

## PREFACE

Global demand for energy consumption is growing dramatically day by day due to the exponential growth of the population, human development of modern society and industrialization. So far, fossil fuel reserves have met the world's current major energy requirements, which are limited in supply and rapidly depleting. Furthermore, the production and use of fossil fuels release a significant amount of contaminants e.g., CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>, dust, soot and smoke into our atmosphere, which raises serious environmental concerns such as environmental pollution and global warming which adversely affect human health. A growing awareness of the environmental crisis is driving world scientists and researchers to develop an interest in alternative energy sources that are cost-effective with fossil fuels, as well as cleaner, sustainable, renewable and environmentally friendly. The direct ethanol fuel cells (DEFC) is considered to be one of the most promising technologies for powering portable electronic devices and stationary equipment due to its low emission levels, high efficiency, simplicity, the convenience of storage and handling, and high energy density of liquid ethanol.

However, the critical issues in DEFC are the major problems like breaking the C-C bond of the ethanol molecule and slow reaction kinetics at low temperatures using current Pt-based electrocatalysts. Moreover, the surface of Pt active sites gets poisoned quickly by strongly adsorbed intermediate species e.g., CH<sub>x</sub> and CO generated during the dissociative adsorption of ethanol. Hence, tremendous efforts have been made to develop advanced electrocatalysts and support materials with high electrocatalytic activity for ethanol electrooxidation and durability. To address these issues, coupling Pt with other less expensive metals such as Ru, Sn, Pd, W or Rh to form bi-metallic electrocatalysts has been extensively investigated for ethanol electrooxidation.

The appropriate electrocatalyst for ethanol electrooxidation is still in the developing stage. Thus, it is difficult to suggest the most suitable electrocatalyst which could split the C-C bond of ethanol molecule. This C-C bond reduces the probability of molecule to cross energy hills thereby lowering the anode kinetics. Although, many efforts have been given to synthesize suitable electrocatalyst for ethanol electrooxidation, in most of the studies the single cell DEFC performance is not optimistic. It is also seen from literature that almost no work on Pt-based bi-metallic and tri-metallic electrocatalysts supported on functionalized black acetylene ( $C_{AB}$ ) and functionalized multi-walled carbon nanotubes (f-MWCNTs) have been found in the open literature for DEFC applications. No detailed studies on direct ethanol fuel cell (DEFC) in acidic medium have been performed using tri-metallic Pt-Ru-Re/f-MWCNT electrocatalysts of different metal combinations as anode. Thus, in the present study development of highly efficient carbon supported Pt-based anode electrocatalysts has been considered for ethanol electrooxidation. It is evident that electrocatalyst is most active and key component of any fuel cell, thus special emphasis was given in the present work to synthesize different types of Pt-based bi-metallic and tri-metallic electrocatalysts supported on functionalized acetylene black carbon ( $C_{AB}$ ) or functionalized multi-walled carbon nanotubes (f-MWCNT) via adopting the two different synthesis routes such as the polyol reduction method (PLM) and the formic acid reduction method (FAM). The physicochemical properties of synthesized electrocatalysts were evaluated using the X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) analyses.

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The laboratory synthesized different carbon supported Pt-based bi-metallic and tri-metallic electrocatalysts were assigned as anodic electrocatalysts, while the commercial Pt/C<sub>HISPEC</sub> (40 % wt.) electrocatalyst was used as cathodic electrocatalyst. To fabricate the electrodes, the electrocatalyst ink was made by ultrasonically mixing the required amount of electrocatalyst powder in a mixture of acetylene black carbon, isopropyl alcohol, Nafion<sup>®</sup> ionomer, and PTFE dispersion to form uniform ink. Nafion<sup>®</sup> ionomer and PTFE 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. The electrocatalytic activities of the electrodes were evaluated by cyclic voltammetry (CV) and chronoamperometry (CA) techniques using a three electrode cell assembly at room temperature.

The post-treated bi-metallic electrocatalyst Pt-Ru/C<sub>AB</sub>-H<sub>2</sub>-RT under H<sub>2</sub> flow at room temperature electrocatalyst showed the improved surface morphology with the highest alloying degree of about 40.84 % Ru with Pt noble metal than that of without post treated bi-metallic Pt-Ru/C<sub>AB</sub>-PLM. The TEM and SEM analysis of electrocatalyst indicate that the metal nanoparticles are homogeneously dispersed with a size range of 1.5-6 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.

Tri-metallic electrocatalyst by addition of Re to Pt-Ru/C showed improved electrocatalytic activity in half cell and single DEFC. The synthesized tri-metallic Pt-Ru-Re (1:1:0.5)/f-MWCNT showed excellent electrocatalytic activity for ethanol electrooxidation among all synthesized bi-metallic and tri-metallic electrocatalysts. The TEM analyses of tri-metallic Pt-Ru-Re (1:1:0.5)/f-MWCNT reveals that the electrocatalyst nanoparticles were well dispersed on the surface of f-MWCNT, with

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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. It was noted the desired elements composition obtained from EDX analysis was nearly in good agreement with the nominal ones for all the electrocatalysts.

The performances of synthesized electrocatalysts as anode in single cell DEFC were evaluated using ethanol as fuel. The commercial Nafion<sup>®</sup> 117 membranes were used as solid electrolyte for MEA fabrication. 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 mW/cm<sup>2</sup> at a current density of 19.52 mA/cm<sup>2</sup> were achieved at room temperature of 35 °C for fuel ethanol concentration of 1 M. Whereas, the maximum OCV of 0.717 and the maximum power density of 5.13 mW/cm<sup>2</sup> at a current density of 18.70 mA/cm<sup>2</sup> were generated using the commercial Pt-Ru/C electrocatalyst as an anode under the same conditions. The peak power density of Pt-Ru/C<sub>AB</sub>-PLM (6.02 mW/cm<sup>2</sup>) electrocatalyst was superior to that of Pt-Ru/C<sub>PAB</sub>-PLM (5.47 mW/cm<sup>2</sup>), Pt-Ru/C<sub>PAB</sub>-FAM (3.85 mW/cm<sup>2</sup>), Pt-Ru/C<sub>AB</sub>-FAM (4.54 mW/cm<sup>2</sup>) and commercial Pt-Ru/C (5.13 mW/cm<sup>2</sup>) electrocatalysts. Moreover, it was also noted that electrocatalysts supported on functionalized carbon support (C<sub>AB</sub>) resulted in improved cell performance compared to pristine carbon support (C<sub>PAB</sub>) when adopted the same synthesis process.

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

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(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 room temperature of 40 °C with same anode loading of 1 mg/cm<sup>2</sup> and 2 M ethanol fuel. 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.

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. 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 room 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 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 results obtained are discussed and presented in this thesis. For ease of understanding to the readers, the subject matter contained in the thesis has been broadly divided into six different chapters.

**Chapter 1** provides a general introduction to the energy scenario, the basic concept of the fuel cell, ethanol as fuel along with its advantages over methanol, anode electrocatalysts, supporting materials and electrocatalyst synthesis methods. **Chapter 2** describes the literature on important DEFC components like electrocatalyst materials, electrocatalyst

characterizations and membrane electrolytes. In particular, the progress made in the development of anode electrocatalyst materials for ethanol electrooxidation has been addressed extensively. It includes the summary of single cell DEFC performances using various anode electrocatalysts along with the investigated operating parameters of the process. At the end of this chapter, the scope of further study on the basis of the literature review and specific objectives of the present work are presented. **Chapter 3** explains the materials used in the experiment and the experimental specifics related to the formulation of anode electrocatalysts such as the functionalization of supporting materials, the synthesis of supported nano-electrocatalysts, fabrication of working electrodes cyclic voltammetry and chronoamperometry for electrochemical measurements, the manufacture of anode, cathode and membrane electrode assembly, the fabrication of single cell set-up to evaluate the DEFC cell performance. **Chapter 4** elaborates the descriptions of the surface response methodology technique that was also used to optimize the DEFC process parameters and validated with experimental data for the same process parameter actual DEFC set-up. **Chapter 5** presents the findings and discussions on physicochemical characterization of synthesized electrocatalysts, surface morphology, crystal structure, particle size and dispersion of the metal nano-particles on the supporting materials. The electrochemical characterization of synthesized electrocatalysts using cyclic voltammetry and chronoamperometry is also discussed. The experimental results of a manufactured single cell using a synthesized electrocatalyst as an anode material are also discussed in detail. Finally, **Chapter 6** summarizes the main findings and discussions of the present work, as well as some significant suggestions for further work in this field. At the end of the thesis, the future scope of research work, the appendices and the references are given.