

# Development of Platinum-based Bimetallic Cathode Electrocatalysts for Proton Exchange Membrane Fuel Cell Application



Thesis submitted in partial fulfillment for the  
Award of Degree

**Doctor of Philosophy**

By

*Abhay Pratap Singh*

DEPARTMENT OF CHEMICAL ENGINEERING & TECHNOLOGY  
INDIAN INSTITUTE OF TECHNOLOGY  
(BANARAS HINDU UNIVERSITY)  
VARANASI - 221005  
INDIA

Roll No. 17041008

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(Prof. Hiralal Pramanik)

Supervisor

Department of Chemical Engg. & Tech.

Indian Institute of Technology

(Banaras Hindu University)

Varanasi – 221005, India

प्रचार्य/Professor  
रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग  
Deptt. of Chemical Engg. & Tech.  
भारतीय प्रौद्योगिकी संस्थान  
Indian Institute of Technology  
काशी हिन्दू विश्वविद्यालय  
Banaras Hindu University  
वाराणसी/Varanasi-221005

  
(Dr. Sweta)

Co-Sopervisor

Department of Chemical Engg. & Tech.

Indian Institute of Technology

(Banaras Hindu University)

Varanasi – 221005, India

सहायक प्राचार्य  
Assistant Professor  
रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग  
Deptt. of Chemical Engg. & Tech.  
भारतीय प्रौद्योगिकी संस्थान  
Indian Institute of Technology  
काशी हिन्दू विश्वविद्यालय  
Banaras Hindu University  
वाराणसी/Varanasi-221005

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Place: Varanasi

Abhay

(Abhay Pratap Singh)

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<p style="text-align: center;"> (Prof. Hiralal Pramanik) <b>Supervisor</b> Department of Chemical Engg. &amp; Tech. Indian Institute of Technology (Banaras Hindu University) Varanasi -221005 प्राचार्य/Professor रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग Deptt. of Chemical Engg. &amp; Tech. भारतीय प्रौद्योगिकी संस्थान Indian Institute of Technology काशी हिन्दू विश्वविद्यालय Banaras Hindu University वाराणसी/Varanasi-221005</p>	<p style="text-align: center;"> (Dr. Sweta) <b>Co-Supervisor</b> Department of Chemical Engg. &amp; Tech. Indian Institute of Technology (Banaras Hindu University) Varanasi -221005 सहायक प्राचार्य Assistant Professor रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग Deptt. of Chemical Engg. &amp; Tech. भारतीय प्रौद्योगिकी संस्थान Indian Institute of Technology काशी हिन्दू विश्वविद्यालय Banaras Hindu University वाराणसी/Varanasi-221005</p>
<p style="text-align: center;"> Signature of Head of Department (Prof. M. K. Mondal) विभागाध्यक्ष/Head रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग Deptt. of Chemical Engg. &amp; Tech. भारतीय प्रौद्योगिकी संस्थान/Indian Institute of Technology काशी हिन्दू विश्वविद्यालय/Banaras Hindu University वाराणसी/Varanasi-221005</p>	

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*Dedicated to My Beloved*

*Parents &*

*Family Members*

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Date: 20/7/23

Place: Varanasi

Abhay

(Abhay Pratap Singh)

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## NOMENCLATURE

<b>Abbreviations</b>	<b>Meaning</b>
ANOVA	Analysis of variance
BBD	Box behnken design
CCME	Catalyst coated membrane electrode
CNT	Carbon nanotube
CV	Cyclic voltammetry
3D	Three-dimensional
DF	Degree of freedom
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
EDX	Energy dispersive X-ray analysis
EG	Ethylene glycol
EIS	Electrochemical impedance spectroscopy
FCA	Flow channel area
GDL	Gas Diffusion Layer
HSA	High surface area
MPD	Maximum power density
MWCNT	Multi-walled carbon nanotube
NC	N-micro/mesoporous carbon supported
OCV	Open circuit voltage
ORR	Oxygen reduction reaction
PEMFC	Proton exchange membrane fuel cell
RSM	Response surface methodology
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
W	Water
XRD	X-ray diffraction

<b>Greek Symbols</b>	<b>Meaning</b>
$\alpha_0$	Lattice parameter of pure carbon supported Pt
$\beta$	Width of the peak (in radians)
$\beta_0$	Linear parameter
$\beta_{ii}$	Quadratic parameter
$\beta_{ij}$	Interaction parameter
$\lambda$	Scherrer constant
$\theta$	Theta (in degree)
$\eta_{FC}$	Total efficiency
$\eta_F$	Faraday efficiency
$\eta_H$	Heating value efficiency
$\eta_r$	Thermodynamics efficiency
$\eta_U$	Fuel utilization efficiency
$\eta_V$	Electrochemical efficiency
<b>Alphabetic symbols</b>	<b>Meaning</b>
A	Cathode loading
a	Lattice parameter
$a_0$	Lattice parameter of pure carbon supported Pt
B	Cell temperature
C	Hydrogen flow rate
$C_{AB}$	Acetylene black
dc	Average crystallite size
$d_{hkl}$	Interplanar distance between two planes of miller indices (hkl)
k	Number of factors in RSM study
N	Total number of experiments in RSM study
p-value	Probability value
$R^2$	Coefficient of determination
$X_i$ and $X_j$	Independent variables for the studied factor
Y	Predicted response (maximum power density)

## PREFACE

The recent past has shown a sharp growth in energy demand as a result of rising global population. The conventional fuels like crude oil, coal, and natural gas, among others, are used to meet energy needs in the domestic and industrial sectors. Recently, the rate at which conventional energy resources are consumed has greatly increased. The major motivation to consider alternative energy sources, however, is the limited storage of conventional energy sources, such as crude oil, coal, and natural gas. The low temperature fuel cell may be considered as better source of energy compared to the other conventional energy sources. It is well known that, hydrogen-based fuel cell has attracted interest due to their potentially low degree of pollution and better electrical efficiency than other alcohol based fuel cells. No better alternative to the conventional energy sources. However, irrespective of any kind of fuel cell it suffers from different types of losses/polarization viz activation losses, ohmic losses, and concentration losses. Activation polarization is due to the slow electrochemical reactions at the electrode surface, where the species are oxidized or reduced in a fuel cell electrode reaction. Low-temperature fuel cells powered by hydrogen are gaining popularity because of their ability to use a proton exchange membrane (PEM) made of a material like Nafion<sup>®</sup> as an electrolyte with high ionic conductivity. According to numerous published research, oxygen reduction at the cathode is slower in an acidic medium or PEM than anode electro-oxidation of H<sub>2</sub> fuel in the presence of a Pt-based electrocatalyst. Slow reduction kinetics at the cathode for a Pt-based electrocatalyst is thus one of the major challenges for the oxygen reduction reaction. Other challenges of proton exchange membrane fuel cell (PEMFC) are proton conductivity at high temperatures ( $T > 80$  °C), notable activation loss, and the high cost of pure

Pt-based electrocatalyst. Currently, researchers are working very hard to develop a very effective bimetallic cathode electrocatalyst that could reduce the consumption of costly platinum (Pt), reduce activation overpotential and raise the current density to a few folds higher than the existing electrocatalyst. In order to build bimetallic electrocatalysts for oxygen reduction reaction (ORR) at the PEMFC cathode, it is necessary to add other metals, such as Co, Cr, Ni, and W to Pt. This will surely lower the cost of the cathode electrocatalyst and consequently lower the overall fabrication cost of the fuel cell. The platinum (Pt) is a widely used cathode electrocatalyst for the oxygen reduction reaction because it is electrochemically very active. However, Pt-based bimetallic electrocatalysts are not commercially commonplace. As a result, there is an urgent need to synthesize bimetallic Pt-M (where M is Co, Ni, etc.) electrocatalysts to enhance oxygen reduction reaction kinetics and activity.

Despite several attempts to create acceptable Pt-based bimetallic electrocatalysts, no scientific work has yet examined the impact of different solvent types on electrocatalyst development. The solvent, which acts as an agent in the preparation of highly active core-shell electrocatalysts and regulates the size and shape of synthesized particles, also plays a significant role in the synthesis of highly active electrocatalysts. Bimetallic Pt-M/C<sub>AB</sub> (M = Co, Ni) electrocatalysts for efficient ORR in hydrogen-based PEMFC were synthesized using the solvothermal method using four different solvents, namely dimethyl sulphoxide (DMSO), dimethylformamide (DMF), ethylene glycol (EG), and water (W). The EG-based solvothermal method produced a highly effective active cathode electrocatalyst, Pt-Ni/C<sub>AB</sub>-EG, which displayed the best performance for ORR in a half-cell and single PEMFC out of all four solvents employed in the synthesis of cathode electrocatalysts.

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The acetylene black supported with 20 wt.% metal loading, cathode electrocatalysts Pt-M(3:1)/C<sub>AB</sub> (M = Co, Ni) were synthesized using platinum (II) acetylacetonate, cobalt (III) acetylacetonate, H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O and NiCl<sub>2</sub>.6H<sub>2</sub>O precursors by solvothermal method using four types of solvents namely, dimethyl sulphoxide (DMSO), dimethylformamide (DMF), ethylene glycol (EG) and water (W).

The synthesized Pt-based bimetallic electrocatalysts were Pt-Co/C<sub>AB</sub>-DMSO, Pt-Co/C<sub>AB</sub>-DMF, Pt-Co/C<sub>AB</sub>-EG, Pt-Co/C<sub>AB</sub>-W, Pt-Ni/C<sub>AB</sub>-DMSO, Pt-Ni/C<sub>AB</sub>-DMF and Pt-Ni/C<sub>AB</sub>-EG. The synthesized electrocatalysts were characterized by XRD, SEM, EDX, TEM, and electrochemical techniques (CV and EIS). The anode electrocatalyst was commercial Pt/C<sub>HSA</sub> (40 wt. %). For electrode preparation, a gas diffusion layer (GDL) was used. The ink was made by combining the necessary amounts of electrocatalyst, isopropanol (99.0 %), Nafion® dispersion (5 wt %), and PTFE (60 wt. %) dispersion. The prepared ink was painted on carbon paper using a paintbrush for anode and cathode preparation. The experiment was performed to achieve the best cell performance, with synthesized cathode electrocatalyst in PEMFC. The PEMFC operating parameters were optimized using response surface methodology (RSM) using the best cathode electrocatalyst candidate. The XRD analysis confirms, the all synthesized Pt-Co/C<sub>AB</sub> electrocatalyst were crystalline in structure and show their prominent diffraction peaks of the face-centered cubic (FCC) for Pt at plane 220. This prominent shifting of 2θ proved the incorporation of Co into Pt metal of the FCC structure, which results in alloy formation of Pt-Co/C<sub>AB</sub>. The Pt-Ni/C<sub>AB</sub> XRD patterns demonstrated that the Pt-phase in the synthesized electrocatalysts consisted of highly crystalline face-centered cubic (FCC) structure. The lattice parameters of all Pt-Ni/C<sub>AB</sub> alloy electrocatalysts were between those for pure Pt (0.3924 nm) and pure Ni (0.3523 nm). Peaks for Ni were not observed in the XRD patterns of the Pt-Ni/C<sub>AB</sub> synthesized electrocatalyst,

although their presence could be discarded. The SEM images of the prepared electrocatalyst showed that the particles were uniformly dispersed across the support material and were in the nanometer size range. The EDX analysis was performed to determine the surface composition of all active components and elemental mapping, which reveals the existence of C, Pt, Co, and Ni elements in the synthesized electrocatalyst, Pt-Co/C<sub>AB</sub> and Pt-Ni/C<sub>AB</sub>. The TEM study indicated that the particles were between 2 to 20 nm for Pt-Co/C<sub>AB</sub> and 3 to 6.5 nm for Pt-Ni/C<sub>AB</sub> in size. The half-cell analysis using CV showed that Pt-Co/C<sub>AB</sub>-EG and Pt-Ni/C<sub>AB</sub>-EG had low activation losses as compared to other synthesized electrocatalyst. EIS showed that Pt-Co/C<sub>AB</sub>-EG had the lowest charge transfer resistance related to the other Pt-Co/C<sub>AB</sub> electrocatalyst. In the PEMFC, the performance of anode electrocatalysts Pt-Co/C<sub>AB</sub> and Pt-Ni/C<sub>AB</sub> of the same compositions was examined. The performance of PEMFC increased with the increase in electrocatalyst loading but beyond the optimum loading, the performance, got decreased due to an increase in the mass transfer resistance for the flow of reactants (hydrogen and oxygen) from the bulk to reaction sites on the electrode surface. A rise in cell operating temperature improved cell performance by increasing reaction kinetics at anode and cathode. Moreover, the mobility of ions improved, at the high temperature, hence ohmic loss decreases. Excessive increase in cell temperature, reduced the PEMFC performance due to dehydration of membrane as well as the electrode surface. The performance of synthesized electrocatalyst Pt-Co/C<sub>AB</sub>-EG was superior among all the synthesized Pt-Co/C<sub>AB</sub> electrocatalysts in half-cell, as well as in the single PEMFC. Similarly, Pt-Ni/C<sub>AB</sub>-EG showed, a better performance than the other synthesized Pt-Ni/C<sub>AB</sub> electrocatalysts in CV and PEMFC. However, PEMFC performance showed that the synthesized ORR electrocatalyst Pt-Ni(3:1)/C<sub>AB</sub>-EG is better than Pt-Co(3:1)/C<sub>AB</sub>-EG. The Pt-Ni(3:1)/C<sub>AB</sub>-EG in PEMFC at optimum cell conditions i.e., electrocatalyst loading at anode 1 mg/cm<sup>2</sup> and cathode 1 mg/cm<sup>2</sup>, flow rate of

anode/cathode species of 50/60 ml and cell temperature of 60 °C produced a maximum power density of 42.29 mW/cm<sup>2</sup> at a current density of 102.4 mA/cm<sup>2</sup> with an OCV of 0.908 V. The statistical analysis response surface methodology (RSM) was also used to developed a mathematical model and validate the same with experimental data. The optimum condition optimized through the RSM was very close to the experimental result. The % errors of power density between predicted and experimental value at optimum condition was found 0.31 % which is in permissible limit. The subject matter contained in the thesis has been arranged in six different chapters. In the **Chapter 1**, an overview was given about the energy demand and supply in present scenario, overview of fuel cell and its development along with its advantages over the other types of energy sources and use of hydrogen as fuel in the fuel cell for energy applications. At the end of the chapter, discussion about cathode electrocatalyst, synthesis of the cathode electrocatalyst using various non polar and polar solvents along with their advantages and disadvantages are described. **Chapter 2** explains the advancement of PEMFC from its inception along with describing the main components of PEMFC i.e., membrane electrolyte, electrocatalyst used as anode and cathode, gas diffusion layer along with the physical and chemical characterization techniques of electrocatalyst. This chapter also includes details about literature review of cathode electrocatalyst for PEMFC, PEMFC performance comparison about different types of cathode electrocatalyst. At the end of the chapter 2, objectives of the present thesis work is discussed. **Chapter 3** covers the material used in the experiment along with their experimental specifications for the synthesis of cathode electrocatalyst. The fabrication of working cathode electrode for half-cell and preparation of anode, cathode and forming a membrane electrode assembly (MEA) for the evaluation of PEMFC performance in a single cell setup are discussed in this chapter 3. **Chapter 4** covers the optimization of the PEMFC performance by considering the synthesized cathode

electrocatalyst loading as the factor along with cell temperature and hydrogen flow rate as other factors for maximizing the power density of the PEMFC by using box behnken design model.

**Chapter 5** covers the results and discussion which provides discussion about the physical characterization of the synthesized cathode electrocatalyst types, chemical characterization of the cathode electrocatalyst including cyclic voltammetry and electrochemical impedance spectroscopy and various findings interpreted from the characterization techniques. The performance of PEMFC using synthesized cathode electrocatalyst types is also discussed in this chapter. **Chapter 6** concludes the findings and discussion about the present work along with suggestions. At the end of the thesis, future scope of present research work, references and appendices are provided.