"Metal-organic networks-based materials for electrochemical water splitting"

Anna Dymerska

Abstract

The doctoral dissertation comprehensively explores metal-organic frameworks (MOF), particularly emphasizing their potential applications in electrochemistry. The study focuses on three distinct approaches to modifying a zeolitic imidazolate framework based on cobalt centers (ZIF-67), a MOF class. Additionally, different nickel-based MOF (NiMOF) variations are presented to optimize their effectiveness in electrochemical reactions. The varying types of NiMOF-based catalysts include powdered NiMOF, nickel foam (NiF) impregnated with NiMOF (NiF/MOF), NiMOF deposited by drop-casting on NiF (NiF+NiMOF), and NiF/MOF with deposited NiMOF (NiF/MOF+NiMOF). Summarized experimental work is presented in a graphical abstract.

The first approach involves low-temperature thermal treatment of ZIF-67 (at temperatures of 150, 200, 250, and 300 °C). The most optimal sample (ZIF-67 200) is characterized by an overpotential of 318 mV and a Tafel slope (TS) of 105 mV/dec during an oxygen evolution reaction (OER). The electrocatalytic properties were boosted concerning pristine ZIF-67 due to the presence of cobalt species on the surface, facilitating favorable OER-active reactions, along with optimized pore distribution and a higher number of exposed active sites.

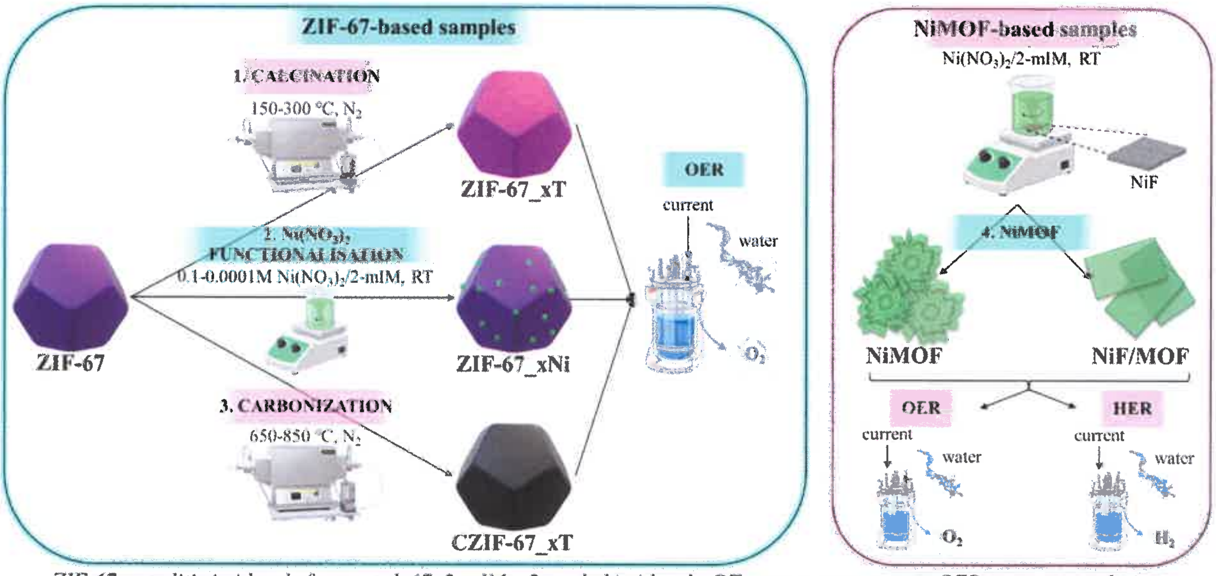
The second approach entails the ZIF-67 functionalization with nickel salt (with nickel(II) nitrate hexahydrate salt concentrations of 0.0001, 0.001, 0.01, and 0.1 M). The most optimal sample in the context of electrocatalytic activity (ZIF-67 0.001Ni) reached an overpotential of 299 mV and a TS of 94 mA/dec, which was due to the formation of active nickel dimers (Ni^{2+}) with superparamagnetic properties and enhanced specific surface area (SSA).

The third approach to ZIF-67 modification involves carbonization (at temperatures of 650, 750, and 850 °C). The most optimal sample (CZIF-67 750C) has an overpotential of 288 mV and a TS of 69 mV/dec. Here, the enhanced electrochemical properties arise from its surface rich in Co_3O_4 islets and the highest electrochemically active surface area (ECSA).

Moreover, a bifunctional NiMOF is analyzed, demonstrating superior efficiency during

both OER and a hydrogen evolution reaction (HER). The most optimized sample for OER (NiF/MOF+NiMOF) demonstrates an overpotential of 186 mV and a TS of 104 mV/dec. The most optimized sample for HER (NiF/NiMOF) has an overpotential of 210 mV and a TS of 69 and 272 mV/dec at lower and higher current ranges, respectively. For the OER, the boosted performance of NiF/MOF+NiMOF is attributed to the highest ECSA due to its unique flower-like architecture and 3D network structure, which create new pathways for oxygen release and a synergy effect between nickel particles. Conversely, in the HER, NiF/MOF demonstrates optimal performance due to its unique rectangular-shaped flakes providing a high ECSA and abundant active sites, along with the synergy effect between Ni origin from NiF and NiMOF.

The materials underwent detailed characterization, including transmission and electron microscopy (TEM and SEM, respectively), X-ray diffraction (XRD), atomic absorption spectrometry (AAS), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma optical emission spectrometry (ICP-OES), Raman spectroscopy, and electron paramagnetic resonance (EPR). What is more, *ex-situ* monitoring of the electrocatalyst morphology and phase composition alterations at different stages of electrochemical processes (conducted at a defined voltage) enabled the proposal of reaction mechanisms by defining the most active species, which contributed significantly to the advancement of research on MOF in the context of their application in electrochemical water decomposition.



ZIF-67 – zeolitic imidazole framework 67, 2-mIM – 2-methyl imidazole, RT – room temperature, OER – oxygen evolution reaction, NiMOF – metal-organic framework based on Ni, HER – hydrogen evolution reaction, NiF – nickel foam

Graphical abstract for doctoral thesis "Metal-organic networks-based materials for electrochemical water splitting".

04.05.2024

Anna Dymerska