

Metal-Organic Frameworks and Nanomaterials for Oxygen Evolution Reaction



Thesis Submitted for the Degree of

Doctor of Philosophy

By

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Summary and Future Outlook

7.1 Summary

Non-noble transition-based materials like spinels and metal-organic frameworks (MOFs) have a crucial role in improving the OER (oxygen evolution reaction) performance in water-splitting. The thesis outlines the synthesis of spinel materials; nickel ferrite (NFO), cobalt-doped nickel ferrite (cobalt ferrite, CFO, and cobalt-nickel ferrite, CNFO), and metal-organic frameworks (MOFs); Co-MOF, ZnDTO (zincdithioamide) MOF and Ni-Fe-PBA-NC (Prussian blue analogue nanocube). Further, various nanostructures are derived from MOFs like heteroatom-doped porous carbon from ZnDTO MOF, Ni-Fe PBA nanocage, and Ni-Fe mixed oxide from Ni-Fe PBA nanocubes.

The spinel materials are synthesized by a facile sol-gel method and used the same for OER. Among all the spinel materials (NFO, CFO and CNFO) nickel based-spinel materials show better performance. The finding reveals that the lower Tafel slope and low overpotential as well as the higher oxygen vacancies and porosity were accountable for improving their catalytic performance. The Tafel slope values for NFO-800, CFO-800 and CNFO-800 are 93 mVs^{-1} , 139 mVs^{-1} , and 105 mVs^{-1} , respectively which shows that NFO-800 has the least Tafel slope among them and the respective onset potential is found to be 1.52, 1.59 and 1.53 V which imply the value of an overpotential $\sim 300 \text{ mV}$ for NFO-800. Further, our study presents a simple and more effective method for the synthesis of spinel materials than the earlier reported methods which are time-consuming and tedious. Further, Rose-like-structured Co-MOF is synthesized via a simple precipitation approach using cobalt salts as a metal ion and Anthranilic acid (AA) as an organic linker and no such reports are available in reference to this type of morphology of the Co-MOF using AA. The complexation of Co^{2+} with AA in Co-MOF is well-explained by the characterization techniques such as FT-IR (Fourier transfer infrared), UV-Vis.

(Ultraviolet-visible), XPS (X-ray photoelectron spectroscopy), XRD (X-ray diffraction) and mass spectrometry. The morphology and elements distribution is analyzed by HR-SEM (high-resolution scanning electron microscopy) and EDX (energy dispersive X-ray analysis), and the structure is concluded through DFT (density functional theory) analysis which supports our proposed reaction mechanism. It shows the excellence in OER performance than the commercially available RuO₂ having a lower Tafel slope (58 mV dec⁻¹) and overpotential of 520 mV at 10 mA cm⁻² current density. After that, the spherical ZnDTO MOF is synthesized with DTO (dithioamide) ligand and Zn²⁺ ions and derived the N/S/Zn doped porous carbon matrix (NSC) by carbonizing ZnDTO at different temperatures 500, 700 and 900 °C. Then the thermally optimized carbon matrix (NSC-7) is treated with acid (2 M HCl) to examine the role of the Zn in the OER activity of NSC-7, and using Co₃O₄ nanoparticles; a nanocomposite is constructed with these carbon matrixes (NSC-7 and NSC-7AW) to enhancing the OER performance. Co₃O₄|NSC-7 exhibits enhanced OER performance than Co₃O₄|NSC-7AW and Co₃O₄ nanoparticles due to the Zn and heteroatoms' participation. Acid treatment of NSC-7 causes a loss of Zn percentage that leads to poor performance of Co₃O₄|NSC-7AW, which evidences that the contribution of Zn is also much more significant in stabilizing the higher oxidation state of Co, which is responsible for the high conductivity of composites. Further, PBA (Prussian blue analogue) type MOF is explored as an electrocatalyst for OER. Novel Ni-Fe-PBA nanocubes are synthesised by a facile method and using the nanocubes as templates, different two nanostructures with varying chemical compositions pertaining to cubic shapes are generated. The precursor nanocubes undergo a very unusual structural evolution on reaction with ammonia solution and transform into a cage-like nanostructure, which is likely due to the inhomogeneous surface reactivity of the cubes. At the same time, when nanocubes are annealed (at 350 °C) in the presence of air, it

transforms into the oxide (NiFe-oxide), a porous cube. Both the structures (nanocage and oxide) exhibit higher OER performance than the solid counterparts (nanocube) due to the increased surface area. A comparative list of different types of OER electrocatalysts is given below.

Table 7.1 Comparison of OER performance of different types of electrode materials.

S.No.	Electrode materials	Electrolyte	Potential (vs. RHE / V) at 10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)	References
1.	NiFe ₂ O ₄	0.1 M KOH	1.67	98	[248]
2.	CuFe ₂ O ₄	0.1 M KOH	1.64	94	[248]
3.	NiCOOH	0.1 M KOH	1.51	36	[249]
4.	Ni-Fe LDH	1M KOH	1.53	40	[250]
5.	g-C ₃ N ₄ Ti ₃ C ₂	0.1 M KOH	1.65	74.6	[251]
6.	CoMnP	1 M KOH	1.56	61	[252]
7.	Ni ₃ Se ₂	0.3 M KOH	1.53	122	[253]
8.	BSCF900N ₂	0.1 M KOH	1.65	143	[254]
9.	NiCo-bimetal MOF	1 M KOH	1.48	42	[255]

10.	Ti ₃ C ₂ T _x -CoBDC	0.1 M KOH	1.64	48.2	[256]
11.	NFO-800	0.1 M KOH	1.79	93	This work
12.	Co ₃ O ₄ NSC-7	0.5 M KOH	1.83	62	This work
13.	Co ₃ O ₄ NSC-7AW	0.5 M KOH	1.86	75	This work
14.	Co-MOF	0.5 M KOH	1.75	58	This work
15.	NiFe-oxide	0.1 M KOH	-	47.5	This work

From this Table it is evident that and NiFe-oxide show greater activity than other materials in terms of Tafel slope and potential at 10 mAcm⁻² in which NiFe-oxide has the lowest Tafel slope among Co₃O₄|NSC-7 and Co-MOF. But NiFe-oxide show very low magnitude of current density while Co₃O₄|NSC-7 and Co-MOF possess higher current density. Co₃O₄|NSC-7 and Co-MOF show almost comparable activity (the value of Tafel slope and potential at 10 mAcm⁻² is close to each other).

7.2 Future Outlook

In the thesis, we employed a sol-gel method to synthesise the spinel materials. The sol-gel method is reasonably an easier and time-saving process than other methods, providing a new and facile way to develop various spinels with different combinations of transition

metals. Further, the synthesis approaches for MOFs offer a new strategy to evolve highly efficient catalysts through diverse pre- and post-treatments in MOFs. Structural modification, doping, and composite synthesis are quite easy through these techniques, which will be advantageous in developing highly active electrocatalysts for water-splitting that can produce H₂ and O₂ simultaneously on a large scale for continuously generating electricity in the fuel cell. Apart from this, the crystalline structure and chemical functionalities of MOFs can be regulated through the judicious choice of organic ligands and inorganic metal ions, which has directed their exploitations in other fields such as gas storage and separation, photolysis, biosensors etc.