CHAPTER- 8

CONCLUSIONS AND FUTURE SCOPES

CHAPTER 8: Conclusions and Future Scopes

8.1 Conclusion of the Present Investigation

The main objective of the research work presented in the thesis has focussed on the systematic study of Lanthanum Ferrite-based material for its use as electrodes and catalysts. Lanthanum Strontium Ferrite ($La_{0.5}Sr_{0.5}FeO_3$) and Lanthanum Strontium Ferrite Titanate ($La_{0.5}Sr_{0.5}Fe_{0.5}Ti_{0.5}O_3$) have studied alongside their base materials Lanthanum Ferrite ($LaFeO_3$) and Strontium Titanate ($SrTiO_3$), for their potential use as electrode materials in fuel cells. Additionally, their reaction kinetics were studied under different pH conditions and analyzed for use as a catalyst, observeing their enhanced performance in the enviromenmtal friendly mediums. The structural, microstructural, and thermal properties of the system have been investigated with their electrochemical properties and reaction processes, which are essential requirements for electrode materials near the eletrolyte end as well as for the use as a catalyst. Conductivity and impedance spectroscopy techniques have been studied to understand the electrical conductivity behavior. The major conclusions drawn from the entire study carried out during this work are summarized below:

1. Lanthanum Ferrite ($LaFeO_3$), Lanthanum Strontium Ferrite ($La_{0.5}Sr_{0.5}FeO_3$), and Lanthanum Strontium Ferrite Titanate ($La_{0.5}Sr_{0.5}Fe_{0.5}Ti_{0.5}O_3$) were synthesized via the solid-state reaction route at the sintering temperature of 1300 ℃ for 2 h. XRD data revealed the orthorhombic phase with pbnm space group. The conductivity spectra were used to study the dynamics of ions. The band gap of the sample was estimated and correlated with the charge transfer coefficient calculated through electrochmeical studies. The activation energy calculated with the help of Arrhenius equation suggested a change in the charge

carrier and more polaronic behavior observed in Lanthanum Strontium Ferrite ($La_{0.5}Sr_{0.5}FeO_3$). The electrochemical study indicated a high cathodic current observed in Lanthanum Strontium Ferrite ($La_{0.5}Sr_{0.5}FeO_3$) with high ORR values. In addition, the Tafel slope calculation suggested that a high OER present in the LSF, as the lower slope was observed in it. The chronopotentimetry stability shows that, like $LaFeO_3$, $La_{0.5}Sr_{0.5}FeO_3$, $La_{0.5}Sr_{0.5}Fe_{0.5}Ti_{0.5}O_3$ were also stable for a long duration irrespective of current. All results suggests that hole substitution and, consequently, co-substitution of electrons increases the conductivity and the redox activity of the $LaFeO_3$ and is a promising material for use in FCs.

2. In continuation of the above, ion dynamics and electrochemical studies of the base material $SrTiO_{3-\delta}$ sample were investigated. In this context, $SrTiO_3$ was synthesized via a solid-state reaction route. XRD confirmed the cubic structure with the pm3m space group. The conductivity data isotherms with frequency showed non-linear variation and were well-fitted with Jonscher power law. Conductivity spectra analysis yielded the dc conductivity, hopping frequency, and exponent values. The activation energy estimated through bulk conductivity and hopping frequency is 1.25eV and 1.77 eV, respectively, suggesting oxide ion participation in the conduction. Impedance and modulus spectroscopy were studied. The conduction process remains unaffected by frequency and temperature confirmed by the Ghosh scaling. Additionally, the reaction kinetics and electrochemical behavior of the sample were studied through cyclic voltammetry across a wide range of pH conditions. The sample showed better activity and stability in the neutral and alkaline conditions than in acidic conditions. High redox reactivity and ORR/OER were observed in the neutral

medium compared to alkaline conditions. Also, reversibility was shown in the neutral medium, called as environment-friendly medium, compared to alkaline conditions.

3. To study the influence of different pH media on the electrochemical properties of hole substitution at the La-site and electron co-substitution at the Fe-site formed Lanthanum Strontium Ferrite Titanate ($La_{0.5}Sr_{0.5}Fe_{0.5}Ti_{0.5}O_3$). This co-substitution improved the conductivity and electrochemical reactivity of the sample. In this work, LSFT was explored as a bifunctional catalyst for the fuel cell and widely analysed in different pH conditions. Sodium sulphate (Na_2SO_4, neutral), potassium hydroxide (KOH, alkaline), and sulphuric acid (H_2SO_4, acidic) were used as the electrolyte medium for the catalytic studies. Higher current density in OER and ORR regimes with higher stability was observed in a neutral medium. It was explored as a bifunctional catalyst for simultaneous H2 (HER/ORR) and O2 (OER) production. Also, LSFT was stable for 600 cycles in the neutral medium compared to alkaline and acidic media. The chronopotentiometry stability with a potential of 2 V (vs Ag/AgCl) at a higher current of 150 mA/cm^2. This suggests that LSFT showed bifunctional catalyst behavior in the neutral medium compared to the harsh media (alkaline and acidic).

4. Continuing from the previous chapter, this section discusses heterostructures formed via Pulse Laser Deposition (PLD). X-ray diffractograms of all the compositions confirmed the presence of the orthorhombic phase (Pbnm) of LSFT and the hexagonal phase (P63mc) of ZnO. These heterostructure LSFT/ZnO/LSFT were explored as multifunctional catalysts for the simultaneous HER/OER/ORR in the neutral medium. A relative conductivity is four times higher for all four heterostructures formed compared to parent LSFT. Variation of I/I_o vs time shows the mixed ionic-electronic conducting (MIEC) behavior of the

heterostructures, which is why these heterostructures were also termed as double heterostructure mixed-ionic electronic conducting (DH-MIECs) materials. The activation energy calculated from the Arrhenius equation gives 75 meV, suggesting polaronic conduction in all DH-MIECs. XPS analysis shows that metal-O bonds (Fe-O, Ti-O, Sr-O, La-O) are present in LSFT and $n = 15$, while metal-OH is present in parent LSFT,10, and 15 DH-MIECs. Electrochemical characterization was carried out in neutral medium Na_2SO_4, and a significant change in OER/ORR and HER behavior is observed in all DH-MIECs with parent LSFT. ORR increases with the thickness, whereas HER and OER potential shifted to a more positive potential, and a significant increase in OER current was observed. A lesser transient response was observed in all the DH-MIECs, making them suitable for hole transport behavior. Mott Schottky's analysis suggests a p-type nature for all DH-MIECs, including parent LSFT. In addition, in the chronopotentiometry stability test of the DH-MIECs, only $n = 15$ were stable for 24 h at the applied voltage of 2V, which is also confirmed through the post and pristine FTIR, AFM, and XPS characterizations.

5. The influence of A-site substitution on the structure, morphological, and electrochemical properties of the Lanthanum Strontium Ferrite ($La_{0.5}Sr_{0.5}FeO_3$) sample was investigated in the previous chapter. In this chapter, LSF was synthesized via hydrothermal method. This preparation route helps to produce fine particles with a better surface area compared to the solid-state reaction route. The TEM of the sample confirmed the formation of the nanoparticles. With the help of a W-H plot, the crystallite size of the materials was estimated, suggesting a nanometer order in the hydrothermal method, and micrometer (μm) in the SSR method. Further, electrochemical properties were analyzed and compared to B-LSF. Here, the current density is higher in the case of B- LSF compared to N-LSF. The B-

LSF was adequately involved in the redox activity, whereas for N-LSF, only reduction properties were favourable. That is why the specific capacitance of both samples was estimated, and a ∽ ten times higher specific capacitance (mF/g) was observed in the case of N-LSF. The calculated transient time decay value is consistent with the capacitive properties. The chronoamperometry stability test was observed for 4000 sec, and both samples were stable for that period.

8.2 Outlook for Future Perspective

The extrinsic properties of the materials for FCs depend on their processing route, dopants, and microstructures. Processing variables like sintering temperature, environment utilized during sintering, and processing routes will change their properties. Therefore, a thorough investigation of the impact of these processing factors on the structural, microstructural, thermal, electrical, and electrochemical properties of the compositions under investigation is necessary.

Some of the following points may be noted for future prospects in this area:

- To explore these materials in the regenerative fuel cell or H2/O2 fuel cell for the multipurpose.
- To investigate these materials in hydrogen production and water splitting process.
- Explore their performance as an individual fuel cell by depositing them as the electrode material and incorporating compatible components.
- Understanding their role in fuel cells is of great interest for various catalytic applications.

- Investigation as the catalyst supporting layer GDL replaced by these materials in terms of reduced thickness and composition.