvement on current methods to stabilize Mn oxide for OER under acidic conditions.

Keywords: Acidic conditions, catalyst, oxygen-evolution reaction, silicate stabilized manganese oxide, stability

References

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