Abstract

The growing urgency of climate change and the rising atmospheric concentration of CO_2 have necessitated the development of sustainable energy solutions, positioning the electrochemical CO_2 reduction reaction as a promising route for producing carbon-neutral fuels and value-added chemicals. In parallel, the oxygen reduction reaction is likewise a key process in sustainable energy conversion and storage systems, including fuel cells and metal-air batteries. This dissertation focuses on the rational synthesis and structural tuning of novel electrocatalysts, emphasizing the relationship between material structure, product selectivity, and reaction kinetics within the framework of the sustainable energy transition.

This thesis integrates a range of advanced characterization techniques to elucidate catalyst properties, including X-ray diffraction (XRD) for crystallinity analysis, Scanning Electron Microscopy (SEM) for morphological evaluation, and X-ray Photoelectron Spectroscopy (XPS) for surface chemical state determination. Electrochemical testing was performed in both three-compartment flow cells and zero-gap membrane electrode assemblies (MEA), while product distribution was analysed using Gas Chromatography (GC) for gas-phase species and High-Performance Liquid Chromatography (HPLC) for liquid-phase species.

The research first investigates Zeolitic Imidazolate Frameworks (ZIFs) prepared via a green, solvent-free steam-assisted dry-gel synthesis route. It is demonstrated that while ZIF-8 (Zn-based) achieves selective CO production with a Faradaic efficiency of approximately 60%, the isostructural ZIF-67 (Co-based) predominantly favours the competing hydrogen evolution reaction, highlighting the decisive role of the metal centre over surface area or CO_2 adsorption capacity alone. Expanding toward multi-carbon products, a nitrogen-coordinated Cu-MOF with a hierarchical flake morphology was engineered. In MEA, this catalyst achieved a maximum ethylene Faradaic efficiency of 51.6% at 200 mA cm^{-2}, with operando X-ray absorption spectroscopy revealing reversible Cu redox transitions during the reaction.

To address operational robustness, the study explores nickel sulfide (NiS_x) nanostructures supported on nitrogen-doped mesoporous carbon (NiS_x@NMC). Following strategic acid leaching, the resulting NiS_x@NMC_AL catalyst exhibits near-unity CO selectivity across a broad pH range, including under strongly acidic conditions with a pH of 1, while significantly outperforming sulfur-free Ni-based samples and the non-acid-treated NiS_x@NMC. The sulfur-enriched NiS_x surface effectively suppresses the competing hydrogen evolution reaction and promotes selective CO_2-to-CO conversion. By adjusting the anolyte to a mildly acidic pH of 3,

salt deposition at the cathode is effectively mitigated, enabling stable continuous operation for 450 minutes at 100 mA $cm^{-2}$with a sustained full-cell energy efficiency of 43.7%. Finally, the thesis examines Fe-doped nitrogen-rich mesoporous carbons for the oxygen reduction reaction, showing that Fe_3C active sites promote an efficient four-electron pathway, particularly in alkaline media.