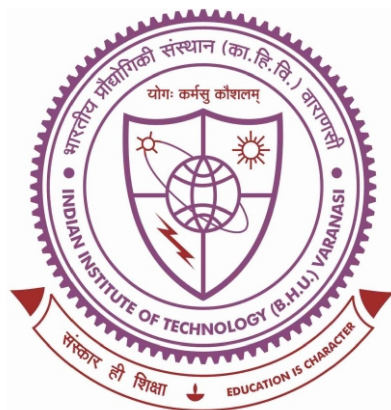


Understanding of Redox Interactions of Transition Metal Ions in Different Lattices to Develop Superior Water Splitting Electrocatalysts



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By

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Conclusion

This thesis primarily focuses on the various strategies to be utilized for the enhancement of electrochemical oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) by different 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 prioritizes the different strategies utilized for the development of metal oxides and tuning the redox energy level based on their intrinsic properties.

The summary and conclusion for each chapter, highlighting the valuable outcomes obtained from the work done during my Ph.D. tenure, are presented as follows:

- ✓ **In the first chapter** the global energy consumption and environmental challenges have been presented, highlighting the necessity for sustainable energy sources to generate zero-emission H_2/O_2 gas. This chapter addresses the fundamental principle of electrochemical water splitting, which involves the production of O_2 and H_2 gases, along with various strategies aimed at improving the overall efficiency of water splitting catalysts.

A concise overview of the existing literature on the current state-of-the-art as well as challenges related to the modification of transition metal oxides are discussed. The chapter further discussed the HER and OER activity parameters for water splitting. At last, this chapter is concluded with the objectives of the present thesis.

- ✓ **The second chapter** provides a fundamental overview of the experimental methodology, detailing the synthesis techniques employed to produce materials with controlled structure and composition. The discussion also includes various instrumental techniques and the experimental setups employed for the characterization of the as-

synthesized electrocatalyst. Concluded the discussion on the electrochemical methods employed to assess the electrocatalytic performance of the fabricated electrodes for hydrogen evolution reaction and oxygen evolution reaction using the synthesized catalyst.

- ✓ **In chapter third**, a series of cubic rock salt NiO structures with 3 to 10% Ti doping ($\text{Ni}_{1-2x}\text{Ti}_x\text{V}_x\text{O}$, $0 < x < 0.1$) have been synthesized using the sol-gel method and the effect of Ti doping on electrocatalytic activity toward the OER has been examined. 5% Ti-doped NiO shows remarkable performance as an OER catalyst compared with state-of-the-art RuO_2 . The origin of the observed higher activity of Ti-doped NiO is due to the formation of cation vacant lattice sites (supported by Raman studies) on surfaces for H_2O adsorption and the inductive effect brought about by Ti substitution on the Ni site in the rock-salt NiO structure. Ti dopant being a stronger Lewis acid as compared to Ni ion is shown to positively shift the formal redox potentials of $\text{Ni}^{2+}/\text{Ni}^{3+}$ of the parent active species, as evident from our CVs studies. $\text{Ni}^{2+}/\text{Ni}^{3+}$ is the active site for OER and Ti^{4+} enhances the ionicity of the Ni-O bond in the lattice through the inductive effect. Both FT-IR and Raman studies confirm the elongation of the Ni-O bond and XPS study confirms high electro-positivity of Ni ions. The higher ionicity of Ni-O leads to a greater overlap between Ni 3d and O 2p orbitals resulting in higher catalytic activity of the doped catalysts. However, further increase in the Ti concentration leads to a decrease in the concentration of $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox-active sites at the surface due to the formation of a higher concentration of cation vacancies and an increase in the concentration of non-active Ti on surfaces. Therefore, an increase in the Ti concentration beyond an optimum level lead to a decrease in the OER activity. An optimum concentration of 5% Ti doping leads to the best activity via its inductive effect on the redox potential of the active species, namely $\text{Ni}^{2+}/\text{Ni}^{3+}$ parent species. Also, this

optimum concentration of 5% Ti in NiO shows the best OER activity, and $\text{Ni}_{0.9}\text{Ti}_{0.05}\text{O}$ depicts a Tafel slope of 67 mV/dec^{-1} and an overpotential of 304 mV at a current density of 10 mA/cm^2 , confirming a comparable electrocatalytic OER activity to that of the commercial benchmark RuO_2 catalyst, measured under similar experimental conditions.

- ✓ **In chapter four**, a series of ilmenite type Co-doped NiTiO_3 with doping levels 5 to 25% ($\text{Ni}_{1-x}\text{Co}_x\text{TiO}_3$, $0 < x < 0.25$) has been synthesized using the sol-gel method and examined for the effects of Co doping on electrocatalytic activity towards the oxygen evolution reaction. In the series of $\text{Ni}_{1-x}\text{Co}_x\text{TiO}_3$ ($0 < x < 0.25$), 17.5% Co-doped NiTiO_3 emerges as the most effective OER catalyst. The observed increased activity of Co-doped NiTiO_3 attributed to the inductive effect produced by the substitution of Co at the Ni site within the ilmenite NiTiO_3 structure. $\text{Ni}^{2+}/\text{Ni}^{3+}$ serves as the active site for the oxygen evolution reaction, as the $\text{Ni}(3d)$ orbitals are pinned over $\text{O}(2p)$ orbitals. The Co^{3+} enhances the ionicity of the Ni–O bond within the lattice via the inductive effect, as evidenced by XPS (see Figure 4.3a). The increased ionicity of Ni–O results in enhanced overlap between $\text{Ni}(3d)$ and $\text{O}(2p)$ orbitals, which in turn contributes to the higher catalytic activity of the doped catalysts. An increase in Co concentration beyond an optimal level results in a decline in the OER activity of the catalyst, as higher substitution of Co on the Ni site reduces the concentration of catalytic active centers ($\text{Ni}^{2+}/\text{Ni}^{3+}$) within the catalyst. The optimum level of 17.5% Co doping results in the highest activity due to its inductive influence on the redox potential of the active species, specifically the $\text{Ni}^{2+}/\text{Ni}^{3+}$ parent species. Furthermore, the optimal concentration of 17.5% Co in NiTiO_3 exhibits the highest OER activity with $\text{Ni}_{0.825}\text{Co}_{0.175}\text{TiO}_3$ demonstrating 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 (NaYTiO_4), $\text{Na}_{1-x}\text{K}_x\text{YTiO}_4$ ($x \leq 0.2$), and $\text{NaY}_{1-x}\text{Gd}_x\text{TiO}_4$ ($x \leq 0.2$) synthesized by the sol-gel method has been explored as an efficient electrocatalyst for the HER. The crystal structure, morphology and composition of the materials were confirmed by XRD, XPS, SEM, HR-TEM and ICP-MS analysis. Tuning the relative position of the redox energies with Fermi levels in different oxides is important for designing novel electrocatalysts and electrodes for electrochemical conversion devices. The incorporation of interlayer potential to tune the relative redox energies of the Ti(IV)/Ti(III) redox couples in K- and Gd-doped NaYTiO_4 , i.e., $\text{Na}_{1-x}\text{K}_x\text{YTiO}_4$ ($x \leq 0.2$) and $\text{NaY}_{1-x}\text{Gd}_x\text{TiO}_4$ ($x \leq 0.2$), is envisaged here to develop a superior HER electrocatalyst. Electrochemical studies reveal good HER activity of the electrocatalyst; NaYTiO_4 exhibits good HER activity that is not only superior to that of TiO_2 but also comparable to or surpassing the majority of oxide electrocatalysts examined for the HER. Electrochemical investigations demonstrate impressive hydrogen evolution reaction performance of NaYTiO_4 , exhibiting an overpotential of 148 mV and a Tafel slope of 64.9 mV/dec, alongside remarkable stability of 24-hour continuous 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 NaYTiO_4 ($\text{NaY}_{1-x}\text{Gd}_x\text{TiO}_4$) compared to that for NaYTiO_4 .