

*Dedicated*  
*To*  
*Mahadev*



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It is certified that the work contained in the thesis titled "INVESTIGATIONS ON DOUBLE PEROVSKITE  $\text{PrBaCo}_2\text{O}_{6-\delta}$  AS AN AIR ELECTRODE FOR FUEL CELL APPLICATIONS" by "AJAY SHANKAR BANGWAL" (Roll No. 16171004), in partial fulfillment of the requirement for award of 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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**DECLARATION BY THE CANDIDATE**

I, **AJAY SHANKAR BANGWAL** (Roll No. 16171004), certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of **PROF. PRABHAKAR SINGH** from **JULY, 2016** to **FEBRUARY 2022** at the **DEPARTMENT OF PHYSICS**, Indian Institute of Technology, Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied from any other's work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports dissertations, theses, *etc.*, or available at websites and have not included them in this thesis and have not cited as my own work.

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It is certified that the above statement made by the student is correct to the best of our knowledge.

  
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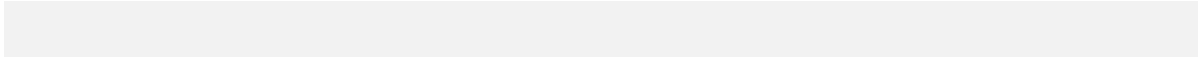
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## LIST OF SYMBOLS AND ABBREVIATIONS

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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
PBCO	$\text{PrBaCo}_2\text{O}_{6-\delta}$
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetry analysis
XRD	X-ray diffraction
JCPDS	Joint Committee on Powder Diffraction Standards
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy

XPS	X-ray Photoelectron Spectroscopy
STM	Scanning Tunneling Microscopy
FWHM	Full width at Half Maximum
SSR	Solid State Route
ACR	Auto Combustion Route
P-SSR	Pallet Synthesized through SSR
P-ACR	Pallet Synthesized through ACR
K	Kelvin
N	Avogadro's Number
JT	Jahn-Teller
$\Delta G$	Gibbs Free Energy
$\Delta S$	Entropy
$\Delta H$	Enthalpy
G	Gram
SAED	Selected Area Electron Diffraction
V	Volt
OD	Orthorhombic Distortion
DFPT	Density Functional Perturbation Theory
DOS	Density of State
HS	High Spin
LS	Low Spin
IS	Intermediate Spin
RS	Randles-Ševčík
CR	Corrosion Rate





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## PREFACE

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The demand of energy is growing day by day due to increase in industrialization and population, 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 cell.

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 hold 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, double perovskite  $\text{PrBaCo}_2\text{O}_{6-\delta}$  has been chosen for further investigation. Double perovskite  $\text{PrBaCo}_2\text{O}_{6-\delta}$  (PBCO), in particular, is one of the most interesting materials due to the stronger tendency of A-site ordering. However, there are lots of ambiguity regarding its synthesis techniques. Thus, PBCO was synthesized by two well-known methods Solid state route method (SSR) and auto-combustion route method (ACR). It was found that optimized temperature was less in case of SSR as compare to the ACR and also the samples are phase pure in case of SSR. This is the violation of the general belief of synthesis that chemical synthesis (ACR) reduced the sintering temperature. The details of this anomaly were studied experimentally and theoretically. The catalytic study of the PBCO was also studied and observed that PBCO has an issue of degradation during cyclic voltammetry for ORR.

In order to understand the behavior of PBCO and its compositions as catalyst, a series of Pr rich perovskite was synthesized by using the SSR method. The compositional effect on

ORR was studied for this series of double perovskite. The structural, microstructural, electronic along with catalytic studies was performed by XRD, SEM, XPS and CV. It was found that a particular composition of this series is suitable for ORR with more production of hydrogen gas.

Along with ORR, oxygen evolution reaction (OER) is also important for many electrochemical devices and double perovskites has an ability to function like electrocatalyst for OER as well. Therefore, another series was synthesis from PBCO (i.e., Ba rich double perovskite) by solid state route method and their catalytic behavior was studied especially for OER. 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.

Finally, in the last part of this research work, a comparative study was performed for the ORR in bulk sample and thin film. The sample used for this investigation was the best optimized sample for ORR and PBCO. Their catalytic activity was again studied by using cyclic voltammetry. It was observed that thin film reduces the transient response of the electrode making them suitable for ORR.

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 cobaltite-based perovskite and layered perovskite materials along with an overview of  $\text{PrBaCo}_2\text{O}_{6-\delta}$  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** aims to describe the violation of the paradigm that chemical synthesis reduces the sintering temperature as compared to the solid-state synthesis in the case of double perovskite  $\text{PrBaCo}_2\text{O}_{6-\delta}$ . Our results show that this anomalous synthesis behavior is due to anisotropic surface nucleation growth. Thermodynamically, the higher decomposition temperature in the chemical route is mainly occurs due to the stronger electron-phonon coupling and the higher value of change in entropy. The variation in the Co-O-Co bond angle reveals Jahn-Teller vibrational anisotropy in the b-plane leading to the anisotropic synthesis behavior. This anisotropy is the reason for the violation of the paradigm.

In **Chapter 4**, compositional effect on oxygen reduction reaction (ORR) has been studied. In order to understand to inspect the ORR mechanism with substitution, a series of  $\text{Pr}_{1+x}\text{Ba}_{1-x}\text{Co}_2\text{O}_{6-\delta}$  are prepared using conventional solid state ceramic route. The structural, microstructural, electronic and catalytic studies was performed using XRD, SEM, XPS and CV. The triple phase boundary reaction suggest the formation of  $\text{Co}(\text{OH})_3$  along with the  $\text{H}_2$  gas on reaction of these composite electrode with  $\text{H}_2\text{O}$  during electrochemical dissolution. Sample with higher ORR and liberation of  $\text{H}_2$  gas at room temperature from this compositional series may be utilized for further studies.

In **Chapter 5**, a series of double perovskite oxide materials  $\text{Pr}_{1+x}\text{Ba}_{1-x}\text{Co}_2\text{O}_{6-\delta}$  ( $x=0.05, 0.10, 0.15$  and  $0.20$ ) was synthesized using the high temperature solid-state route and their catalytic activity and stability in 1M KOH alkaline solution are probed. Powder X-ray diffraction was used to determine the phase formation and structure of the prepared oxides. SEM analyses confirm the morphology of prepared catalysts. Electrochemical measurements were used to investigate the catalytic performance of the prepared catalyst in alkaline solution for both oxygen evolution reaction (OER) and oxygen reduction reactions (ORR). This series of double perovskite oxide materials exhibit catalytic activity for both OER and ORR. Power law gives a hint of oxide-ion intercalation pseudo capacitance in one composition. On the other hand, one composition exhibits potential behavior for ORR. Overall, our findings highlight the collective effects of incorporating Ba into double perovskite  $\text{PrBaCo}_2\text{O}_{6-\delta}$  for OER and ORR properties.

In **Chapter 6**, a comparative study was performed on the catalytic behavior of the  $\text{PrBaCo}_2\text{O}_{6-\delta}$  and  $\text{PrBaCo}_2\text{O}_{6-\delta}$  in bulk and thin film. The thin film was deposited on silica substrate by using pulse laser deposition technique. Cyclic voltammetry was mainly employed to investigate the catalytic behavior and it was found that transient response time is less in case of thin film as compared to that of the bulk sample.

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