

Effect of the Heterogeneous Catalyst Attachment Method

On O₂ Production of WO₃ Photoanodes in Acidic

Aqueous Electrolyte

J. M. Spurgeon, J. M. Velazquez

WO₃ is a promising candidate for a photoanode material in an acidic electrolyte, in which it is more stable than most metal oxides, but kinetic limitations combined with the large driving force available in the WO₃ valence band for water oxidation make competing reactions such as the oxidation of the acid counterion a more favorable reaction. The incorporation of an oxygen evolving catalyst (OEC) on the WO₃ surface can improve the kinetics for water oxidation and increase the branching ratio for O₂ production. Ir, Ru, and Co-based OECs were attached to WO₃ photoanodes by a variety of methods including sintering from metal salts, sputtering, drop-casting of particles, and electrodeposition to analyze how attachment strategies can affect photoelectrochemical oxygen production at WO₃ photoanodes in 1 M H₂SO₄. Current density vs. potential (*J-E*) measurements of OEC/WO₃ electrodes showed that high temperature processing of the catalyst on the WO₃ surface degraded the performance unless the catalyst was already in its metal oxide state when deposited. High surface coverage of catalyst on the semiconductor was necessary to ensure that most minority-carrier holes contributed to water oxidation through an active catalyst site rather than a side-reaction through the WO₃/electrolyte interface. Sputtering of OEC layers on WO₃ did not detrimentally affect the energy-conversion behavior of the photoanode and improved the O₂ yield at 1.2 V vs. RHE from ~ 0% for bare WO₃ to 50 – 70% for a thin, optically transparent catalyst layer to nearly 100% for thick, opaque catalyst layers. Of the OECs tested, only IrO₂ displayed extended stability under the anodic operating conditions in acid as determined by XPS.