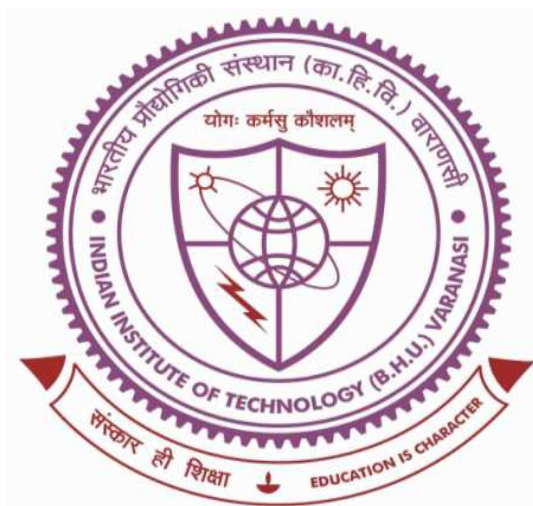


# **Development of Anode Electrocatalysts for Proton Exchange Membrane Based Direct Ethanol Fuel Cell**



**Thesis submitted in partial fulfillment**

**for the Award of Degree**

**Doctor of Philosophy**

**by**

**ABHAY KUMAR CHOUDHARY**

**DEPARTMENT OF CHEMICAL ENGINEERING & TECHNOLOGY**

**INDIAN INSTITUTE OF TECHNOLOGY**

**(BANARAS HINDU UNIVERSITY)**

**VARANASI-221005**

**Roll No: 15041001**

**2021**

---

## CHAPTER 6

### CONCLUSIONS

The difficulty of C-C bond cleavage of ethanol molecule for complete ethanol electrooxidation at low temperatures has inspired scientists to design a low-cost, highly-active, and selective anode electrocatalyst. The electrooxidation of ethanol occurs via both parallel and successive oxidation reaction mechanisms result partially oxidized products and strongly adsorbed poisoning species thereby reducing the fuel efficiency. A considerable effort has been made to establish the suitable anode electrocatalyst to split the C-C bond of ethanol molecule for complete oxidation to CO<sub>2</sub> successfully. However, still there is a lack of highly active and selective anode electrocatalysts that can initiate the complete electrooxidation of ethanol to CO<sub>2</sub> and H<sub>2</sub>O giving the highest number of electrons (12e<sup>-</sup>) per molecule with faster anode kinetics which limits their potential use in DEFC. Thus, in this study, carbon-supported Pt-based bi-metallic and tri-metallic electrocatalysts were successfully synthesized in the laboratory and characterized extensively. The synthesized electrocatalysts were also tested in a direct ethanol fuel cell using ethanol as fuel and pure oxygen or oxygen from air as oxidant. Various parameters were optimized to get maximum power density and current density.

#### 6.1 Direct ethanol fuel cell (DEFC) components and construction

The DEFC experiments were carried out using fabricated membrane electrode assemblies (MEAs) with an area of 6.25 cm<sup>2</sup> in the laboratory. The commercial Pt/C<sub>HISPEC</sub> (40 wt. %) electrocatalyst was used as cathodic electrocatalyst, while the corresponding laboratory synthesized Pt-Ru/C<sub>PAB</sub>-PLM, Pt-Ru/C<sub>PAB</sub>-FAM, Pt-Ru/C<sub>AB</sub>-PLM, Pt-Ru/C<sub>AB</sub>-FAM, Pt-

Ru/C<sub>AB</sub>-syn, Pt-Ru/C<sub>AB</sub>-H<sub>2</sub>-RT, Pt-Ru/C<sub>AB</sub>-H<sub>2</sub>-160, Pt-Ru/C<sub>AB</sub>-Air-160, Pt-Ru (1:1)/f-MWCNT, Pt-Re (1:1)/f-MWCNT, Pt-Ru-Re (1:1:1)/f-MWCNT, Pt-Ru-Re (1:1:0.5)/f-MWCNT, Pt-Ru-Re (1:1:0.25)/f-MWCNT and commercial Pt-Ru/C (30 %: 15 % by wt.) were assigned as anodic electrocatalysts, respectively. The electrodes were fabricated using the electrocatalyst ink made by ultrasonically mixing the required amount of electrocatalyst power in a mixture of acetylene black carbon, isopropyl alcohol, Nafion<sup>®</sup> ionomer, and PTFE dispersion to form uniform ink. The Nafion<sup>®</sup> ionomer and as proton conductor and PTFE dispersion function as binders and assist in the creation of pores and channels. The ink was coated onto the porous carbon paper/GDL of area 6.25 cm<sup>2</sup> using a thin brush. The coated electrodes were sintered at a high temperature. For fabricating MEA, the commercial Nafion<sup>®</sup> 117 membranes were used as a solid electrolyte. The membrane electrode assembly (MEA) was fabricated by holding the commercial Nafion<sup>®</sup> 117 membrane/electrolyte in between the sintered anode and the cathode, followed by clamping the assembly together. The assembled MEAs were then placed between graphite plates with serpentine flow channels for the reactant flow. The single cell DEFC tests were evaluated with constant feeding of an aqueous solution of ethanol fuel to the anode using a peristaltic pump (Electrolab, India), while the cathode was delivered with the humidified oxygen (80 % relative humidity).

## 6.2 Physical characterization of support and electrocatalyst

It is reported in the literature that chemical oxidation/functionalization of the supporting materials significantly affects the electrochemical activity of the electrocatalyst towards ethanol electrooxidation. Thus, first of all, support materials such as pristine acetylene black (C<sub>PAB</sub>) and pristine MWCNTs (P-MWCNT) were subjected to acid treatment to generate oxygenated surface functional groups. The FTIR analysis showed that after

chemical oxidation of carbon support i.e.,  $C_{PAB}$  and p-MWCNT materials, sufficient oxygenated functional groups were created on the surface. The obtained functionalized acetylene black carbon ( $C_{AB}$ ) and functionalized multi-walled carbon nanotubes (f-MWCNT) were used as support material for the synthesis of highly dispersed electrocatalysts. The oxygenated surface functional groups created after chemical oxidation of carbon supports has been documented to be advantageous for improved metal dispersion and anchoring of the electrocatalytic active phase to the carbon surface. Besides, the oxygenated surface functional groups also improve the hydrophilic character of carbon support and facilitate the diffusion of reagents to active sites.

The acetylene black carbon supported Pt-based bi-metallic anode electrocatalysts were successfully synthesized with nominal metal loading of 40 wt. % on carbon support ( $C_{AB}$  or  $C_{PAB}$ ) of 60 wt. % using two different methods i.e., the polyol reduction method (PLM) and the formic acid reduction method (FAM) for application in DEFC. The electrocatalysts were designated as Pt-Ru/ $C_{AB}$ -PLM for polyol reduction and Pt-Ru/ $C_{AB}$ -FAM for formic acid reduction method, respectively.

In another attempt, highly dispersed Pt-Ru nano electrocatalysts supported on functionalized acetylene black carbon ( $C_{AB}$ ) were synthesized by a modified polyol reduction route followed by post-treatment under three different conditions. The synthesized Pt-Ru/ $C_{AB}$ -syn electrocatalysts after post-treatment were designated as Pt-Ru/ $C_{AB}$ -H<sub>2</sub>-RT when treated under H<sub>2</sub> atmosphere at room temperature of 40 °C, and Pt-Ru/ $C_{AB}$ -H<sub>2</sub>-160 when treated under H<sub>2</sub> atmosphere at 160 °C and Pt-Ru/ $C_{AB}$ -Air-160 when treated under air at 160 °C, respectively.

Finally, bi-metallic Pt-Ru, Pt-Re and tri-metallic Pt-Ru-Re nano electrocatalysts supported on f-MWCNTs with fixed metal loading of 40 wt. % on f-MWCNT support of 60 wt. % were synthesized using the modified polyol reduction method (PLM). The obtained electrocatalysts were designated as Pt-Ru (1:1)/f-MWCNT, Pt-Re (1:1)/f-MWCNT, Pt-Ru-Re (1:1:1)/f-MWCNT, Pt-Ru-Re (1:1:0.5)/f-MWCNT, and Pt-Ru-Re (1:1:0.25)/f-MWCNT.

The size of metal nanoparticles and their distribution over the support material are strongly influenced by the nature of support material and synthesis method used to prepare the electrocatalysts in the fuel cells. The average crystallite size obtained for the synthesized electrocatalysts supported on pristine acetylene black ( $C_{PAB}$ ), i.e., Pt-Ru/ $C_{PAB}$ -PLM and Pt-Ru/ $C_{PAB}$ -FAM is larger than that of the functionalized acetylene black ( $C_{AB}$ ) supported electrocatalysts Pt-Ru/ $C_{AB}$ -PLM and Pt-Ru/ $C_{AB}$ -FAM, respectively. The size of Pt-Ru alloy electrocatalysts nanoparticles supported on  $C_{AB}$  resulted in smaller particle size and thus, the high surface area of synthesized electrocatalysts Pt-Ru/ $C_{AB}$ -PLM ( $22.26 \text{ m}^2/\text{g}$ ) and Pt-Ru/ $C_{AB}$ -FAM ( $24.31 \text{ m}^2/\text{g}$ ) were observed. Although the average crystallite size is a little larger for PtRu/ $C_{AB}$ -PLM (3.6 nm) than electrocatalyst Pt-Ru/ $C_{AB}$ -FAM (3.4 nm), the polyol method (Pt-Ru/ $C_{AB}$ -PLM) results in higher Ru alloying of 37.0 wt. % with Pt noble metal.

The post-treated electrocatalyst under  $H_2$  flow at room temperature (Pt-Ru/ $C_{AB}$ - $H_2$ -RT) showed the improved surface morphology with the highest alloying degree of about 40.84 % Ru with Pt noble metal. The XRD analysis verified the typical fcc Pt crystalline structure and the formation of Pt-Ru alloy for carbon-supported Pt-Ru bi-metallic nano electrocatalysts. The modified surface composition and microstructures of the Pt-Ru/ $C_{AB}$ - $H_2$ -RT electrocatalyst can be attributed to interconnection and the phase separation of

metal nanoparticles such as Pt and Ru under H<sub>2</sub> flow at room temperature. The TEM and SEM analysis of electrocatalyst indicate that the metal nanoparticles are homogeneously dispersed with a size range of 1.5 nm to 6 nm on the surface of functionalized carbon nano support for the Pt-Ru/C<sub>AB</sub>-H<sub>2</sub>-RT electrocatalyst and were very similar to commercial Pt-Ru/C (1.5-5.5 nm) electrocatalyst.

Similarly, the characterization of the functionalized MWCNT supported bi-metallic and tri-metallic electrocatalysts showed that tri-metallic Pt-Ru-Re (1:1:0.5)/f-MWCNT is better than all the other synthesized electrocatalysts in terms of crystallite size, particle size and dispersion. The TEM analysis reveal that the electrocatalyst nanoparticles were well dispersed on the surface of f-MWCNT, with spherical shapes and small average particle sizes (2.68-3.53 nm). The XRD analysis and FE-SEM element mapping showed the formation of a homogeneous alloy structure of Pt, Ru, and Re in tri-metallic Pt-Ru-Re (1:1:0.5)/f-MWCNT electrocatalyst with an average crystallite size of 2.11 nm. The presence of dispersed Pt, Ru, Re, O and C are observed by SEM-EDX analysis, which corresponds to synthesized metal species and C as support, respectively. It was noted the desired elemental composition obtained from EDX analysis was nearly in good agreement with the nominal ones for all the electrocatalysts. Very minute discrepancies in actual metal loading of electrocatalysts with the nominal weight were noted, which could be associated with the metal losses during the separation and purification process.

### 6.3 Electrode characterization

Electrocatalytic properties of the fabricated anodes using synthesized electrocatalysts were thoroughly studied using electrochemical methods including cyclic voltammetry (CV) and chronoamperometry (CA) tests. The cyclic voltammetry (CV) and

chronoamperometry (CA) analyses of synthesized electrocatalysts for ethanol electrooxidation in a half cell were further substantiated with the single cell DEFC experiments with similar conditions. The cyclic voltammograms (CVs) analysis of all the electrocatalysts showed two well-defined electrooxidation peaks for ethanol fuel in the forward and backward scans. The prominent electrooxidation peak during the forward scan is attributed to the electrooxidation of freshly chemisorbed ethanol species, while the electrooxidation peaks at the backward scan were related to the further oxidation of adsorbed carbonaceous species.

In the CV study, the ethanol electrooxidation activity of anode electrocatalysts increased in the following order: Pt-Ru/C<sub>PAB</sub>-FAM < Pt-Ru/C<sub>AB</sub>-FAM < commercial Pt-Ru/C < Pt-Ru/C<sub>PAB</sub>-PLM < Pt-Ru/C<sub>AB</sub>-PLM based on their peak current densities. The CV and CA tests showed that the electrocatalytic activity of the synthesized PtRu/C<sub>AB</sub>-PLM for ethanol electrooxidation was superior to that of PtRu/C<sub>AB</sub>-FAM and commercial Pt-Ru/C electrocatalysts, which could be attributed to the positive effect of functionalized acetylene black (C<sub>AB</sub>) as support having high electrical conductivity and large pore volume.

The electrochemical tests of all the post treated electrocatalysts revealed that well alloyed synthesized PtRu/C<sub>AB</sub>-H<sub>2</sub>-RT had greater electrocatalytic activity and stability for ethanol electrooxidation than the low alloyed synthesized PtRu/C<sub>AB</sub>-Air-160, Pt-Ru/C<sub>AB</sub>-H<sub>2</sub>-160 electrocatalyst by the modified polyol reduction method.

The electrochemical test results demonstrated that tri-metallic Pt-Ru-Re (1:1:0.5)/f-MWCNT had higher electrocatalytic activity and stability towards ethanol electrooxidation than that of bi-metallic Pt-Ru (1:1)/f-MWCNT and Pt-Re (1:1)/f-

MWCNT and trimetallic Pt-Ru-Re (1:1:1)/f-MWCNT and Pt-Ru-Re (1:1:0.25)/f-MWCNT electrocatalysts. The Pt-Ru-Re (1:1:0.5)/f-MWCNT had the highest ECSA of  $150.77 \text{ m}^2/\text{g}$ , which could be attributed to the smaller size of electrocatalyst nanoparticle size and better distribution of nanoparticles on the f-MWCNT surface and results in the best activity of Pt-Ru-Re (1:1:0.5)/f-MWCNT electrocatalyst in the half cell and single cell DEFC tests for ethanol fuel.

#### 6.4 Performance of DEFC

The direct ethanol fuel cell fabricated with the all mentioned anode and cathode electrocatalysts using ethanol as fuel were tested and polarization and power density characteristic curves were generated by varying experimental parameters such as electrocatalyst type at the anode and cathode side, ethanol concentration, electrocatalyst loading at the anode side and operating cell temperature.

The cell performance increases initially with the increase in fuel ethanol concentration but it does not increase proportionally with the further increase in fuel concentration. The optimum concentration of 2 M was observed for the maximum power density of the fuel cell. The performance of the direct ethanol fuel cell increases with the increase in anode electrocatalyst loading from  $0.5 \text{ mg}/\text{cm}^2$  to  $1 \text{ mg}/\text{cm}^2$  of fuel ethanol used at the anode. However, beyond the electrocatalyst loading of  $1 \text{ mg}/\text{cm}^2$ , the cell performance starts decreasing. The cell performance of the single cell DEFC also increases with the temperature for fuel ethanol because of the improved reaction kinetics, reduced cell overpotentials mainly activation and ohmic losses at high temperatures.

In a single cell DEFC experiments, using synthesized Pt-Ru/C<sub>AB</sub>-PLM electrocatalyst as the anode, the maximum OCV of 0.71 V and power density of  $6.02 \text{ mW}/\text{cm}^2$  at a current



density of  $19.52 \text{ mA/cm}^2$  were achieved at room temperature of  $35 \text{ }^\circ\text{C}$  for fuel ethanol concentration of  $1 \text{ M}$ . Whereas, the maximum OCV of  $0.717$  and the maximum power density of  $5.13 \text{ mW/cm}^2$  at a current density of  $18.70 \text{ mA/cm}^2$  were generated using the commercial Pt-Ru/C electrocatalyst as an anode under the same conditions. The peak power density of Pt-Ru/ $C_{AB}$ -PLM ( $6.02 \text{ mW/cm}^2$ ) electrocatalyst was superior to that of Pt-Ru/ $C_{PAB}$ -PLM ( $5.47 \text{ mW/cm}^2$ ), Pt-Ru/ $C_{PAB}$ -FAM ( $3.85 \text{ mW/cm}^2$ ), Pt-Ru/ $C_{AB}$ -FAM ( $4.54 \text{ mW/cm}^2$ ) and commercial Pt-Ru/C ( $5.13 \text{ mW/cm}^2$ ) electrocatalysts. Moreover, it was also noted that electrocatalysts supported on functionalized carbon support ( $C_{AB}$ ) resulted in improved cell performance compared to pristine carbon support ( $C_{PAB}$ ) when following the same synthesis process. The presence of oxygenated surface groups at functionalized carbon  $C_{AB}$  results in improved ethanol electrooxidation kinetics and favors the diffusion of reactants at a higher rate to the active sites. It is observed that the performance of DEFC using Pt-Ru/ $C_{AB}$ -PLM as anode increases with the increase in ethanol concentration of up to  $2 \text{ M}$  at a temperature of  $35 \text{ }^\circ\text{C}$ . The optimum concentration of DEFC using Pt-Ru/ $C_{AB}$ -PLM as an anode was  $2 \text{ M}$ , with a maximum OCV of  $0.712 \text{ V}$  and a maximum power density of  $8.28 \text{ mW/cm}^2$  at a current density of  $27.36 \text{ mA/cm}^2$  achieved from the single cell. Moreover, the maximum power density of the cell was further increased from  $8.28 \text{ mW/cm}^2$  at  $35 \text{ }^\circ\text{C}$  to  $15.12 \text{ mW/cm}^2$  at  $80 \text{ }^\circ\text{C}$ , i.e. approximately 1.83 times higher when Pt-Ru/ $C_{AB}$ -PLM was used as an anode and  $2 \text{ M}$  ethanol as anode feed.

Similarly, when the most active post-treated Pt-Ru/ $C_{AB}$ -H<sub>2</sub>-RT was used as anode electrocatalyst for the operation of DEFC, OCV of  $0.718 \text{ V}$  and maximum power density of  $9.15 \text{ mW/cm}^2$  were obtained, and these results are better than that of Pt-Ru/ $C_{AB}$ -syn ( $0.658 \text{ V}$ ,  $4.97 \text{ mW/cm}^2$ ), Pt-Ru/ $C_{AB}$ -Air-160 ( $0.68 \text{ V}$ ,  $5.79 \text{ mW/cm}^2$ ), Pt-Ru/ $C_{AB}$ -H<sub>2</sub>-160

(0.712 V, 6.84 mW/cm<sup>2</sup>) and commercial Pt-Ru/C (0.72 V, 7.86 mW/cm<sup>2</sup>) electrocatalysts at a temperature of 40 °C with same anode loading of 1 mg/cm<sup>2</sup> and 2 M ethanol fuel. The improved performance of post treated Pt-Ru/C<sub>AB</sub>-H<sub>2</sub>-RT electrocatalyst could be ascribed to mild post treatment in acidic atmosphere which results improved surface morphology with higher alloying degree of Ru, negligible agglomeration of metal nanoparticles and homogeneously dispersed on the surface functionalized carbon C<sub>AB</sub> support. The single cell performance of Pt-Ru/C<sub>AB</sub>-syn was lowest of all post treated electrocatalysts due to lower crystallinity and alloying degree of Ru. The Pt-Ru/C<sub>AB</sub>-syn showed the lowest performance of all post-treated electrocatalysts due to lower crystallinity and Ru atomic fraction ( $x_{Ru}$ ). The single cell DEFC adopting Pt-Ru/C<sub>AB</sub>-H<sub>2</sub>-RT as anode electrocatalyst yielded the maximum OCV of 0.737 V and peak power density of 16.23 mW/cm<sup>2</sup> at a cell temperature of 80 °C. It should be noted that the performance of post treated electrocatalyst Pt-Ru/C<sub>AB</sub>-H<sub>2</sub>-RT is better than the polyol synthesized electrocatalyst Pt-Ru/C<sub>AB</sub> without any post treatment.

The tri-metallic Pt-Ru-Re (1:1:0.5)/f-MWCNT as anode electrocatalyst exhibited the highest electrocatalytic performance in terms of power density than the bi-metallic Pt-Ru (1:1)/f-MWCNT and Pt-Re (1:1)/f-MWCNT and tri-metallic Pt-Ru-Re (1:1:1)/f-MWCNT and Pt-Ru-Re (1:1:0.25)/f-MWCNT electrocatalysts. Even the maximum power density produced by the best tri-metallic electrocatalyst Pt-Ru-Re (1:1:0.5)/f-MWCNT was higher than the all synthesized acetylene black (C<sub>AB</sub>) bi-metallic Pt-Ru/C<sub>AB</sub>-PLM (best electrocatalyst, without post treatment), Pt-Ru/C<sub>AB</sub>-H<sub>2</sub>-RT (best electrocatalyst, post treatment), functionalized MWCNT bi-metallic Pt-Ru (1:1)/f-MWCNT, Pt-Re (1:1)/f-MWCNT and tri-metallic Pt-Ru-Re (1:1:1)/f-MWCNT and Pt-Ru-Re (1:1:0.25)/f-MWCNT electrocatalysts. The highest peak power density of 9.52 mW/cm<sup>2</sup> was obtained

for Pt-Ru-Re (1:1:0.5)/f-MWCNT at a temperature of 30 °C. Whereas, at the same operating temperature of 30 °C, bi-metallic Pt-Re (1:1)/f-MWCNT and Pt-Ru (1:1)/f-MWCNT resulted in a lower power density of 4.74 mW/cm<sup>2</sup> and 7.48 mW/cm<sup>2</sup>, respectively. The peak power density of the cell increased significantly from 9.52 mW/cm<sup>2</sup> to 23.2 mW/cm<sup>2</sup> i.e., 2.44 times higher when cell temperature was raised from 30 °C to 80 °C for Pt-Ru-Re (1:1:0.5)/f-MWCNT as anode electrocatalyst. The high cell performance delivered by the tri-metallic Pt-Ru-Re (1:1:0.5)/f-MWCNT electrocatalyst towards ethanol electrooxidation, advocates it as a promising advanced electrocatalyst with excellent activity and durability for the application in DEFC.

The experimental results demonstrate that the developed electrocatalyst Pt-Ru-Re (1:1:0.5)/f-MWCNT has the potential to be used as commercial electrocatalysts which might be available at low cost and recommended for moderate temperature DEFC application as it is giving higher power density among all the synthesized commercial electrocatalysts. The results of cyclic voltammetry (CV) and chronoamperometry (CA) measurements substantiate the experimental data of a single direct ethanol fuel cell.

### **6.5 Process parameters optimization using response surface methodology (RSM)**

The response surface methodology (RSM) based on the Box-Behnken design (BBD) technique was successfully applied to optimize the effect of three key independent parameters i.e., ethanol concentration (A), anode electrocatalyst loading (B), and cell temperature (C) on the maximum power density as a response (Y) of a DEFC. A series of various runs were executed at varied ethanol concentrations (1-3 M), anode electrocatalyst loading (0.5-1.5 mg/cm<sup>2</sup>), and operating cell temperature (40-80 °C) according to the Box-Behnken design (BBD). The Nafion<sup>®</sup> 117 membrane as solid

electrolyte and synthesized Pt-Ru-Re (1:1:0.5)/f-MWCNT as anode and commercial Pt/C<sub>HISPEC</sub> (40 % wt.) as cathode electrocatalysts were used, respectively. A quadratic model was developed to simulate the power density with regard to the input data obtained experimentally using RSM and ANOVA tests. The fitted quadratic model is statistically significant as implied by the F-value (177.4) and p-value (< 0.0001) of the model. The developed quadratic model equation could be used for the power density (response function) prediction based on input parameters. The ANOVA results reveal that the linear, square and interaction coefficients of all the parameters are statistically significant, except for the interaction of ethanol concentration and anode electrocatalyst loading. It was noted from ANOVA analysis that the effect of cell temperature on the power density was significant, while the effect of anode electrocatalyst loading and ethanol concentration were minimal. The increase in cell temperature leads to a significantly increase in electrode reaction kinetics and proton conductivity of Nafion<sup>®</sup> membrane and subsequently improves the cell performance. From RSM analysis, the optimum values of ethanol concentration, anode electrocatalyst loading and cell operating temperature were obtained as 2.03 M, 1.14 mg/cm<sup>2</sup> and 79.48 °C, respectively. The predicted response value i.e., maximum power density (22.10 mW/cm<sup>2</sup>) under optimum conditions from the quadratic model was in good agreement to the experimental value (21.53 mW/cm<sup>2</sup>) with 2.58 % deviation from the predicted value and the R<sup>2</sup> of the model was 0.9956. Overall, it can be concluded that optimizing the operating conditions of DEFC favors two aspects (i) achieving optimum performance of DEFC and (ii) it enables the DEFC to operate in high-efficiency mode to achieve greener and cleaner electricity output.

## 6.6 Future scope

The performance of direct ethanol fuel cell using synthesized anode electrocatalyst shows that it hold a promising future for applications in portable electronic and electrical vehicles. The other considerable advantages are simplicity, low operation temperatures, high energy conversion efficiency, and renewable in nature. The developed DEFC using the synthesized best tri-metallic electrocatalyst i.e., Pt-Ru-Re(1:1:0.5)/f-MWCNT working under optimized conditions could be used as roadmap for further improvement and development of direct ethanol fuel cell (DEFC) in terms of higher current density and power density.

However, several critical issues need to be resolved for the successful commercialization of DEFC. The costs of DEFC are determined by the materials cost associated to fabricate the cells like electrocatalyst and electrolyte mainly. Till now, platinum (Pt) based metal alloy electrocatalysts are recommended and extensively used for ethanol electrooxidation. However, the limited supply of noble metal Pt in nature and extensive use of costly metal Pt are making this technology difficult to reach the common people for their use as a power source. As various studies shows that the anodic electrode, the pure Pt electrocatalysts are highly susceptible to poisoning by adsorbed intermediates such as  $\text{CO}_{\text{ad}}$  and  $\text{CH}_{\text{x,ad}}$  generated during the ethanol electrooxidation process. Additional factors that impede the development of DEFC include slow reaction kinetics, a complex reaction mechanism, and an ethanol crossover from the anode to the cathode. In this context, the urgent matter to address is to develop advanced, cost-effective, durable, and catalytically active or even non-precious metal anode electrocatalysts for ethanol electrooxidation that could contribute to lowering the cost and improve the catalytic activity and durability. So far, tremendous research efforts have been concentrated to reduce the above problems by

alloying Pt with 3d transition metal such as Ru, Sn, Rh, Ce, Ir, Ni, Mo, or W to form Pt-based bi-metallic and tri-metallic electrocatalysts with improved electrocatalytic activity due to their better capability of modulating structure, geometric as well as electronic effects. On the other hand, effective multi-metallic electrocatalysts should have the ability to activate the C-C bond cleavage of the ethanol molecule to achieve complete oxidation product (CO<sub>2</sub>) at a low overpotential at low temperatures and lower loading of electrocatalysts. The carbon-supported Pt-based bi-metallic and tri-metallic electrocatalysts developed in this work exhibit well under low operating temperature conditions. Thus the future work could focus on developing highly active pluri-metallic electrocatalysts with low Pt content supported on novel support materials for ethanol electrooxidation at high operating temperatures. Single cell performance study of pluri-metallic electrocatalysts as anode materials for other aliphatic alcohols and mixtures of alcohol could be studied in the future research work. To operate the DEFC at high temperature, the polymer membrane electrolyte like Nafion<sup>®</sup> must be modified, so that the membrane conducting for ion transport does not damage at high temperature due to membrane degradation. Thus, the membrane synthesis and modification of the present membrane electrolyte also could be taken as a future work. Although single cell DEFC shows promising results, the stack development using optimized conditions obtained from the single cell study and testing is required to obtain useful and workable voltage and current, making the direct ethanol fuel cell commercially viable.