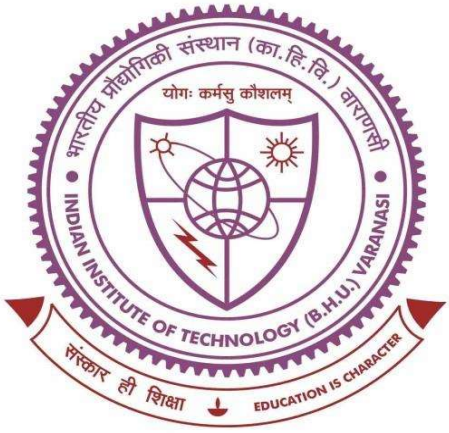
INVESTIGATIONS ON NICKELATE BASED SYSTEM AS AIR-ELECTRODES FOR FUEL CELL APPLICATIONS



THESIS SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

In

Physics

By

Manisha Chauhan

Under the supervision of

Prof. Prabhakar Singh

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY
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Dedicated

To

my beloved Family

and my Preceptor

CERTIFICATE

It is certified that the work contained in the thesis titled **"INVESTIGATIONS ON NICKELATE BASED SYSTEM AS AIR-ELECTRODES FOR FUEL CELL APPLICATIONS"** by "**MANISHA CHAUHAN"** (Roll No. **17171014**), in partial fulfillment of the requirement for the award of the degree of **Doctor of Philosophy** at **Indian Institute of Technology (B.H.U), Varanasi** is a record of her own work carried out under my supervision and guidance and this work has not been submitted elsewhere for a degree.

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Acknowledgments

“The journey of thousands of miles, begins with a single step.”

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Date:

Place: Varanasi **(Manisha Chauhan)**

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LIST OF SYMBOLS AND ABBREVIATIONS

AFC	Alkaline Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
DMFC	Direct Methanol Fuel Cell
PAFC	Phosphoric Acid Fuel Cell
MCFC	Molten Carbonate Fuel Cell
SOFC	Solid Oxide Fuel Cell
ORR	Oxygen Reduction Reaction
TEC	Thermal Expansion Coefficient
RT	Room temperature
ASR	Area Specific Resistance
MIEC	Mixed Ionic-Electronic Conductor
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
IDEP	Isotope Exchange Depth Profile
OER	Oxygen Evolution Reaction
HER	Hydrogen Evolution Reaction
IT-SOFC	Intermediate Temperature Solid Oxide Fuel Cell
YSZ	Yttrium Stabilized Zirconia
CGO	Gadolinium Doped Ceria
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetry analysis
XRD	X-ray diffraction
JCPDS	Joint Committee on Powder Diffraction Standards

SEM	Scanning Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
AFM	Atomic Force Microscopy
ATR	Attenuated Total Reflection
SR	Specular Reflection
FTIR	Fourier-Transform Infrared Spectroscopy
FWHM	Full width at Half Maximum
SSR	Solid State Route
SAED	Selected Area Electron Diffraction
V	Volt
RP	Ruddlesden Popper
TR	Transpassive Region
C_P	Specific Capacitance
C_{dl}	Doble Layer Capacitance
SC	Supercapacitor
RS	Randles–Ševčík
CR	Corrosion Rate
TS	Tafel Slope
RT	Room Temperature
RHE	Reversible Hydrogen Electrode

Preface

Global energy demand is continually rising as a result of ongoing industrial development and population increase, meanwhile the conventional fossil fuels such as oil, coal, natural gases, etc., are exhausting swiftly. Presently, these fossil fuels are the primary fuel source that meets to our current energy needs. However, the availability of fossil fuels in the forthcoming years is of enormous matter of concern. The burning of fossil fuels not only leads to several environmental threats by releasing toxic gases but also restricts the accessibility of traditional energy sources. These detrimental effects on environment enable the global warming. The awareness about the energy crisis and greenhouse gas emission has led to the hunt for alternative routes. In order to find an alternative possibility for alternatives routes, the research is focused into two parts namely, in which one part is focused on the sources that are renewable and ecofriendly while second part is focused on those electrochemical devices which can harvest green and clean energy such as fuel cells.

Electrochemical devices for energy storage play a vital part in the energy dependent world for meeting the situation of rapid diminution of fossil fuels. Electrochemical devices either generate electricity from a chemical reaction (like a battery) or use electrical energy to trigger a chemical reaction (like a catalyst). Among the various available electrochemical devices, fuel cell is highly efficient and holds many diversified pros associated with mobile and stationary power generation including both large scale centralized power production as well as in individual homes and businesses, *etc.*

These days, there are various types of fuel cells accessible in the market. Fuel cells are usually categorized via their electrolyte material. They vary in their power outputs, operating

temperatures, electrical efficiencies, and typical applications. Solid oxide fuel cells (SOFCs) correspond to one of the cleanest and most effective options for the direct conversion of a wide variety of fuels to electricity. For example, SOFCs driven by natural gas are preferably suited for distributed power generation. However, the commercialization of SOFC technologies pivots on advances in materials development to significantly reduce the cost while enhancing performance and durability. One of the crucial hurdles to achieve high-performance SOFC systems is the cathodes for oxygen reduction reaction (ORR), which perform inadequately at low temperatures and degrade over time under operating conditions. Similarly, these investigated cathodes can be used as an electrode in many other electrochemical devices as catalyst for oxygen evolution reaction (OER).

In the present research work, Ruddlesden-Popper perovskite $SmSrNiO_{4-\delta}$ has been chosen for further investigation. Ruddlesden–Popper perovskites (RP perovskites) have shown electrocatalytic properties along with excellent performance in oxygen-solid oxide fuel cells and hydrogen-solid oxide fuel cells. Their performance is basically attributed to fast surface oxygen exchange property and proton and oxygen transport mechanisms. The microstructural design of electrode materials plays an important role, not only in electron and oxygen ion conduction at the electrolyte–electrode and electrode–air interfaces (ORR), but also on the life time of fuel cells. In this regards, $SmSrNiO_{4-\delta}$ was synthesized by Solid state route method (SSR) at different optimization temperature. The porous and pore-free sample was synthesized at two different temperature and influence of catalysis on the structure after voltammetry was comprehensively studied. It was found these samples synthesized at two different temperatures that pore-free sample with a higher ionic conductivity and catalytic

activity is suitable for use as a buffer layer in between the electrolyte and electrode for solid oxide fuel cells.

In order to understand the influence of active site alteration on the catalytic behaviour of Ruddlesden-popper oxide, a series was synthesized by altering the amount of Sm and Sr using the SSR method. In order to understand the active site engineering more effectively, thin film was also synthesized by picking up the two best optimized samples. The electrocatalytic behaviour was studied for this series of Ruddlesden-popper perovskite. The structural, microstructural, electronic along with catalytic studies was performed by YGA, XRD, SEM, XPS and CV. It was found that moderate electroactivity can be achieved with an increase in active sites on miniaturization with the phase change.

Along with ORR, oxygen evolution reaction (OER) is also important for many electrochemical devices and Ruddlesden-popper perovskite has an ability to function like electrocatalyst for OER as well. Therefore, another series was synthesis from $SmSrNiO_{4-\delta}$ with doping on Lanthanum and Calcium on A-site by solid state route method and their catalytic behavior was studied especially for OER and also their suitability for energy storage application. It was observed that one of the compositions of this series has a large value of specific capacitance and double layer capacitance, making it suitable choice as the catalyst for OER and also shows its prominence for energy storage application as hybrid capacitor electrode.

It was observed that Nickel is playing the crucial role in the catalytic activity of all the sample synthesized till now. Therefore, in the last part of this research work, thin film of nickel oxide was synthesized by sol gel method by taking different number of depositions and the effect of pH was studied on their catalytic activity. In this regard, solution of three different

medium (acidic, neutral and alkaline) was chosen as electrolyte solution for catalytic studies. It was observed that a particular sample of synthesized thin films shows promising behaviour for electrocatalysis in two media.

The present thesis is divided into seven chapters and a brief description is given below:

Chapter 1 Provides introduction about fuel cell, as well as comprehensive review of the literature. This chapter describes the motivation of the research work, the background and fundamentals of fuel cell, the essential requirements of fuel cell components, the mechanism and kinetics for the cathode, the materials selection for cathode, the current scenario of nickelate-based perovskite and layered perovskite materials along with an overview of $SmSrNiO_{4-\delta}$ based on the systems. The main objective of the present work is also included in this chapter.

Chapter 2 Discusses various experimental techniques used for the present investigations. It represents the details of implemented experimental instruments, analysis techniques and various synthesis routes adopted to synthesize the samples. Solid-state reaction route, sol-gel, and pulse laser deposition techniques were discussed, which were used to synthesize the proposed systems. A detailed description of employed instruments such as TGA, DSC, XRD, SEM, TEM, XPS, and CV measurements, etc. along with the important analysis techniques like Rietveld Refinement analysis has also been discussed in this section.

Chapter 3 Ruddlesden–Popper structured layered perovskite, $(SmSr)NiO_{4-\delta}$, was synthesized at different sintering temperatures using a solid-state reaction technique. Porous and dense microstructures were obtained at sintering temperatures of 1250 °C and 1425 °C, respectively. The influence of electrocatalysis on the structures of both surfaces was studied comprehensively. Post cyclic voltammetry structural studies show the presence of $Ni–(OH)_2$

and Ni–OOH species for the samples, respectively, suggesting that they undergo different oxygen reduction reaction mechanisms.

Chapter 4 The influence of compositional engineering via active site alternation on catalytic behaviour has been studied for the Ruddlesden–Popper-based system $Sm_{2-x}Sr_xNiO_{4-\delta}$. A phase change from orthorhombic (x = 0.6) to tetragonal (x = 1.0) in bulk $Sm_{2-x}Sr_xNiO_{4-\delta}$ is confirmed by Rietveld (XRD) analysis, thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). To alter the active sites, we fabricated thin films for x = 0.6 and x = 1.0 using a pulsed laser deposition technique. The electrocatalytic behaviour has been studied in an environmentally friendly medium, i.e., a neutral medium (pH = 7), for both bulk and thin films, and parameters such as transient response, electrochemical reversibility and oxygen evolution reactivity are measured. The cyclic voltammetry curves suggest that electrochemical reversibility for thin films is governed by adsorption as opposed to the diffusion observed for bulk samples. Our investigation further suggests that moderate electroactivity can be achieved with an increase in active sites on miniaturization with the phase change.

Chapter 5 A series of Ruddlesden popper oxide materials $Sm_{1-x}La_xSr_{1-x}Ca_xNiO_{4-\delta}$ (x = 0.00, 0.05, 0.10, 0.15, and 0.20) were synthesized and their electrochemical behavior was investigated in 1M KOH alkaline solution. Phase formation in all the sample is confirmed through XRD. SEM depicts the porous morphology of all the samples. FTIR confirms the presence of -OOH and -OH groups in several compositions. The Cyclic voltammetry curve of $Sm_{0.90}La_{0.10}Sr_{0.90}Ca_{0.10}NiO_{4-\delta}$ and $Sm_{0.80}La_{0.20}Sr_{0.80}Ca_{0.20}NiO_{4-\delta}$ indicates the presence of the combination of both pseudo capacitance and electrochemical double layer capacitance in these two electrodes. However, only the sample $Sm_{0.90}La_{0.10}Sr_{0.90}Ca_{0.10}NiO_{4-\delta}$ satisfy the condition of general power law for pseudo capacitance. This material also shows the highest value of

specific capacitance (910.20 F/g) and electrochemical double layer capacitance (238.25 mF/cm^2) among all the samples. XPS analysis reveals that oxidation states of the Nickel and Oxygen play a crucial role for the better electrochemical performance of the electrode.

Chapter 6 Thin films of Nickel oxide (NiO) was synthesized by using sol gel method through spin coating technique on silica substrate with different number of layers deposition of NiO. XRD confirms the cubic phase formation of thin films and SEM and AFM confirm the well deposition of thin films on substrate. The catalytic activity was investigated of two extreme samples for oxygen evolution reaction and oxygen reduction reaction in all three mediums i.e., acidic, neutral, and alkaline mediums. It was found that the sample with highest number of deposition layers shows its suitability for electrocatalysis in alkaline and acidic mediums.

Chapter 7 Concludes the outcomes of the research works of this thesis and also propose the future scope of the present investigations.