

Abstract

The growing global demand for energy, the instability of fossil fuel supplies and related environmental issues have all driven the need for alternative green energy solutions.

Electrocatalytic water splitting reaction is one of the key technologies for the large-scale energy storage in the form of hydrogen fuel and oxygen evolution reaction (OER) is the bottleneck of the reaction. The water splitting reaction plays a central role in the hydrogen economy, where hydrogen acts as an energy carrier for a variety of uses, such as fuel cells, transportation and industrial processes, helping to lessen reliance on fossil fuels.

For the large-scale application of these technologies, there is a need for electrocatalysts that are highly efficient, affordable and stable. Transition metal-based oxide materials have attracted considerable interest as promising electrocatalysts for the OER and hydrogen evolution reaction (HER) due to their abundance in the Earth and cost-effectiveness.

The thesis entitled **“Understanding of Redox Interactions of Transition Metal Ions in Different Lattices to Develop Superior Water Splitting Electrocatalysts”** primarily focuses on the various strategies to be utilized for the enhancement of electrochemical OER and HER activity by different transition metal oxides. The electrochemical efficiency of the metal oxides was altered through various techniques such as foreign element doping and cation defect introduction. The sol-gel route was chosen for the synthesis of the electrocatalysts (metal oxides) due to its simplicity, cost-effectiveness and environmentally friendly characteristics. The thesis emphasizes the development of metal oxides and the tuning of redox energy levels by leveraging their intrinsic properties.

The following chapters comprise the structure of current thesis:

In the first chapter, global energy consumption and environmental challenges are discussed, emphasizing the urgent need for sustainable energy sources to produce zero-emission H₂/O₂ gases. This chapter explores the fundamental principles of electrochemical water splitting, focusing on the production of H₂ and O₂ gases, as well as various strategies to enhance the efficiency of water-splitting catalysts.

A concise review of existing literature is provided, highlighting the state-of-the-art advancements and challenges associated with modifying transition metal oxides. Additionally, the chapter discusses key parameters for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activity in water splitting. Finally, the chapter concludes by outlining the objective of the current thesis.

The second chapter presents a fundamental overview of the experimental methodology, focusing on the synthesis techniques used to create materials with controlled structure and composition. It also covers the instrumental methods and experimental setups utilized for characterizing the synthesized electrocatalyst. The chapter concludes with a discussion of the electrochemical methods employed to evaluate the electrocatalytic performance of the fabricated electrodes for HER and OER using the synthesized catalyst.

In chapter 3, cubic rock salt NiO structures with 3 to 10% Ti doping ($\text{Ni}_{1-2x}\text{Ti}_x\text{V}_x\text{O}$, $0 < x < 0.1$) were synthesized using the sol-gel method, and the impact of Ti doping on electrocatalytic activity towards the OER has been investigated. Among these, NiO doped with 5% Ti exhibited remarkable performance as an OER catalyst which is comparable to the state-of-the-art RuO₂ catalyst.

The enhanced activity of Ti-doped NiO is attributed to the formation of cation vacancy sites on the surface (as evidenced by Raman studies), which promote water adsorption and the inductive effect caused by Ti substitution at the Ni site within the rock-salt NiO lattice. FT-IR

and Raman studies revealed an elongation of the Ni–O bond, while XPS analysis indicated increased electro-positivity of Ni ions. The higher ionicity of the Ni–O bond improves the overlap between Ni 3*d* and O 2*p* orbitals, thereby enhancing the catalytic activity of the doped material. However, increasing the Ti concentration beyond 5% reduces the concentration of Ni²⁺/Ni³⁺ redox-active sites at the surface due to a higher number of cation vacancies and an increased presence of non-active Ti species. Which leads to a decrease in OER activity.

Therefore, 5% Ti doping is identified as the optimal concentration, maximizing the inductive effect on the redox potential of the active Ni²⁺/Ni³⁺ species and delivering superior catalytic performance.

In chapter four, a series of ilmenite-type Co-doped NiTiO₃ materials with doping levels ranging from 5 to 25% (Ni_{1-x}Co_xTiO₃, 0 < x < 0.25) were synthesized using the sol-gel method to study the effects of Co doping on OER activity. Among these, the 17.5% Co-doped NiTiO₃ composition found as the most efficient OER catalyst.

The enhanced activity of Co-doped NiTiO₃ is attributed to the inductive effect arising from Co substitution at the Ni site within the ilmenite NiTiO₃ lattice. The Ni²⁺/Ni³⁺ redox pair serves as the active site for the OER, as the Ni(3*d*) orbital are pinned over O(2*p*) orbitals. The incorporation of Co³⁺ increases the ionicity of the Ni–O bond through the inductive effect, as confirmed by XPS analysis. This increased ionicity enhances the overlap between the Ni(3*d*) and O(2*p*) orbitals, resulting in higher catalytic activity of the doped catalysts. However, Co concentrations beyond the optimal level lead to a decrement in OER activity. This is due to the reduced concentration of catalytically active Ni²⁺/Ni³⁺ centers caused by Co substitution. The optimal 17.5% Co doping level results the highest activity due to the inductive influence on the redox potential of the Ni²⁺/Ni³⁺ active species.

Notably, the 17.5% Co-doped NiTiO₃ composition (Ni_{0.825}Co_{0.175}TiO₃) exhibits highest OER activity, achieving a Tafel slope of 56 mV dec⁻¹ and an overpotential of 395 mV at a current density of 10 mA cm⁻².

In chapter five, polycrystalline sodium yttrium titanate (NaYTiO₄), Na_{1-x}K_xYTiO₄ (x ≤ 0.2), and NaY_{1-x}Gd_xTiO₄ (x ≤ 0.2), synthesized using the sol-gel method, has been explored as efficient electrocatalysts for the hydrogen evolution reaction. The crystal structure, morphology and composition of these materials are characterized through XRD, XPS, SEM, HR-TEM and ICP-MS analysis. Tuning the relative positions of redox energies with Fermi levels in different oxides is crucial for designing novel electrocatalysts and electrodes for electrochemical conversion devices. The incorporation of interlayer potential to adjust the redox energies of the Ti(IV)/Ti(III) couples in K and Gd-doped NaYTiO₄, specifically Na_{1-x}K_xYTiO₄ (x ≤ 0.2) and NaY_{1-x}Gd_xTiO₄ (x ≤ 0.2), is envisaged here to develop a superior HER electrocatalyst.

Electrochemical studies show the excellent HER performance of electrocatalyst; NaYTiO₄ exhibits good HER activity that is not only superior to that of TiO₂ but also comparable to or surpassing the majority of oxide electrocatalysts examined for the HER. NaYTiO₄ demonstrates an overpotential of 148 mV (@ 10 mA cm⁻²), a Tafel slope of 64.9 mV/dec and exceptional stability during a 24-hour chronoamperometry test at -0.15 V vs RHE. With the selection of suitable active cation, superior HER catalytic activity was obtained for electropositive Gd-doped NaYTiO₄ (NaY_{1-x}Gd_xTiO₄) compared to that for NaYTiO₄.

The concluding sixth chapter briefly summarizes the research findings of current thesis for the Ti doped NiO and Co doped NiTiO₃ for oxygen evolution reaction and Gd, K doped NaYTiO₄ as hydrogen evolution reaction electrocatalyst.

Herein, it also discusses the possible modification in the near future that can be done with the metal oxides to enhance electrocatalytic performance.