
PREFACE

Global energy demand is continuously increasing due to exponential industrial development. Most of the energy demand are met through fossil fuels that causes severe effect on human kind. In the 21st century, one of the most urgent technological challenges is meeting the global demand for energy with secure, environment friendly, and sustainable sources. Fossil fuels like coal, gas, and natural oils are the most consumed fuel, and they are available in limited amounts. Alternatively, wind, solar, and hydro-power systems are rapidly growing and gaining popularity worldwide. However, these renewable energy sources generally depend on external factors like weather and atmosphere, so their extensive use is limited. Also, these are not cost-effective, non-portable, and have less scalability and efficiency. Several sophisticated, sustainable technologies like water electrolyzers, batteries, fuel cells, and unitized regenerative fuel cells have been explored extensively for alternative future energy requirements to address these constraints. They are cost-effective and environment friendly and, at the same time, have high conversion efficiency.

Our present work is focused on the study of the Lanthanum Ferrite materials for energy applications. Perovskite-structured Lanthanum Ferrite (LaFeO_3) exhibits mixed ionic-electronic conductivity with variation in dopants and has interesting structural, physical, and electrochemical properties. Therefore, they are used for various energy applications such as fuel cells, batteries, photocatalysis, water splitting etc. The incorporation of various substituents tends to improve their properties. In the present investigation, the effect of alkaline earth metal and transition metal ion doped- LaFeO_3 and their structural, electrical,

and optical properties are demonstrated along with their electrochemical and catalytic properties.

Thus, the synthesis of LaFeO_3 and substitution of alkaline earth metal (Strontium, Sr) and transition metal (Titanium, Ti) with A- and B- sites were investigated. Sr doped at the La site of LaFeO_3 (LF) forms $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$, exhibiting air electrode behavior with high cathodic current and maximum oxygen reduction reactivity. Co-substituting Sr at the La- and Ti at the Fe- site forms $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_3$ in LaFeO_3 , showing electrode behavior with bifunctional catalyst properties for energy application. The prepared samples were characterized using XRD, SEM, TGA, UV-visible, XPS, impedance spectroscopy, and cyclic voltammetry.

Besides the LF, Strontium titanate, SrTiO_3 (ST) was also synthesized to understand the electrochemical and catalytic behavior in a wide pH range. It is systematically investigated for its application as an electrode material for fuel cells and batteries. The structural, morphological, optical, and elemental analyses of the system were carried out using the XRD, FESEM, TGA, UV -Vis, and XPS techniques. The impedance analysis technique was used to investigate the electrical behavior and conduction mechanism. With the help of cyclic voltammetry, we studied the electrochemical behavior of the sample at various electrolyte media (pH= 1, 7, 14).

Structural, microstructural, optical, thermo-dynamic, and electrical properties of the investigated systems have been probed, and the correlation among them is established. This bound volume, submitted for the Doctoral degree at IIT (BHU) Varanasi, comprises eight chapters followed by conclusions, future work, and a list of publications. A brief description is given below:

Chapter 1 deals with the broad energy scenario, a general introduction of energy, the solutions available, and a few renewable /alternative energy resources, followed by a brief literature survey. A general introduction to perovskite structure, properties, and applications, including ferrites and Fe-based materials, are also explained in this chapter. This chapter illustrates the motivation and plan of research work. Moreover, this chapter deals with possible conduction and electrochemical reaction mechanisms occurring in the investigated system. The primary goals of the present work are also included in this chapter.

Chapter 2 discusses the experimental and analysis techniques employed in the present work. Solid-state reaction route and hydrothermal synthesis route were adopted to synthesize the samples. Pulse laser deposition is also used to form the heterostructures. This chapter includes a description of these techniques. A complete description of the characterization techniques such as XRD, FESEM, TEM, XPS, DSC, UV-visible, and Impedance Spectroscopy measurements, as well as significant analysis techniques, including Rietveld Refinement and Impedance analysis are incorporated. The basic physics behind the measurements is also discussed briefly.

Chapter 3 aims to describe the structural properties and electrochemical behavior of samples, synthesized via a solid-state reaction route. Phase formation of LaFeO_3 (LF), $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ (LSF), and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (LSFT) was studied by powder X-ray diffraction technique. The Rietveld refinement confirms the space group, atomic positions, and the occupancies of the component. The dc conductivity and the activation energy were calculated from the conductivity spectra analysis suggests a change in the charge carrier and more polaronic behavior in LSF. The electrochemical studies of the samples were performed with the help of cyclic voltammetry in the neutral medium (Na_2SO_4), indicates a high OER

and ORR present in LSF, alongwith the chronopotentiometry stability for the long duration of 72 h irrespective of current.

Chapter 4 presents the systematic study of the charged dynamics and the electrochemical behavior of pure SrTiO₃. Phase formation of SrTiO₃ (ST) was studied using the powder X-ray diffraction technique and confirmed through Rietveld refinement. Impedance spectra were analyzed to understand the charge dynamics. The dc conductivity, hopping frequency, and exponent values were extracted from the Jonscher Power Law fitting of conductivity data. We observed that the system follows Ghosh scaling. Electrochemical studies were performed with the help of Cyclic Voltammetry in three different, neutral (Na₂SO₄), basic/alkaline (KOH), and acidic (H₂SO₄) media and confirmed that better redox activity is available in environment friendly medium (Na₂SO₄). The system exhibits electrochemical reversibility in the neutral medium as well.

In **Chapter 5**, Lanthanum Strontium Ferrite Titanate, i.e., La_{0.5}Sr_{0.5}Fe_{0.5}Ti_{0.5}O₃ (LSFT), was studied for its catalytic activity and stability in three different electrolyte media. Electrochemical measurements were used to investigate the catalytic performance of the prepared catalyst in neutral (environment friendly) medium, alkaline medium and acidic medium for the oxygen evolution reaction (OER), oxygen reduction reaction (ORR), and hydrogen evolution reaction (HER). LSFT demonstrates high current density in both OER and ORR in an environment friendly medium compared to other two, acidic and alkaline media. It was also stable for 600 cycles in the neutral medium alongwith chronopotentiometry stability more than 1500 h at a higher current 150 mA/cm².

Chapter 6 describes the multifunctional behavior of the heterostructure formed with the help of the Pulse laser deposition method (PLD). Here, LSFT and ZnO are selected as the target

materials, with LSFT as the substrate material. A thin layer of ZnO and LSFT is deposited sequentially on the substrate LSFT, with the variation in the number of laser shots, i.e., $n = 550, 1050, 1550, 2050$. The thickness of the layer deposited is calculated with the help of Scanning Electron Microscopy (SEM), and it increases with the number of laser shots. A comparative analysis of the conductivity behavior of all the heterostructure formed was performed with the parent LSFT ($n = 0$). It was observed that for the $n = 1050$, the conductivity was highest. Transient response and stability behavior were studied and $n = 1050$ showed better stability with good time response. It shows better redox activity and multifunctional behavior compared to other laser shots (n).

Chapter 7 describes the variation of characteristics in LSF via different synthesis methods, namely solid-state and hydrothermal techniques. Phase formation of the samples was confirmed through XRD and Rietveld refinement. TEM analysis confirms the nanoparticle formation of the synthesized sample via the Hydrothermal method. A comparative study was performed on the catalytic behavior of both the sample in the bulk and nano form with the help of cyclic voltammetry.

In Chapter 8, we conclude the outcomes of this thesis's research works and list the possibilities of future investigations.