

# Investigation of Ni, Co and Cu-Doped Iron Oxide Coatings for AEM Electrolysis

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Recent advancements in catalyst development for anion exchange membrane (AEM) water electrolysis have identified transition metal compounds doped with non-noble metals as viable, non-precious alternatives to noble metal-based electrocatalysts for both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Doping transition metal compounds with heteroatoms, such as Ni, Co or Cu, can alter structural, optical, and electronic properties, enhance electrical conductivity, modify adsorption energies, and increase active sites density [1]. Recent discoveries highlight the catalytic OER activity of transition metal oxides (TMOs) or (oxy)hydroxides (TM-(O)OH), with Fe-based oxides demonstrating low overpotentials, fast kinetics, excellent long-term durability, natural abundance, cost-effectiveness, and environmental adaptability [2]. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) characterized by a hexagonal structure with Fe<sup>3+</sup> in octahedral coordination, is recognised as a promising OER catalyst due to its abundance, non-toxicity, and eco-friendly properties. Spinel-type Fe<sub>3</sub>O<sub>4</sub> where Fe ions are partially substituted by other TM ions could offer a variety of oxidation states, high electrical conductivity, and optimal binding energies between active sites and OER intermediates. Ni incorporation increases oxide group adsorption efficiency, modifies Gibbs free energy, and activates HO-O bond. Cu doping causes lattice deformation and produces additional defects, increasing active sites density [1]. Co doping can increase intrinsic conductivity and reduce the Gibbs free energy of H\* adsorption, leading to highly active catalytic sites.

This study systematically investigates transition metal oxides, specifically Ni-, Co-, and Cu-doped iron oxides, as high-activity, robust OER catalysts. The thin films were fabricated using reactive magnetron sputtering (MS), a precise deposition technique enabling control over film composition, microstructure, thickness, particle size, and crystallinity by modifying parameters. MS technique enables to obtain doped compact films that can help prevent undesirable side processes, such as slow pore diffusion and clogging which can hinder the OER. Doped iron oxide coatings were deposited on commercially available AISI304 type stainless steel substrates using pure hematite and metallic Ni, Co, and Cu targets, with a 70%:30% argon-to-oxygen ratio maintained in the deposition chamber to ensure oxide formation.

Comprehensive characterization revealed enhanced catalytic activity and stability in doped thin films compared to undoped ones. Dopant concentrations ranged from 2% to 32%, depending on the metal. Structural analysis using X-ray diffraction (XRD) and Raman spectroscopy indicated that heteroatom incorporation peculiarly adjusts crystallinity, induces phase transitions from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, and optimizes electronic/surface properties. Higher dopant content contributed to the formation of amorphous structures, which enrich active sites, chemical composition, and structural flexibility [4]. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) provided insights into the surface morphology and uniformity of the films, factors directly impacting their electrochemical performance. Detailed electrochemical investigations described dopant-specific influences on iron oxide behavior, both at reaction onset and industrially relevant current densities.

## References:

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