

Title: Design and development of efficient bi-functional catalyst by tuning the electronic properties of cobalt-manganese tungstate for oxygen reduction and evolution reaction

Authors: Guruprakash Karkera, Tanmay Sarkar, Mridula Dixit Bharadwaj, Annigere S Prakash

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Abstract: Solid state electrochemistry is drawing considerable interest as the inter conversion of O₂ and water playing an important role in energy conversion and storage technology. With an aim of developing an efficient bi-functional catalyst by tuning the electronic properties and local structure around 3d metal in CoWO₄, solid solutions Co_{1-x}Mn_xWO₄ are investigated. Nanocrystalline Co_{1-x}Mn_xWO₄ (x= 0 to 1) phases with a unique exposure of low surface energy planes are synthesised by hydrothermal method. Replacing optimum amount of Co with Mn to enhance the catalytic activity correlates with a negative shift observed in the Co²⁺/³⁺ redox wave and onset of OER indicating strong electronic interaction between the two elements. Composition corresponds to Co_{0.5}Mn_{0.5}WO₄ has demonstrated great ability to catalyse both OER and ORR with a combined overpotential of 0.89 V. It exhibited an OER current density of 10 mA cm⁻² at an overpotential of 400 mV. While, ORR current density of 3 mA cm⁻² is reached at a potential of 0.74 V vs. RHE. The density functional theory revealed that the substitution of Mn in CoWO₄ elevate the 3d metal d band centre closure to fermi energy and hence ease the electron transfer to facilitate ORR-OER.