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It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. Degree.

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DECLARATION BY THE CANDIDATE

I, **"Deoashish Panjiara"**, certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of **"Prof. Hiralal Pramanik"** from "July 2015 to March 2021" at the "Department of Chemical Engineering & Technology", Indian Institute of Technology (BHU), 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 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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Dedicated to My Beloved

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Date:

Place: Varanasi **(Deoashish Panjiara)**

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NOMENCLATURE

Alphabetic symbols	Meaning
A	Glycerol concentration
a	lattice parameter
B	Anode electrolyte concentration
C	Anode electrocatalyst loading
C_{AB}	Acetylene black carbon
C_p	Central points
D	Cathode electrolyte concentration
d_c	average crystallite size
d_{hkl}	interplanar distance between two planes of Miller index (hkl)
d_h	Hydraulic diameter
2FI	Two factor interaction
F	Faraday’s constant
k	number of factors in RSM study
N	Total number of experiments in RSM study
p-value	Probability value
R	universal gas constant
R^2	Coefficient of determination
T	operating temperature
x_i and x_j	Independent variables for the studied factor
Y	Predicted response
z	Downstream length

Abbreviations	Meaning
ANOVA	Analysis of variance
AFC	Alkaline fuel cell
BBD	Box-Behnken Design
CEA	Central electricity authority
CV	Cyclic Voltammetry
3D	Three-dimensional
DF	Degree of freedom
EDX	Energy dispersive X-ray spectroscopy

SEM	Scanning Electron Microscopy
GDL	Gas Diffusion Layer
LFFC	Laminar flow fuel cell
MWCNT	Multi-walled carbon nanotube
MCFC	Molten Carbonate Fuel Cell
MFC	Microfluidic fuel cell
OCV	Open circuit voltage
ORR	Oxygen Reduction Reaction
PEMFC	Proton Exchange Membrane Fuel Cell
PAFC	Phosphoric Acid Fuel Cell
PRESS	Predicted residual error sum of squares
RSM	Response surface methodology
SOFC	Solid Oxide Fuel Cell
TEM	Transmission Electron Microscopy
XRD	X-Ray Diffraction

Greek Symbols	**Meaning**
α_a	Anodic charge transfer co-efficient
α_b	Cathodic charge transfer co-efficient
β_o	Linear parameter
β_{ii}	Quadratic parameter
β_{ij}	Interaction parameter
μ	Viscosity
β	width of the peak (in radians) at its half-height
κ	Scherrer constant (0.90 for spherical crystallite)
λ	X-ray wavelength used (1.54056 Å for Cu-$K_{\alpha 1}$ radiation)
ρ	Density
$\vec{u}$	Velocity field
δ_x	Broadening width
η	surface overpotential

PREFACE

In the present world scenario, limited resources of fossil fuels with high demand are the major cause for researchers to develop environment friendly power generating devices. The fuel cell device produces energy without any toxic emissions to the environment. Microfluidic fuel cells (MFCs) are one of the most recently developed and investigated micro fuel cell device which has created interest among the researchers these days for further studies due to its possible potential uses in portable electrical and electronic devices. In MFC, the electrodes are fixed in a microchannel with a distance between electrodes of less than 1 mm without having any solid membrane electrolyte. The anode and cathode streams are maintained in laminar flow and with a low Reynolds number. Recently, a new type of microfluidic fuel cell was developed by Jayashree et al., (2005) known as air breathing microfluidic fuel cell consisting air breathing cathode. There are several advantages of using air breathing cathode in MFC e.g., cathode electrocatalysts sites get exposed to the higher concentration of oxygen via air breathing cathode in comparison to that of oxygen dissolved in aqueous solution due to low solubility of oxygen. Thus, in the present study Y-shaped and T-shaped air breathing microfluidic fuel cell was fabricated for experimental studies and validation of developed model equation through Response surface methodology (RSM). Glycerol fuel has comparable energy density to that of methanol and ethanol and it is a byproduct of biodiesel manufacturing via transesterification of vegetable oils and readily available. It is non-toxic, non-flammable, non-volatile and having high boiling point (290 ^{o}C). Thus, glycerol was selected as most promising fuel for the present study in a specially design MFC. The anode electrocatalyst of different metal compositions of Pd-Pt/C and Pd-Ni/C were synthesized to improve the electrooxidation kinetics and activity via a suitable reaction pathway which allows to split the C-C bond of glycerol at low activation energy. whereas, commercial Pt (40 wt.%)/C_{HSA} was used as cathode electrocatalyst.

The Y-shaped and T-shaped air breathing MFC were fabricated from perpex sheet (PMMA) using CNC milling machine. Pottasium hydroxide (KOH) was used as electrolyte. The acetylene black supported anode electrocatalyst was synthesized using $PdCl_2$, H_2PtCl_6. $6H_2O$ and $NiCl_2.6H_2O$ precursors by impregnation reduction method. The synthesized bimetallic anode electrocatalyst were Pd/C, Pd-Pt (16:4)/C, Pd-Pt (10:10)/C, Pd-Pt (4:16)/C, Pd-Ni (16:4)/C, Pd-Ni (10:10)/C and Pd-Ni (4:16)/C. The prepared electrocatalysts were analysed by X-ray Diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and transmission electron microscopy (TEM) for physcical characterization. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed for electrochemical characterizations of the synthesized anode electrocatalysts. The cathode electrocatalyst was commercial Pt (40 wt. %)/C_{HSA}. The Toray carbon paper (TGP-H-60) was used for electrode preparation. The ink was made by adding required quantity of electrocatalyst, isopropanol, Nafion® dispersion (D-520, 5 wt. %) and PTFE dispersion (60 wt. %). The prepared ink was painted with the help of paintbrush on carbon paper for anode and cathode preparation.

The experiment was performed using synthesized anode electrocatalysts for both type of MFC to obtain maximum cell performance. The electrode area was 0.6 cm^2 (3 cm × 0.2 cm) and 0.9 cm^2 (3 cm × 0.3 cm) for Y-shaped MFC and T-shaped MFC, respectively. Important cell parameters such as flow rate, glycerol concentration, electrolyte concentration, anode electrocatalyst type, anode electrocatalyst loading, cathode electrocatalyst loading, oxidant type and cell temperature were thouroughly and systematically studied in fabricated MFC. Further, the optimization study using response surface methodology in MFC was performed. The dimensionless numbers and cell efficiency were evaluated for both type of MFC. Finally the stability test were performed for both type of MFC using best anode electrocatalyst.

The performance of anode electrocatalyst Pd-Pt/C and Pd-Ni/C of different compositions were evaluated in both Y-shaped and T-shaped air breathing MFC. The synthesized electrocatalyst Pd-Pt (16:4)/C shows better performance than other ratios in half cell and single cell studies. Similarly, Pd-Ni (10:10)/C shows better performance than other ratios in half cell and single cell studies. However, Pd-Pt (16:4)/C exhibited better perfomance than the Pd-Ni (10:10)/C electrocatalyst in both type i.e., Y-shaped and T-shaped design, respectively. The Pd-Pt (16:4)/C in Y-shaped MFC at optimum cell conditions i.e., flow rate of anode and cathode streams of 1 ml/min, glycerol concentration 0.5 M, electrolyte/KOH concentration of 0.5 M at anode and 0.5 M at cathode, electrocatalyst loading at anode 2 mg/cm^2 and cathode 2 mg/cm^2, and cell temperature of 75 ^oC produced highest OCV of 0.93 V and maximum power density of 2.11 mW/cm^2 at a curent density of 5.14 mA/cm^2. The same electrocatalyst Pd-Pt (16:4)/C in T-shaped produced little lower OCV of 0.78 V and maximum power denisty of 4.03 mW/cm^2 at the optimum cell conditions i.e., flow rate of 1.2 ml/min at anode and 1 ml/min at cathode, glycerol concentration 1 M, electrolyte/KOH concentration of 1.5 M at anode and 0.5 M at cathode, electrocatalyst loading at anode 1 mg/cm^2 and cathode 1 mg/cm^2, and cell temperature of 75 ^oC.

The Pd-Ni (10:10)/C in Y-shaped MFC at optimum cell conditions i.e., flow rate of anode and cathode streams of 1 ml/min, glycerol concentration 0.5 M, electrolyte/KOH concentration of 0.5 M at anode and 0.5 M at cathode, electrocatalyst loading at anode 1.5 mg/cm^2 and cathode 1.5 mg/cm^2, and cell temperature of 75 ^oC produced highest OCV of 0.8 V and maximum power density of 1.6 mW/cm^2 at a curent density of 4.41 mA/cm^2. The same electrocatalyst Pd-Ni (10:10)/C in T-shaped produced little lower OCV of 0.51

V and maximum power denisty of 2.14 mW/cm^2 at the optimum cell conditions i.e., flow rate of 1.2 ml/min at anode and 1 ml/min at cathode, glycerol concentration 1 M, electrolyte/KOH concentration of 1 M at anode and 1 M at cathode, electrocatalyst loading at anode 1 mg/cm^2 and cathode 1 mg/cm^2, and cell temperature of 75 ^oC.

After, optimization of process parameters using RSM, the predicted maximum power density was 2.79 mW/cm^2 at the optimum condition and the actual/experimental power density obtained was 2.76 mW/cm^2. The RSM study indicates that cathode side KOH concentration has the least effect on cell performance. The stability test shows that the performance decreases with time due to poisoning of the electrode surface.

The subject matter contained in the thesis has been arranged in six different chapters. **Chapter I** is Introduction of thesis. Literature review and objectives are presented in **Chapter II**. **Chapter III** is Experimental which describes about material used and then experimental setups and methods. Process optimization by RSM is discussed in the **Chapter IV**. Results and Discussion are thoroughly represented in Chapter V. Finally, the conclusions of thesis is presented in **Chapter VI**.