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Structural reconstruction and performance of IrO_x-NiSe₂ for OER

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Water electrolysis is a promising method for producing green hydrogen, offering a carbon-free alternative to conventional techniques like the steam reform of natural gas. Nickel selenide-based electrocatalysts are promising candidates for catalyzing the oxygen evolution reaction (OER) in alkaline media, the rate-limiting step in water splitting [1]. However, nickel selenide catalysts tend to oxidize during the OER, forming an active nickel-oxy(hydroxide) phase. This active phase formation is hampered by the catalyst's limited structural stability and number of active sites [2]. In some cases, the presence of a second species in the structure adjusts the electronic structure and improves the exposure of active sites [3]. Therefore, iridium and its oxides are known to be excellent OER catalysts, so that incorporating small amounts of IrO_x into nickel selenide-based catalysts could potentially improve their performance.

Herein, nickel selenide catalysts modified with iridium oxide nanoparticles were synthesized and analyzed for the OER in 1M KOH electrolyte to assess how the modification influences reaction kinetics and electrochemical stability. Characterization techniques, including XRD, EDS, and XPS, confirmed the formation of a composite of the NiSe₂ phase with amorphous IrO_x nanoparticles (IrO_x-NiSe₂). The IrO_x nanoparticles incorporation impacted their nucleation, reducing particle size. Additionally, the incorporation of IrO_x improves the onset potential for OER. Voltammetric analysis suggests that the formation of a NiOOH active phase is accompanied by the fast oxidation of selenium species (Se⁻) to Se^{3+/4+} (as SeO₃⁻² and SeO₄⁻²), and by the Ni²⁺ species being oxidized to Ni³⁺ involving a redox process, which is assumed to be responsible for the structural reconstruction to form the active phase. Analysis by scanning flow cell combined with inductively coupled plasma mass spectrometry (SFC-ICP-MS)[4] indicates the dissolution of Se species in the corresponding range of oxidation potentials (Se⁻ to Se^{3+/4+}), confirming that the selenide is sacrificed during the formation of the NiOOH phase. Accelerated stress tests confirmed that the active NiOOH phase remains stable, despite a reduction in surface area due to particle coalescence. This study underscores the importance of controlling the chemical composition and structure to achieve durable and efficient OER electrocatalysts.

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