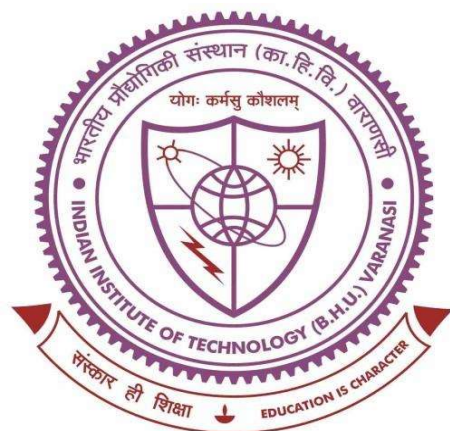


INVESTIGATIONS ON NICKELATE BASED SYSTEM AS AIR-ELECTRODES FOR FUEL CELL APPLICATIONS



THESIS SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

In

Physics

By

Manisha Chauhan

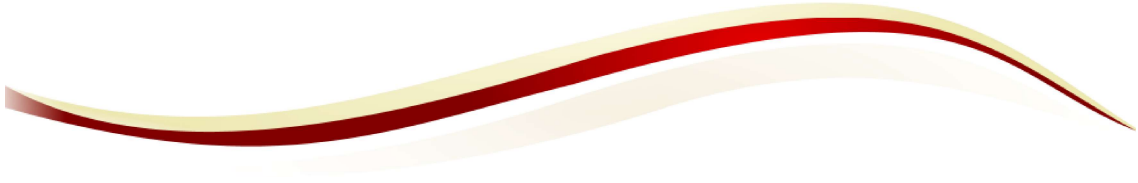
Under the supervision of

Prof. Prabhakar Singh

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY
VARANASI-221005
INDIA

17171014

2022



Chapter-7

Conclusions and Future Scopes



CHAPTER 7: Conclusions and Future Scopes

7.1 Conclusion of the Present Investigation

One of the primary objectives of the current thesis work was to understand the behavior of Nickel based Ruddlesden-Popper based perovskite for fuel cell applications. Therefore, strontium doped samarium nickelate system was used as primary system for investigation. The optimization condition was first analyzed for this system and after that electron and oxygen ion conduction at the electrolyte- electrode and electrode-air interfaces (ORR) for this system and its compositions. The structural, microstructural characteristics, thermal and electronic properties along with the catalytic behavior were investigated of these systems. On the basis of work accomplished, results procured and the discussion followed by conclusion represented in the preceding chapters, the overall conclusion of thesis work can be summarized as below:

In SOFCs, the microstructural designing of electrode materials is an important aspect for electron and oxygen ion conduction at the electrolyte-electrode and electrode-air interfaces. To investigate this feature, the Ruddlesden-Popper structured layered perovskite (SmSr)NiO_{4-δ} is synthesized at different sintering temperatures using solid-state reaction technique. The porous and dense microstructure is obtained with sintering temperatures 1250 °C and 1425 °C, respectively. The pore free sample is more ionic than the porous sample, while both the samples are highly conducting. The influence of electro-catalysis on the structure of both surfaces is studied comprehensively. The electrocatalysis and redox reaction are influenced by the microstructure. It altered the surface adsorption mechanism from 4 step pathway (for porous sample) to 2 step pathway (for pore free sample). Post cyclic voltammetry structural studies show the presence of Ni-(OH)₂ and Ni-OOH species

for both samples, respectively suggesting different oxygen reduction reaction mechanisms. Conclusively, it can be proposed that the pore free sample with higher ionic conductivity and catalytic activity is suitable as a buffer layer in between electrolyte and electrode for Solid oxide fuel cells.

A systematic study on the influence of compositional engineering via active site alternation on catalytic behavior has been studied for the Ruddlesden–Popper-based system $\text{Sm}_{2-x}\text{Sr}_x\text{NiO}_{4-\delta}$. Here, the value of x varies from 0.4 to 1.0. The series is synthesized through conventional solid state route method at sintering temperature of 1425 °C. A phase change from orthorhombic ($x = 0.6$) to tetragonal ($x = 1.0$) in bulk $\text{Sm}_{2-x}\text{Sr}_x\text{NiO}_{4-\delta}$ 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 behavior has been studied in an environmentally friendly medium, i.e., a neutral medium ($\text{pH} = 7$), 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. The lattice mismatch increases with the phase change, consequently enhancing the number of active sites, proving the suitability of $x = 1.0$ (i.e., $\text{SmSrNiO}_{4-\delta}$) thin films as nano-electrocatalysts in a neutral medium.

In the extension of this, the effect of A-site substitution was investigated for electrocatalytic activities and for electrochemical devices. For this purpose, a series of

Ruddlesden popper oxide materials $\text{Sm}_{1-x}\text{La}_x\text{Sr}_{1-x}\text{Ca}_x\text{NiO}_{4-\delta}$ ($x = 0.00, 0.05, 0.10, 0.15,$ and 0.20) were synthesized and their electrochemical behavior was investigated in 1 M 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 $\text{Sm}_{0.90}\text{La}_{0.10}\text{Sr}_{0.90}\text{Ca}_{0.10}\text{NiO}_{4-\delta}$ and $\text{Sm}_{0.80}\text{La}_{0.20}\text{Sr}_{0.80}\text{Ca}_{0.20}\text{NiO}_{4-\delta}$ indicates the presence of the combination of both pseudo capacitance and electrochemical double layer capacitance in these two electrodes. However, only the sample $\text{Sm}_{0.90}\text{La}_{0.10}\text{Sr}_{0.90}\text{Ca}_{0.10}\text{NiO}_{4-\delta}$ sample 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 revealed that oxygen and nickel play a crucial role on the high capacitive behavior of sample $\text{Sm}_{0.90}\text{La}_{0.10}\text{Sr}_{0.90}\text{Ca}_{0.10}\text{NiO}_{4-\delta}$. Formation of high oxidative ion species (O^{2-}/O^-) and high ratio of $\text{Ni}^{3+}/\text{Ni}^{2+}$ in $\text{Sm}_{0.90}\text{La}_{0.10}\text{Sr}_{0.90}\text{Ca}_{0.10}\text{NiO}_{4-\delta}$ is resulting the enhanced electron transfer properties and also surface charge storage capacity. This study concludes that $\text{Sm}_{0.90}\text{La}_{0.10}\text{Sr}_{0.90}\text{Ca}_{0.10}\text{NiO}_{4-\delta}$ is a suitable material for energy storage application to be used as a hybrid capacitor electrode.

Since B-site element (i.e., nickel) in all the sample has great impact on the catalytic behaviour of all the sample as discussed. Therefore, it is necessary to investigate the behaviour of metal oxide (NiO) for the electrocatalytic behaviour. In this regard, thin film of Nickel oxide was prepared by using the sol gel method. The electrolyte has a great influence on the electrocatalytic behaviour in cyclic voltammetry towards oxygen reduction and evolution reactions. Therefore, the electrocatalytic activity was investigated in three different types of mediums. The behaviour of NiO thin film was investigated in 0.5M Na_2SO_4 , H_2SO_4 ,

and KOH solutions. It was found that pH effect the electrocatalytic activity severely. Sample with 6 depositions i.e., N₆ shows promising behaviour for electrocatalytic activity towards oxygen reduction reactions and oxygen evolution reactions at acidic and alkaline medium.

Overall, it can be concluded that layered perovskites (SmSr)NiO_{4-δ} exhibit a competent feature for an air electrode material in porous structure and feature for buffer layer in pore free structure. In addition, thin films of (SmSr)NiO_{4-δ} act as a nano-electrocatalysts in a neutral medium. Subsequently, its compositions Sm_{0.90}La_{0.10}Sr_{0.90}Ca_{0.10}NiO_{4-δ} is a suitable material for electrocatalyst for oxygen evolution reactions and also has potential to be used as electrode for energy storage application in hybrid capacitor.

7.2 Scope for Future Work

Future work can be pursued in various directions. Some of the following points may be noted for future prospects in this area:

- The study of the effect of B site substitution on the catalytic behavior of (SmSr)NiO_{4-δ} and its compositions.
- To Synthesize and analyses the properties of the higher order layered perovskites and study their electrochemical behavior for electrochemical energy storage devices Synthesis approaches may be alter to obtain the best performance of the material.
- Preparation of new RP phases and their deposition as cathode material (air electrode), and testing in a symmetrical cell mode of operation and incorporation into a single solid oxide fuel cell device.
- To explore the new and wide range of cathode (as well anode) materials for fuel cells.