3D NiMnCo trimetallic electrocatalysts with cauliflower curd-shaped micro-sized nodular morphology for an efficient and sustainable hydrogen evolution reaction in alkaline media and simulated seawater

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Significance and Relevance

Hydrogen is a versatile energy carrier, which has the advantages of clean combustion products with zero CO_2 emission, high gravimetric energy density, and large resource reserves, thus, can be one of the potential alternatives to traditional fossil fuel. Electrocatalytic seawater splitting instead of inadequate freshwater is an ideal strategy for the production of green and renewable hydrogen energy. Compared to scarce freshwater, ocean seawater, which covers 97% of the Earth's water reserves, can be considered as an unlimited resource. Thus, seawater splitting could be a more recommended approach than the freshwater electrolysis for sustainable high-purity hydrogen production on an industrial scale.

Preferred presentation: Poster.

Introduction and Motivations

In this work, we report an affordable one-step synthesis of self-supported 3D nickel-manganese-cobalt (NiMnCo) trimetallic coatings, whose electrocatalytic activity and durability were evaluated for the hydrogen evolution reaction (HER) in both alkaline media (1 M KOH) and simulated seawater (1 M KOH + 0.5 M NaCl). These ternary coatings were electrodeposited on a titanium substrate by a straightforward electrochemical deposition using a dynamic hydrogen bubble template technique. Scanning electron microscopy characterization of the optimal NiMnCo/Ti-2 coating revealed a unique cauliflower curd-shaped, micro-nodular architecture with grain particle diameters of 7–14.5 µm.

Materials and Methods

Nickel sulfate hexahydrate ($NiSO_4.6H_2O$, >98%), manganese chloride tetrahydrate ($MnCl_2.4H_2O$, >99%), cobalt nitrate hexahydrate [$Co(NO_3)_3.6H_2O$, >99%] salts were used as a source of metal ions and ammonium sulfate [$(NH_4)_2SO_4$, >99%], boric acid (H_3BO_3, >99.5%), H_2SO_4 (96%) and HCl (35-38%) were the additives used for plating baths. The HER activity of these catalysts was investigated using Linear Sweep Voltammetry in alkaline media and simulated seawater at variuos temperatures. NiMnCo/Ti-1 and NiMnCo/Ti-2 electrocatalysts were synthesized using two electroplating bath solutions containing Ni^{2+}:Mn^{2+}:Co^{3+} molar ratios of 1:5:1 and 1:5:2, respectively.

Results and Discussion

The optimal NiMnCo/Ti-2 electrocatalyst demonstrated excellent HER activity in alkaline media, requiring a low overpotential of 56 mV to reach the benchmark current density of 10 mA cm^{-2}. Impressively, an ultra-low overpotential of 29 mV was needed to achieve the same current density in simulated seawater.

The high-performance NiMnCo/Ti-2 electrocatalyst not only exhibits enhanced HER activity in both electrolytes, but also demonstrates excellent long-term stability, sustaining a constant potential of -0.23 V (vs. RHE) and a constant current density of 10 mA cm^{-2} for 50 hours. In addition, it performed robust performance in a multi-step chronopotentiometry test with current densities ranging from 20 mA cm^{-2} to 100 mA cm^{-2}, indicating sustainable durability and suitability for practical seawater-splitting applications.