



## **Chapter-7**

### **Conclusions and Future Scopes**





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## CHAPTER 7: Conclusions and Future Scopes

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### 7.1 Conclusion of the Present Investigation

One of the primary objectives of the current thesis work was to resolve the ambiguity regarding the synthesis of the double perovskite  $\text{PrBaCo}_2\text{O}_{6-\delta}$ . Therefore, it was designed to synthesize the PBCO by using two methods—solid state ceramic and auto combustion routes. 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:

The optimized sintering temperature for the double perovskite  $\text{PrBaCo}_2\text{O}_{6-\delta}$ . Is found to be 1000 °C for SSR (P-SSR) and 1050 °C (P-ACR). Thus, the paradigm that chemical synthesis reduces the sintering temperature as compared to solid state synthesis, seems to be violated. The X-ray diffraction patterns showed that both optimized samples exhibit the orthorhombic crystal structures with Pmmm symmetry. The thermodynamic parameters validates that the reaction kinetics for the formation of perovskite are feasible for both samples. HRTEM and XPS studies reveal that both samples are highly crystalline and have an orderly arrangement. HRTEM, Raman and STM studies reveal that there is crystal growth on a smooth surface with a preferred orientation. Thus, the anomalous synthesis behavior is due to anisotropic surface nucleation crystal growth and a high value of entropy change is expected in both samples. The high entropy change increases the contribution from two stable configurational vibrational modes (JT modes) which leads to a reduction in bond energy and surface energy in the case of ACR as compared with SSR. Also, the smaller

chemical potential gradient observed for ACR is not far from thermodynamic equilibrium as compared with SSR. Consequently, a higher sintering temperature is expected in the case of ACR. The microstructure (dihedral angle) and JT interaction suggest a high surface energy and a metallic nature, as confirmed through electronic (XPS and DFPT) studies. The porous microstructure and high conductivity for P-SSR make it a very promising candidate for cathode materials for SOFCs. Thus, our results not only explain the observed synthesis anomaly observed, but also account for the high conductivity in  $\text{PrBaCo}_2\text{O}_{6-\delta}$ . Further, these outcomes will stimulate research on the correlation between the processing of magnetic cathode materials for SOFCs and their quantum behavior.

A systematic study on compositional effect on ORR in perovskite series  $\text{Pr}_{1+x}\text{Ba}_x\text{Co}_2\text{O}_{6-\delta}$  from  $x = 0.0$  to  $1.0$  in the steps of  $0.2$  was performed. All the compositions were synthesized at the best optimized condition for  $\text{PrBaCo}_2\text{O}_{6-\delta}$  (solid state route- $1050\text{ }^\circ\text{C}$ ). The compositions are observed to be in double phase (confirmed from XRD and DSC studies) with single morphology as no composite behavior is revealed in the SEM micrographs. The Rietveld refinement revealed that the XRD data can be fitted with *Pmmm* and *Pnma* symmetries for the substituted compounds. At  $x = 0.6$ , Ba content  $0.4$  is critical for band center formation and decreases the bulk oxygen vacancy and increases ORR with the higher Pr content. When  $\text{Ba} > 0.4$  and  $\text{Ba} < 0.4$ ,  $\text{Co}^{2+}$  creates electron traps at the surface which can decrease in conductivity leading to an overall decrease in ORR. Thus, sample  $x = 0.6$  has higher ORR with the more production of  $\text{H}_2$  gas in comparison to other substituted samples.

In the extension of this, the perovskite series  $\text{Pr}_{1+x}\text{Ba}_{1-x}\text{Co}_2\text{O}_{6-\delta}$  from  $x = 0.0$  to  $0.2$  in the step size of  $0.05$  were synthesized and their catalytic behavior for ORR along with OER were studied. XRD and Rietveld refinement confirm the phase formation in all electrode samples

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except for  $x=0.15$  and SEM images depict the electrocatalyst morphology. The detailed electrochemical investigations revealed that  $x = 0.05$  ( $\text{Pr}_{0.95}\text{Ba}_{1.05}\text{Co}_2\text{O}_{6-\delta}$ ) exhibits good ORR activity and a strong redox peak corresponding to the high value of cathodic current with the presence of various oxidation states of Cobalt. The specific capacitance for  $x=0.05$ ,  $x=0.10$  and  $x=1.20$  (phase pure perovskite) is estimated to be 235.7, 598.4, and 408.37 F/g, respectively. Power law indicates that oxide ion dominates the energy storage mechanism in  $x=0.10$ , leading to the oxygen-ion intercalation pseudo capacitance, which is corroborated through RS equations. A high value of Double-layer capacitance in  $x=0.05$  and  $x=0.10$  reveals the high number of active sites in these two perovskites establishing the high OER activity. However,  $x=0.10$  is observed to be more suitable for OER catalysts. Since A site substitution of double perovskites praseodymium-based cobaltite is not claimed for the considerable electrocatalyst toward ORR or OER, this study could provide a pathway for efficient and potential application of Pr based double perovskites as an efficient catalyst for OER and ORR.

The likelihood of investigated catalytic behavior of studied sample in thin film, thin films of two samples ( $\text{PrBaCo}_2\text{O}_{6-\delta}$  and  $\text{Pr}_{1.6}\text{Ba}_{0.4}\text{Co}_2\text{O}_{6-\delta}$ ) were fabricated successfully by pulse laser deposition method on silica substrate. XRD data revealed phase formation and AFM studies displayed proper deposition of thin film in both the samples. Catalytic study of reveals that transient response time reduced in case of thin film as compared to the bulk sample, even with less current. However,  $\text{Pr}_{1.6}\text{Ba}_{0.4}\text{Co}_2\text{O}_{6-\delta}$  thin film can be proposed as a catalyst for ORR.

Overall, it can be concluded that double perovskite  $\text{PrBaCo}_2\text{O}_{6-\delta}$  exhibit a competent feature for an air electrode material of fuel cell and higher conductivity. Subsequently, its

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compositions  $\text{Pr}_{1.6}\text{Ba}_{0.4}\text{Co}_2\text{O}_{6-\delta}$  demonstrated promising behavior for ORR and  $\text{Pr}_{0.90}\text{Ba}_{1.10}\text{Co}_2\text{O}_{6-\delta}$  is found suitable as catalyst for OER.

## **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  $\text{PrBaCo}_2\text{O}_{6-\delta}$ .
- The study of the behaviour of investigated electrode materials under different atmosphere.
- The catalytic behaviour of synthesised electrocatalyst can be studied in alkaline, acidic and neutral electrolyte solution.
- Preparation of SOFC using standard electrolyte and anode with the investigated cathode material.
- To explore the new and wide range of cathode (as well anode) materials for SOFC.