This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under grant agreement No 101035813

Production and characterization of nanostructured spinel ferrite MOCVD films and their application for water splitting

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The spinel nano-ferrites exhibit both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) due to the combined effects of the M^{2+} cations' involvement and the electronic interactions between the cations at the octahedral and tetrahedral sites. Ferrites are useful materials due to their easy manufacturing, strong chemical stability, redox activity, abundance in nature, non-toxicity, and inexpensive constituent elements. Numerous ferrites, including $ZnFe_2O_4$, $NiFe_2O_4$, $CoFe_2O_4$, and $CaFe_2O_4$, have been studied to be applied in water splitting systems. In this work films of $NiFe_2O_4$, $CoFe_2O_4$, and $ZnFe_2O_4$ have been produced using the MOCVD technique. The synthetic β-diketonate precursors, $M(tta)_2$tmeda (Htta = 2-thenoyltrifluoroacetone, tmeda = N,N,N',N'-tetramethyl-ethylendiamine, M=Ni, Co, Zn), and the commercial iron(III) precursor, Iron(III)tris(2,2,6,6-tetramethyl-3,5-heptanedionate), $Fe(tmhd)_3$, were utilised as metal sources together with O_2 as reactant gas. Thermogravimetric (TG) and differential scanning calorimetry (DSC) investigations were conducted to assess the thermal features of the precursors. XRD measurements were performed to investigate the growth of crystalline films, hence the formation of polycrystalline ferrite phase on silicon, MgO, and Ni-foam substrates was verified. We assessed the cubic shape morphologies of the produced films, with a thickness around 300-400 nm, using FE-SEM. Employing EDX quantitative analysis the 1:2 stoichiometric ratio between the divalent cations was determined. The oxidation state of the cations was evaluated using XPS, moreover XPS provided indications of iron oxide contamination in certain samples and confirmed the presence of ferrite phases and its surface stoichiometry. Lamella specimens were produced using FIB-SEM and subsequently examined using HR-TEM which verify the presence of a polycrystalline phase. The HER and OER activity have been evaluated employing Electrochemical Impedance Spectroscopy (EIS) and Linear Sweep Voltammetry (LSV). Promising results are observed in the preliminary HER and OER measurements of $NiFe_2O_4$, $CoFe_2O_4$, and $ZnFe_2O_4$ samples on Ni-foam, in fact overpotential, Tafel Slope and Rct values obtained through LSV and EIS demonstrate the applicability of these systems in water splitting.