CHAPTER 2

LITERATURE REVIEW AND OBJECTIVES

2.1 Literature review

The overall performance of single direct ethanol fuel cell (DEFC) or stack of DEFC on the individual performance of each components fuel cell like electrocatalysts of anode and cathode, membrane and current collectors or flow field. Thus, selection of most suitable components for cell fabrication is very much essential to achieve highest cell performance in terms of cell voltage, current density and power density. As already mentioned in the introduction (Page no. 2) the DEFC is in the developing stage, the materials or cell components which are commercially available in the open market do not perform so well. In this perspective the main work of thesis focuses on the synthesis of anode electrocatalyst materials for proton exchange membrane (PEM) based DEFC. In the following section, important DEFC components like electrocatalyst materials, electrocatalyst characterizations, membrane electrolytes and their performance in direct ethanol fuel cell are addressed using different sections and subsections. The objectives of this thesis are finalized based on the literature review.

2.1.1 Major components of direct ethanol fuel cell (DEFC)

As literature suggests that the important components of any DEFC are electrode materials i.e., electrocatalyst at anode and cathode, polymer membrane electrolyte and current collectors. The most active and key component of any fuel cell is electrocatalyst which helps to split the fuel molecule at anode electrode and thereby producing electrons (e^-) which gives electrical current. The cathode electrocatalyst helps to reacting electrons (e^-)

with oxidant via reduction reaction. The membrane electrolyte also play important role for the transport of ions which assist in completion of fulfill electrode reactions.

2.1.1.1 Polymeric membrane electrolyte

As mentioned earlier, the membrane electrolyte is considered as one of the core component of the DEFC. The essential functions of the polymeric membrane in the fuel cells are as follows: to distinguish the electrochemical reaction at the anode from that at the cathode, the free movement of the ion carriers i.e., protons (H^+) or hydroxyl anions (OH^-), acts as separator to avoid direct interaction between the liquid alcohol fuel and the oxidant, for functioning as the electronic insulator to force electrons through the external circuit to the cathode instead of passing electrons across membranes due to the electron-repelling properties of SO_3^- and the oriented structural framework to assist electrocatalysts in the case of catalyst-coated membrane (CCM) (Peighambardoust et al., 2010, Zhang and Shen, 2012 and Zakaria et al., 2016). The primary requirements of membrane electrolyte for use in DEFC are as follows: excellent proton or ionic conductivity generally $\geq 100 \times 10^{-3}$ S cm^{-1} to facilitate a large current density with minimal resistive losses, low fuel/oxidant permeability and isolation of electrons. In addition, the polymer membrane electrolyte should have excellent chemical and thermal stability, outstanding mechanical strength in both dry and hydrated states, suppressed water flow by diffusion and electroosmosis, adequate water uptake and moderate swelling, low cost production and good availability (Peighambardoust et al., 2010, Peron et al., 2010 and Zakaria et al., 2016). Generally, membranes for DEFC are made of organic polymers with acidic functionality e.g., sulfonic, carboxylic and phosphonic acid groups. These ionic polymer electrolytes contain gel-like polymeric structures that have been severely swollen under complete hydration and have fixed negative charges which

facilitate movement of positive charges across the membrane. The proton conduction properties of the membranes are closely related to the presence of conductive electrolytes and are highly dependent on their water content, which restricts their operating temperature (Peighambardoust et al., 2010, Di Noto et al., 2012 and Teixeira et al., 2019). To date, different types of membranes have been developed and tested to be used as solid proton exchange membrane in DEFC at low temperature. Currently, perfluorosulfonic acid ionomer membrane like Nafion® membrane, registered trademark of DuPont, USA is the most widely used PEM due to its excellent chemical and electrochemical stability and mechanical properties with outstanding proton conductivity at moderate temperature (0.10 S cm^{-1}). The Nafion® is a sulfonated perfluorinated copolymer that consists of electrically neutral semicrystalline main polymer backbones polytetrafluoroethylene (PTFE) and regularly spaced long perfluorovinyl ether pendant side chains with hydrophilic terminated sulfonic (HSO$_3^-$) or carboxylic ionic functional groups. The chemical structures of Nafion® perfluorinated electrolyte membrane is shown in Fig (2.1) (Shah et al., 2009).
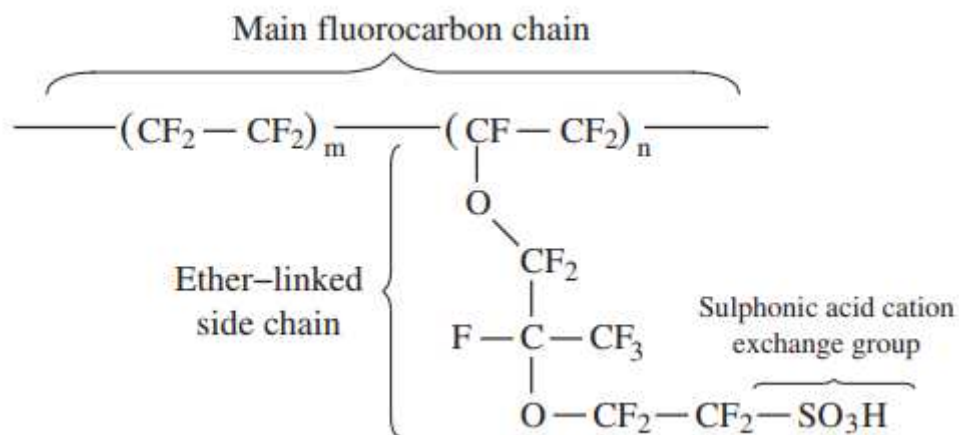

Figure 2.1 Chemical structure of Nafion® membrane (Shah et al., 2009).

The hydrophobic polytetrafluoroethylene (PTFE) backbone of Nafion® offers superior structural integrity as well as thermal and chemical stability, while the hydrophilic perfluorinated side chains have desirable proton conductivity when completely hydrated (Zhang et al., 2012, Zhang and Shen, 2012 and Zakil et al., 2016).

The proton hopping mechanism or Grotthuss mechanism explains the transport of the charge (proton) at low water content with hydronium (H_3O^+) ions consisting of one hydrated sulfonic acid group followed by the transfer of charge across the membrane to the next sulfonic acid group. The proton produced by electrooxidation of the fuel (ethanol/hydrogen) on the anode surface adheres to the water molecule when the provisional hydronium ion is formed. A separate proton is then moved from the same hydronium ion to the other water molecule. The basic schematic of the proton hopping process in PEM is shown in Fig (2.2) (Deluca and Elabd, 2006).
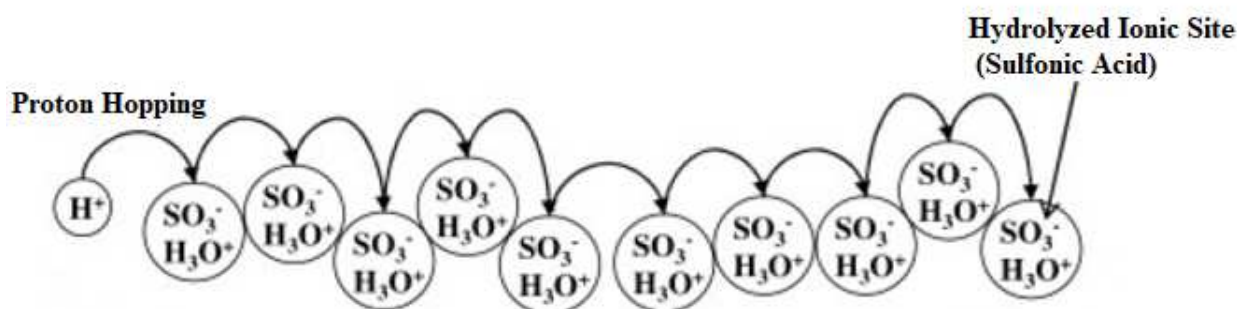

Figure 2.2 The basic diagram of the hopping mechanism of proton in PEM (Deluca and Elabd, 2006).

The second proton transfer mechanism is known as vehicular mechanism. In this mechanism, the transport of hydronium ion (H_3O^+) is diffused through the aqueous medium in response to the electrochemical difference. Fig (2.3) demonstrates the schematic presentation of the vehicle system as the conduction of the proton in the

Nafion[®] membrane. In the vehicular mechanism, the protons bound to the water ($H^+(H_2O)_x$) drag one or more molecules of water through the membrane due to the electroosmotic drag and are moved with them (Kuwertz et al., 2016). The presence of cluster phase domains within the polymer chains in the proton exchange membrane provides a vehicular mechanism route that allows the movement of hydrated protons through the membrane.
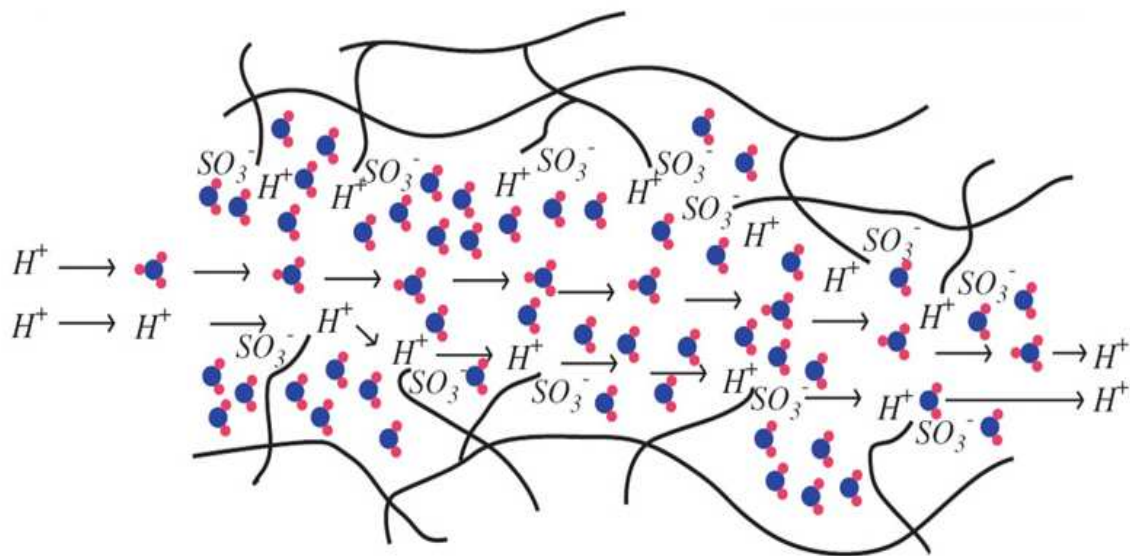

Figure 2.3 The schematic presentation of the Vehicular Mechanism as proton conduction in Nafion[®] membranes (Peighambardoust et al., 2010).

Table (2.1) summarizes the important properties of commercially available Nafion[®] membranes (Peron et al., 2010). The Nafion[®] membranes are often characterized by their thickness, and by their ion exchange capacity (IEC, $mmol_{SO3H}/g_{polymer}$) or equivalent weight (EW) which are used interchangeably. The following correlation (Equation 2.1) is used between EW and IEC for Nafion[®] membrane (Peron et al., 2010).

EW = 1000/IEC   (2.1)

The Nafion® N 1110, Nafion® N 117 and Nafion® N 115 have equivalent repeat unit molecular weights of 1100 and their thicknesses in the dry state are 254 μm, 183 μm and 127 μm, respectively. Whereas, equivalent repeat unit molecular weight of Nafion® NR 212 and Nafion® NR 211 is in the range of 990-1050 and dry state thickness are 50 μm and 25 μm, respectively (Rikukawa and Sanui, 2000 and Peron et al., 2010). The casting procedure was dispersion cast for the Nafion® NR 212 and Nafion® NR 211. The extruded technique was used to cast membrane film for Nafion® N 1110, Nafion® N 117 and Nafion® N 115.

Table 2.1 Properties of commercial Nafion® membranes (Peron et al., 2010).

Commercial name	Casting procedure	Equivalent weight ($g_{polymer}/mole_{SO3H}$) (ionic exchange capacity: $meq_{SO3H}/g_{polymer}$)	Thickness (μm)
Nafion® N 1110	Extruded	1100 (0.91)	254
Nafion® N 117	Extruded	1100 (0.91)	183
Nafion® N 115	Extruded	1100 (0.91)	127
Nafion® NR 212	Dispersion cast	990–1050 (0.95–1.01)	50
Nafion® NR 211	Dispersion cast	990–1050 (0.95–1.01)	25

There are many other advanced perfluorosulfonic acid membranes with identical structures of Nafion® synthesized by Dow Chemical Company (USA), Asahi Chemical Company (Japan) and Asahi Glass Company (Japan). However, they differ slightly from Nafion® by their length of side chains and EW/IEC and sold under different trade names like Dos membrane of Dow Chemical Company, Acriplex® of Asahi Chemical Company and Flemion® of Asahi Glass Company (Peron et al., 2010). The Dow Chemical

Company also manufactured a material with a shorter side chain than Nafion[®] with an equivalent weight of approximately 800 and a thickness of 125 μm, which is no longer available (Rikukawa and Sanui, 2000, Hickner et al., 2004 and Neburchilov et al., 2007). In addition, Asahi Glass Company has produced a series of Flemion[®] R, S, T, which have equivalent repeat molecular weight of 1000 and dry state thicknesses of 50 μm, 80 μm and 120 μm, respectively. Aciplex[®]-S series of membranes developed by Asahi Chemical Industry, which have equivalent repeat unit molecular weights of 1000-1200 and dry state thicknesses in between 25-100 μm (Rikukawa and Sanui, 2000). As already mentioned, the DuPont, USA product Nafion[®] is considered to be superior among the major types of perfluorinated ionomeric membranes due to its reasonable high conductivity (0.10 Scm[-1]), good chemical and electrochemical stability, excellent mechanical properties and commercial availability (Motupally et al., 2000, Peighambardoust et al., 2010 and Zakil et al., 2016). Thus, in the present work Nafion[®] 117 (Alfa Aesar, USA) commercial membrane was used as electrolyte for the DEFC fabrication.

2.1.1.2 Electrode materials

The most active component of fuel cell anode and cathode electrodes are electrocatalysts on which electrooxidation of fuel and reduction of oxidant take place. The electrocatalyst in the DEFC system is a site that provides a surface for the electrooxidation of ethanol to occur at lower activation energy and a higher rate of reaction kinetics. Generally, the active metal electrocatalysts are impregnated and uniform dispersed over a support material which is having high surface area and electrically conducting. The performance of DEFC depends upon the proper selections of electrocatalyst materials which controls electrode kinetics followed by current of the cell. The following sections address the

various types of anode and cathode electrocatalysts for DEFC, their characterization and performance.

2.1.1.2.1 Anode electrocatalysts

Till date several electrocatalysts have been studied as an anode electrode for the use in direct ethanol fuel cells (DEFCs) in acidic media. Since an anode electrocatalyst mainly affects the efficiency of the DEFC system in an acidic medium. Thus, the selected anode electrocatalyst should have the ability to splitting of C-C bond of ethanol molecule together with faster reaction kinetics and resulting in higher cell performance. Mainly electrocatalyst materials are of metallic origin, including platinum (Pt) (Lamy et al., 2001, Singh and Datta, 2011 and Themsirimongkon et al., 2018), gold (Au) (Lamy et al., 2001), palladium (Pd) (Themsirimongkon et al., 2018), rhodium (Rh) (Tóth et al., 2016) iridium (Ir) (Cao et al., 2007) and Ni (Tian et al., 2008 and Vyas et al., 2019). Platinum (Pt), palladium (Pd), iridium (Ir), and gold (Au) are classed as noble metals, while nickel (Ni) is non-noble metal. Of all these metallic electrocatalysts, Pt or Pt-based materials are most commonly used for the adsorption and dissociation of small organic molecules in the acidic medium. Pt-based electrocatalysts are studied in single or bi-metallic or tri-metallic or quaternary forms.

Primarily monometallic platinum (Pt) or platinum supported on high surface area carbon (Pt/C) has been extensively used as anode electrocatalysts for ethanol electrooxidation in low-temperature fuel cells due to its high electrocatalytic activity and passivity under acidic conditions (Li and Pickup, 2006, Rousseau et al., 2006, Vigier et al., 2006, Ghumman et al., 2008, and Singh and Datta, 2011). Rousseau et al., (2006) studied the electrooxidation of ethanol on Pt/C (40 wt. %) in a single DEFC, and reaction products

were detected using high performance liquid chromatography (HPLC). The reaction products analyzed by HPLC showed 47.5 % acetaldehyde (AAL), 32.5 % acetic acid (AA) and 20 % CO_2. The analysis of the reaction products at anode side shows that some ethanol molecules go through partial electrooxidation giving AAL and AA as intermediate products. While a few molecules follow the complete reaction path and thus produce CO_2 as final product. As already discussed in introduction section (Page no. 7, 8) the complete electrooxidation of ethanol molecule releases 12e$^-$ resulting in highest current.

Singh and Datta, (2011) investigated the kinetics and mechanism of ethanol electrooxidation at room temperature on Pt/C electrocatalysts with varying loading i.e., 20 wt. %, 40 wt. % and 60 wt. % which were chemically synthesized by the $NaBH_4$ reduction process. Platinum loading of 40 wt. % Pt/C demonstrated the highest electrocatalytic activity as calculated from the formation of acetic acid during ethanol electrooxidation by ion chromatography technique. The highest electrocatalytic activity of Pt/C (40 wt. %) was due to its homogeneously distributed Pt nanoparticles with smaller particle sizes compared to other electrocatalysts Pt/C (20 wt. %) and Pt/C (60 wt. %). The Pt is required for the dissociative adsorption of ethanol in an acidic medium, while the Pt active sites get easily poisoned by highly adsorbed partially oxidized species such as CO produced during the ethanol electrooxidation phase, resulting in poor electrocatalytic activity of Pt/C and thus efficiency losses in DEFC. In addition, a high over-potential of 0.4 V versus RHE and above is always needed as a start-up potential for ethanol fuel using monometallic Pt/C electrocatalysts. Thus, low current density of DEFC at low potential greatly decreases their practical values in applications (Liu et al., 2011).

As per reported literature, bi-metallic Pt-based alloys are better than monometallic Pt/C electrocatalyst for ethanol electrooxidation. The metal Pt alloyed with other transition metals like ruthenium (Ru), tin (Sn), rhenium (Re) showed better DEFC electrical output in terms of open-circuit voltage (OCV), current density and power density (Zhou et al., 2003, Goel and Basu, 2014 and Tayal et al., 2012). In addition, constructing Pt alloys with second or third transition metals is a handy way to boost electrocatalytic activity of Pt in order to resolve slow kinetics and electrocatalyst poisoning due to formation of CO and CH_x intermediates of ethanol electrooxidation. The alloying of Pt with other transition metals greatly decreases electrocatalyst costs due to the use of the lower quantity of noble metal compared to the pure metal-based electrocatalyst, which is an important aspect for commercialization.

Recently, great efforts has been devoted to overcome the poisoning and quick loss of electrocatalytic activity of pure Pt/C electrocatalysts by incorporation of oxophilic materials such as Ru (Zhou et al., 2003, Li et al., 2007, Şen et al., 2011, Goel and Basu 2014 and Hu et al., 2016), Sn (Zhou et al., 2005, Colmenares et al., 2006, Sim̃oes et al., 2007, Colmati et al., 2007, Almeida et al., 2012, Asgardi et al., 2015 and Romero-Cano et al., 2019), Pd (Seweryn and Lewera, 2012 and Themsirimongkon et al., 2018), Ir (Ribeiro et al., 2007 and Qu et al., 2017), Re (Tayal et al., 2012), Rh (Oliveira et al., 2006, Rao et al., 2014 and Almeida et al., 2019), Ni (Soundararajan et al., 2012, Shen et al., 2015 and Qin et al., 2019), Mo (Dos Anjos et al., 2006 and Herrera-Méndez et al., 2011), Cu (Ammam and Easton, 2013 and Saleem et al., 2013) and Pr (Corradini et al., 2013 and Corradini et al., 2014). Among them, the most promising anode material for ethanol electrooxidation is the bi-metallic Pt-Ru and Pt-Sn combination, due to their lowest overpotential and strong activity at relatively low over potential in acid medium (Zhou et

al., 2003, Antolini, 2007, Li et al., 2007 and Sieben et al., 2012). The enhanced performances of bi-metallic electrocatalysts are often presented by the bi-functional mechanism and/or electronic effects (Datta et al., 2009, Velazquez-Palenzuela et al., 2010, Garcı́a et al., 2012, Muthuswamy et al., 2013 and Gu et al., 2018). Several studies have shown that the incorporation of oxophilic metals such as Ru, Sn, Ir, Re, Rh, Ni or Mo provide surface hydroxides species (-OH groups) by dissociating water at a lower potential that could more easily oxidize the CO or carbonyl species adsorbed at neighboring Pt sites through a bi-functional mechanism (Garcı́a et al., 2012, Shen et al., 2015 and Gu et al., 2018). In addition, ligand or electronic effects suggest that the presence of oxophilic atoms Ru or Sn alters the electronic structure of Pt by interacting with its 5d-band, which weakens the binding strength of Pt-CO adsorbate and decreases the CO coverage during ethanol electrooxidation (Velazquez-Palenzuela et al., 2010 and Shen et al., 2015). In addition, the addition of co-catalysts lowers the Pt content of bi-metallic electrocatalysts and thus lowers the noble metal content. It should be noted that the selection of co-metal/co-electrocatalyst and amount of co-electrocatalyst in bi-metallic electrocatalysts play important role to form most active electrocatalyst for ethanol. Thus, various combination of Pt-based bi-metallic electrocatalysts like Pt_1-Ru_1/C (Zhou et al., 2003), Pt-Ru/C (Li et al., 2007, Sen et al., 2011, Goel and Basu, 2014 and Shen et al., 2015), Pt_1-Sn_1/C (Zhou et al., 2003), Pt-Sn/C (Li et al., 2007, Zhou et al., 2005, Jiang et al., 2005 and Colmenares et al., 2006), Pt_1-W_1/C (Zhou et al., 2003), Pt-Ni/few-layer graphene (FLG) (Shen et al., 2015) and Pt-Pd/C (Zhou et al., 2003) were investigated for ethanol electrooxidation.

Zhou et al., (2003) prepared Pt-based bimetallic electrocatalysts based on carbon XC-72R for ethanol electrooxidation by polyol reduction method. The cyclic voltammetry (CV)

measurements and single direct ethanol fuel cell (DEFC) research together showed that Sn, Ru and W are strong additives, enhanced ethanol electrooxidation activity over Pt in the following sequence: $Pt_1Sn_1/C > Pt_1Ru_1/C > Pt_1W_1/C > Pt_1Pd_1/C > Pt/C$. Li et al., 2007 also investigated ethanol electrooxidation using Pt/C, Pt-Ru (1:1)/C, and Pt-Sn (1:1)/C electrocatalysts with total metal loading of 40 wt. % synthesized by a modified polyol process. The Electrocatalytic activities for ethanol electrooxidation on these electrocatalysts were studied using cyclic voltammetry (CV) and chronoamperometry (CA) methods at room temperature (25 ºC). The ethanol electrooxidation activity on Pt-based electrocatalysts is significantly affected by secondary metal and electrode potential. The single DEFC performance using Pt-Sn/C as anode was better than Pt-Ru/C. They argued that the improvement of ethanol electrooxidation on Pt-Sn/C is mainly attributable to the structural effect due to the extension of the Pt crystal structure, while the promotional effect of Pt-Ru/C electrocatalyst could be explained by the modified bi-functional mechanism resulting from the enhanced activity of H_2O activation on Ru sites.

Similarly, Pt-based bi-metallic electrocatalysts were synthesized by varying amount of co-electrocatalyst/metal by many researchers (Zhou et al., 2005, Colmenares et al., 2006, Colmati et al., 2007 and López-Suárez et al., 2015) to find out the suitable metal loading for achieving highest electrocatalytic activity of the synthesized electrocatalysts towards ethanol electrooxidation. Zhou et al., (2005) tested the ethanol electrooxidation behaviour of Pt-Sn/C synthesized by modified polyol reduction process with different Pt/Sn atomic ratios (1:1, 2:1, 3:1, 3:2 and 4:1) in single DEFC tests. They found that the cell performance of synthesized electrocatalysts with different anode electrocatalysts differed from each other. The single DEFC with Pt_3Sn_2/C anode exhibited better performance at 60 ºC, while the DEFC with Pt_2Sn_1/C and Pt_3Sn_2/C anodes showed similar performance at

75 ℃. However, Pt_2Sn_1/C was identified as a more effective anode electrocatalyst for direct ethanol fuel cells at 90 ℃ in terms of the maximum power density of the fuel cell. The key factors that influence electrocatalytic activity and cell efficiency of the electrocatalyst were the surface oxygen-containing groups, lattice parameters, and ohmic effects which are related to Sn content in electrocatalysts. Colmenares et al., (2006) synthesized Pt/C (20 wt. %), Pt–Ru/C with total metal loading including 20 wt. %, 40 wt. % and 60 wt. %, (Pt:Ru atomic ratio 1:1) and Pt–Sn/C (20 wt. %, Pt:Sn atomic ratio 3:1) electrocatalysts using a modified polyol process and compared the performance of polyol-type synthesized electrocatalysts with that of corresponding commercial electrocatalysts using electrochemical measurements. Incomplete ethanol electrooxidation to C2 products like acetaldehyde and acetic acid produced for both electrocatalysts and CO_2 formation contributes by ≤ 1%. The Polyol-type electrocatalysts demonstrated lower ethanol oxidation reaction (EOR) activity than commercial electrocatalyst activity due to lower activity for acetaldehyde formation. This activity was provisionally attributed to the higher amount of non-alloyed, partially oxidized Ru and Sn surface species in the polyol-type synthesized electrocatalysts and likely to the surface poisoning of polyol-type electrocatalysts by organic residues. Colmati et al., (2007) also studied the ethanol electrooxidation behaviour of Pt–Sn/C electrocatalysts with varying ratios of Pt to Sn i.e., 9:1, 3:1 and 2:1 synthesized by the formic acid reduction process. They explained that the behaviour of PtSn/C for ethanol electrooxidation appears to depend on the amount of both alloyed and non-alloyed Sn. For ethanol electrooxidation, the rate-determining step depends on the reaction temperature and determines the optimal distribution of Sn between the alloyed and non-alloyed states. The removal of CO and CH_3CO species determines the rate of ethanol electrooxidation where ethanol electrooxidation is not rapid at the low temperatures. This rate determination is improved by the presence of Sn

oxides. The dissociative adsorption of ethanol and/or the oxidation of acetaldehyde to acetic acid are the rate-determining step at high temperatures and high current densities of the fuel cell. In this case, due to the increase of the lattice parameter, an increase of the Sn content in the alloyed state of the solid solution Pt-Sn favors these reactions. López-Suárez et al., (2015) synthesized a series of bi-metallic Pt_x-Sn_y/C (20 wt. %, Pt:Sn molar ratio 1:1, 2:1, and 3:1) electrocatalysts by formic acid reduction method and investigated electrocatalytic activity towards ethanol electrooxidation by electrochemical measurements. The introduction of the highest Sn content in Pt_1Sn_1/C created geometric structural changes such as lattice extension with the formation of Pt-Sn solid solution alloy phase, while the intermediate and lowest Sn content Pt_2-Sn_1/C and Pt_3-Sn_1/C promoted the electronic structure modifications of Pt by introducing Sn without the creation of a solid solution. In addition, these findings were controversial in the results published by Colmati et al., (2007) and Zignani et al., (2012) under similar conditions of preparation.

It should be noted that the performance of bi-metallic Pt-Ru and Pt-Sn electrocatalysts for ethanol electrooxidation is superior to Pt alone and other bi-metallic electrocatalysts. However, recent studies prove that most of the electrooxidation products are intermediate species containing the C-C bond, which have a direct adverse effect on the efficiency of DEFCs. Bi-metallic nanoparticles comprising Pt with Ru or Sn are active electrocatalysts for ethanol electrooxidation but inactive for splitting the C–C bond of ethanol molecule to produce CO_2 (Wang et al, 2006 and Drzymała et al., 2020). As a result, scientists claim that the electrocatalyst's activity for ethanol oxidation is dependent not only on its ability for oxidative removal of poisoning species, but also on its activity for C–C and C–H bond breaking (Wang et al, 2006 and Drzymała et al., 2020). Since, it is difficult to oxidize

completely ethanol molecule to CO_2 and water because of its complex molecular structure consisting of the C–C bonds which requires high activation energy (Wang et al, 2006). Thus, it is crucial and necessary for developing novel electrocatalysts or introducing a third metal to modify the structure of the Pt-Ru/C and Pt-Sn/C electrocatalysts to exhibit the higher activity of C-O and C-C bond cleavage, enhance oxidation kinetics and product selectivity during the ethanol electrooxidation.

In the last few years, tri-metallic alloy electrocatalysts have been widely investigated in order to boost ethanol oxidation reaction (EOR) activity and selectivity towards the generation of CO_2. Tri-metallic alloy electrocatalysts such as PtRuSn (Chu et al., 2010 and Cunha et al., 2011), PtRuMo (Wang et al., 2007), PtRuRh (Nakagawa et al., 2012), PtRuNi (Shen et al., 2015 and Sudachom et al., 2017), PtSnRu (Antolini et al., 2007), PtSnMo (Lee et al., 2011), PtSnIr (Ribeiro et al., 2007, Tayal et al., 2011 and Ramos et al., 2012), PtSnW (Ribeiro et al., 2008), PtSnCe (De Souza et al., 2011), PtSnNi (Beyhan et al., 2013 and Beyhan et al., 2014), PtSnRe (Tayal et al., 2012) have been studied to use as anode material for ethanol electrooxidation in direct ethanol fuel cells (DEFCs). Open literature states that all tri-metallic electrocatalysts demonstrate enhanced ethanol electrooxidation behaviour relative to the corresponding bi-metallic Pt-Ru and Pt-Sn electrocatalysts. Till date, many tri-metallic electrocatalysts based on Pt-Ru and Pt-Sn have been tested for ethanol electrooxidation. Generally, the incorporation of the third oxophilic promoter X (where X is Sn, Mo, Rh, Ni, Ru, Ir, W, Ce, and Re) into bi-metallic electrocatalysts during the synthesis of trimetallic electrocatalysts Pt-Ru-X or Pt-Sn-X electrocatalysts has been performed in the recent past. As mentioned earlier (Page no. 26) that metal ratio/composition and metal to carbon support of the synthesized tri-metallic alloy electrocatalysts play a key role in deciding its best catalytic activities. The literature

shows that a series of several synthesized electrocatalysts with differing proportions of metals for a particular category of electrocatalysts, such as Pt-Ru-X and Pt-Sn-X, achieves the highest cell efficiency for their optimum metal ratio. Metals present in the electrocatalyst have a particular position in the C-C bond breaking of ethanol and water molecule dissociation followed by the removal of adsorbed CO from the electrocatalyst surface after CO_2 oxidation.

Several tri-metallic Pt-Ru-X electrocatalysts synthesized by the incorporation of the third (X) metal with Pt-Ru have been documented in the literature, and some of these electrocatalysts with an optimal composition are described here as $Pt_{0.8}Ru_{0.1}Sn_{0.1}/C$ (Cunha et al., 2011), $Pt_{60}Ru_{30}Mo_{10}/C$ (Wang et al., 2007), $Pt_2Ru_1Rh_1/C$ (Nakagawa et al., 2012) and $Pt_{75}Ru_5Ni_{20}$ (Sudachom et al., 2017). Cunha et al., (2011) synthesized tri-metallic PtRuSn/C electrocatalysts using the Pechini process comprising a different Pt/Ru/Sn molar ratio and maintaining carbon to metal ratio at a constant value of 60/40 wt. % by thermal decomposition of polymeric precursor, leads to the formation of nanocatalyst with large roughness factor, and found that the addition Ru and/or Sn to pure Pt electrocatalyst significantly improved electrocatalytic performance towards ethanol electrooxidation. The best composition of tri-metallic electrocatalyst was $Pt_{0.8}Ru_{0.1}Sn_{0.1}/C$ for ethanol electrooxidation which releases acetaldehyde as a main product and traces of CO_2 and acetic acid. Nakagawa et al., (2012) investigated that the additions of Ru to Pt and Rh to PtRu/C increased the current density of DEFC successively like Pt/C < $Pt_1Ru_1Rh_2/C$ < Pt_1Ru_1/C < $Pt_2Ru_1Rh_1/C$ at a cell temperature of 80 °C.

Similarly, many studies on synthesis of tri-metallic Pt-Sn-X have also been carried out. Antolini et al., (2007) synthesized Pt_1Sn_1/C, $Pt_1Sn_1Ru_1/C$, and $Pt_1Sn_1Ru_{0.3}/C$ electrocatalysts using the formic acid reduction process, and highlighted the significance

of the Ru/Sn atomic ratio, which is a key parameter for influencing the ethanol electrooxidation behaviour. The $Pt_1Sn_1Ru_{0.3}$/C electrocatalyst demonstrated greater ethanol electrooxidation activity compared to the bi-metallic Pt_1Sn_1/C and Pt_1Ru_1/C and the tri-metallic $Pt_1Sn_1Ru_1$/C electrocatalysts in both electrochemical measurements and DEFC studies. In addition, the DEFC performance of $Pt_1Sn_1Ru_1$/C was observed to be lower than that of both Pt_1Sn_1/C and Pt_1Ru_1/C bimetallic, which is consistent with the results reported by Zhou et al., (2003) and Zhou et al., (2004) for the tri-metallic $Pt_1Sn_1Ru_1$/C electrocatalyst. Lee et al., (2011) analyzed the activity of Pt_1Sn_1/C, $Pt_1Sn_1Mo_{0.4}$/C and $Pt_1Sn_1Mo_{0.6}$/C electrocatalysts for ethanol electrooxidation synthesized by the polyol reduction method and documented the improved electrocatalytic activity for EOR due to the addition of Mo to Pt-Sn. Electrochemical measurements and single DEFC tests of the $Pt_1Sn_1Mo_{0.6}$/C electrocatalyst revealed enhanced electrocatalytic activity among all, which could be attributed to the cooperative result of the Sn and Mo bi-functional mechanism and the Mo hydrogen spillover effect.

Ribeiro et al., (2007) and Tayal et al., (2011) investigated the effect of Ir incorporation on PtSn for ethanol electrooxidation. In contrast to bi-metallic electrocatalyst PtSn/C, both tri-metallic electrocatalysts $Pt_{68}Sn_9Ir_{23}$/C (Ribeiro et al., 2007) and $Pt_{20}Ir_5Sn_{15}$/C (by wt. %) (Tayal et al., 2011) performed well when tested for ethanol electrooxidation. Ribeiro et al., (2007) developed various compositions of PtSnIr/C electrocatalysts by the Pechini–Adams modified process. The presence of Ir in the bi-metallic PtSn electrocatalyst has been found to increase structural defects or roughness, making the tri-metallic $Pt_{68}Sn_9Ir_{23}$/C electrocatalyst a better choice for EOR. Tayal et al., (2011) synthesized various combinations of tri-metallic PtIrSn/C electrocatalysts using impregnation reduction technique and reported that the addition of Ir in the bi-metallic PtSn/C

electrocatalyst enhances electrocatalytic activity towards ethanol electrooxidation than the $Pt_{20}Sn_{20}$/C (by wt. %).

Ribeiro et al., (2008) and De Souza et al., (2011) studied the addition of W and Ce to PtSn/C. Ribeiro et al. (2008) reported a substantial change in onset potential to lower values and a remarkable improvement in DEFC cell output when W was integrated into PtSn/C. Similarly, De Souza et al., (2011) showed that the presence of Ce in $Pt_{68}Sn_{22}Ce_{10}$/C (mass ratio) electrocatalyst produces almost 40 % higher DEFC performance than that produced by the commercial PtSn/C (E-TEK) electrocatalyst.

Some of the tri-metallic electrocatalysts have been synthesized for ethanol electrooxidation by adding Ni to Pt-Sn/C (Beyhan et al., 2013 and Beyhan et al., 2014). The promoting effect of Ni enhances the C-C bond breaking during ethanol electrooxidation and thus cell performance (Beyhan et al., 2013). The performance enhancement of tri-metallic electrocatalyst could be achieved by adding Re to PtSn/C and this has been studied thoroughly by Tayal et al., (2012). They synthesized various combinations of tri-metallic electrocatalysts and established that Re addition to Pt-Sn/C in low amount is conducive to breaking of C-C bonds in $Pt_{20}Re_5Sn_{15}$/C (by wt. %), and improves the DEFC performance. However, the higher percentage of Re and lesser percentage of Sn in $Pt_{20}Re_{10}Sn_{10}$/C (by wt. %) blocks the further oxidation of intermediates resulting an adverse effect in cell performance.

According to published literature, the addition of Re to Pt-based supported electrocatalysts improves their ability to break the C–C bond of ethanol molecule at low temperatures, which may result in complete ethanol electrooxidation (Goel and Basu, 2012, Tayal et al., 2012, Duke et al., 2017, Parlinska-Wojtan et al., 2019 and Drzymała et

al., 2020). Many researchers also observed that the addition of Re weakened the Pt–CO binding strength, and thus active surface sites were less poisoned by adsorbed CO, which resulted in higher Pt-Re activity (Simonetti et al., 2007, Ciftci et al., 2014, Duke et al., 2015 and Duke et al., 2017). Moreover, rhenium (Re) is a strong oxygen species binder, creating hydroxyl groups (Ciftci et al., 2014), which also would facilitate CO_{ads} removal via conversion of CO_{ads} to CO_2.

Thus, based on thorough literature survey on anode electrocatalysts for ethanol fuel, Pt-based bi-metallic Pt-Ru/C and tri-metallic Pt-Ru-Re/C electrocatalysts were synthesized using various carbon support materials and various synthesizing routes, systematically. In the following sections carbon support materials (Section 2.1.1.2.1.1) and electrocatalyst synthesis routes (Section no. 2.1.1.2.1.2) are discussed.

2.1.1.2.1.1 Electrocatalysts supports

It has been established that interaction between electrocatalyst and support significantly affects the physicochemical and electrochemical characteristics of electrocatalysts and consequently their performance in the fuel cell (Dicks, 2006 and Samad et al., 2018). The nature of the supporting materials plays a very important role in developing/synthesizing well-distributed and scattered electrocatalysts. Supporting materials also play important role by reducing the use of noble metal particles and, at the same time, improving electrocatalytic activity by providing a large surface area for better dispersion, high electrical conductivity and porous structure for better diffusion of reactants at reaction sites (Antolini, 2009 and Samad et al., 2018). In addition, the behaviour and long-term stability of the electrocatalyst are highly affected by the supporting material used.

Supporting material may change the morphology of supported nanoparticles and act as a promoter of the reaction (Goel and Basu, 2014 and Roca-Ayats et al., 2015). It is generally suggested that high electrically conductive carbon materials with ordered structure and graphite characteristics boost fuel cell efficiency. The most widely used electrocatalyst support material in low-temperature fuel cells is Vulcan XC-72, due to its excellent physical characteristics, such as the optimum compromise between pore volume and surface area (Wikander et al., 2006 and Antolini, 2009). However, Vulcan XC-72 comprises around 30 % of the total specific surface area calculated based on Brunauer-Emmet-Teller (S_{BET}) region of micropores smaller than 1 nm, which may not be available to the reactant, and therefore remain unused (Lázaro et al., 2011 and Calvillo et al., 2011). Some researchers stated that due to several good characteristics such as moderate surface area, high conductivity, low cost, availability, and large pore volume, electrocatalyst supported on acetylene black showed promising cell performance (Uchida et al., 1996, Han et al., 2006 and Zhiani et al., 2013). Uchida et al., (1996) studied the effect of carbon support on the synthesis of Pt-Ru bimetallic anode electrocatalysts for direct methanol fuel cells (DMFCs). Among the carbon black support materials tested, the Pt-Ru electrocatalyst supported on acetylene black (AB) with the smallest specific surface area and pore size distribution in the range of 3 to 8 nm performed best. In a similar study on support material, Han et al., (2006) discovered that a high loading of Pt-Ru (80 wt. %) alloy electrocatalyst supported on acetylene black exhibited promising cell performance for methanol fuel in acidic media when compared to other carbon support materials. According to Zhiani et al., (2013), the performance of Pt-Ru (20:10 wt. %)/acetylene black for methanol oxidation in acidic media was superior to that of the commercial electrocatalyst Pt-Ru (20:10 wt. %)/C. In this regard, a commercial pristine/untreated carbon support acetylene black (C_{PAB}) was investigated due to several favorable

properties, including moderate surface area, high conductivity, low cost, availability, and large pore volume.

Over the last few decades, a number of nanostructured carbon materials have been proposed by researchers to synthesize different types of supported electrocatalysts including carbon nanotubes (CNTs) (Chetty et al., 2009, Yang et al., 2012, Cheng et al., 2014, Goel and Basu, 2014 and Sudachom et al., 2017), mesoporous carbons (Calvillo et al., 2007 and Salgado et al., 2010), carbon nanocoils (Lázaro et al., 2011 and Gálvez et al., 2013), graphitic carbon nanofibres (Calvillo et al., 2009 and Rizo et al., 2017a), graphene nanosheets (Dong et al., 2010 and Shen et al., 2015).

In particular, researchers have extensively researched carbon nanotubes (CNTs) as electrocatalyst support material in low-temperature fuel cell applications due to their distinctive properties such as elevated chemical and electrochemical stability and excellent electrical conductivity compared to traditional carbon black such as Vulcan XC-72 and acetylene black carbon, etc (Chetty et al., 2009, Yang et al., 2012, Cheng et al., 2014, Goel and Basu, 2014, Sudachom et al., 2017, You and Kamarudin, 2017 and Samad et al., 2018). The CNTs are two-dimensional tubular nanostructures composed of single sheets of hexagonally organized carbon networks, i.e. graphene and commonly known as single-walled carbon nanotubes (SWNTs) or multi-walled carbon nanotubes (MWCNTs). MWCNTs consist of a series of single-walled, coaxially arranged CNTs with a regularly growing diameter. SWNTs produce a greater surface area, while MWCNTs have a higher electrical conductivity (Goel and Basu, 2014, You and Kamarudin, 2017 and Samad et al., 2018). Despite its enhanced stability and outstanding electronic transport properties, highly graphitized CNTs have inadequate binding sites to anchor the precursor of electrocatalyst nanoparticles and an accessible surface area due to

inert graphite surface and low dispersibility, resulting in high agglomeration in solvents. As a result, carbon nanotubes are functionalized by introducing acid groups to improve hydrophilicity and solve problems related to nanotubes agglomeration, as well as to improve nanoparticle dispersion. The CNTs surface functionalization is usually performed by refluxing in a mixture of HNO_3/H_2SO_4 acid solution to produce defects and functional groups containing oxygen such as hydroxyl (-OH), carboxyl (-COOH) and carbonyl (> C = O) on the CNT surface (Xing, 2004, Yang et al., 2012, Cheng et al., 2014 and Goel and Basu, 2014). In addition, several researchers have stated that the treatment/functionalization of support materials strongly affect the physicochemical and electrochemical features of synthesized electrocatalysts for EOR activities (de La Fuente et al., 2009, Goel and Basu, 2014, Asgardi et al., 2015, Rizo et al., 2017a and Rizo et al., 2017b). The surface of the support material is modified to reinforce the bond between the electrocatalyst and the support material which improves the metal support interaction.

In the present study, to synthesize highly dispersed Pt-based bi-metallic and tri-metallic electrocatalysts for ethanol electrooxidation in half-cell and single DEFC experiments, carbon support materials such as acetylene black (C_{PAB}) and multi-walled carbon nanotubes (MWCNTs) were functionalized and converted to functionalized acetylene black (C_{AB}) and functionalized MWCNTs (f-MWCNT), respectively.

2.1.1.2.1.2 Anode electrocatalyst synthesis routes

It is evident from the published literature that the behaviour of electrocatalyst materials is highly dependent on their structure, surface morphology and particle size. The electrocatalyst synthesis methods have a significant influence on the physical properties of nanoparticle electrocatalysts, such as composition, structure and degree of alloy,

resulting in different electrocatalytic activity and DEFC performance. From this viewpoint, it is essential to study several electrocatalyst synthesis methodologies for the synthesis of highly dispersed metal nanoparticles on high surface carbon or other conducting support materials. There are many methods for the synthesis of supported electrocatalysts in fuel cells including the impregnation reduction process, the colloidal method, the microemulsion method and the polyol reduction method (PLM).

The impregnation reduction method is simple, low-cost and the most widely used chemical preparation technique that has been successfully used for the synthesis of Pt-based bimetallic and trimetallic electrocatalysts (Toyal et al., 2011, Toyal et al., 2012, Goel and Basu, 2014, and Wang et al., 2017). An obvious benefit of this approach is that it avoids filtering and washing procedures and is suitable for large scale production. It consists of impregnating the suitable metal precursors with high surface area carbon black or any other support in an aqueous solution followed by reduction in a flowing hydrogen stream at high temperatures or the chemical reduction of metal precursors using liquid phage reductive agent such as $Na_2S_2O_3$, $NaBH_4$, $Na_4S_2O_5$, N_2H_4 or formic acid. In this electrocatalyst synthesis method, several variables such as different reducing agents and metal precursors, as well as different means of mixing reducing agents and pH modification have a major influence on the surface composition, particle size, morphology, electrocatalyst dispersion of nanoparticles (NPs) and the degree of alloy, resulting in variation of electrocatalytic activity. The main drawback of the impregnation reduction process is the difficulty in regulating the size and distribution of nanoparticles. However, several researchers have successfully used the method for synthesizing dispersed electrocatalyst nanoparticles by carefully monitoring effective preparation procedures. Nakagawa et al., (2012) have used the same method to synthesize a series of

Pt/C, PtRu (1:1)/C, PtRuRh (2:1:1)/C and PtRuRh (1:1:2)/C with high metal loading around 65 wt. % and average metal crystallite sizes ranging from 2.61 nm to 5.24 nm. Wang et al., (2017) developed a well dispersed Pt-Rh/TiO$_2$-C electrocatalyst with an average particle size of 6.49 nm and a narrow size distribution by the impregnation reduction method using sodium borohydride (NaBH$_4$) as a reducing agent.

Highly dispersed Pt-based bi-metallic and tri-metallic supported electrocatalysts for DEFC have also been synthesized by formic acid reduction method (FAM) which is an impregnation reduction method (Antolini et al., 2007, Antolini et al., 2009, Jacob et al., 2015 and López-Suárez et al., 2015). In this methodology, electrocatalysts are formed by suspending appropriate amount of carbon support like Vulcan XC-72 or acetylene black carbon in a concentrated formic acid solution which acts as reducing agent and the resulting mixture is heated to 80 ℃. Subsequently, solutions of suitable metal precursors are applied to the reaction vessel under stirring to achieve better dispersion. After the metal reduction process has been completed, the electrocatalyst obtained is filtered, washed with distilled water and dried. Antolini et al., (2007) used this methodology to develop bi-metallic Pt–Sn/C (1:1) and tri-metallic Pt–Sn–Ru/C (1:1:0.3 and 1:1:1) electrocatalysts with the desired catalytic composition and well distributed nanoparticles ranging from 1.5 nm to 8 nm on the carbon surface for ethanol electrooxidation.

The colloidal method is another extensively studied electrocatalyst synthesis route for Pt-based electrocatalysts used in fuel cell applications (Beyhan et al., 2013 and Beyhan et al., 2014). It involves formation and deposition of metal colloids onto the support surface followed by the chemical reduction of the mixture. This method provides an effective way to control nucleation and growth, thereby resulting in the nanoparticle sizes with uniform shape and homogeneously distributed on the surface of carbon support (Wang et

al., 2011 and Zhu et al., 2015). There are several colloidal routes i.e., Bönnemann colloidal route, the modified Watanabe's colloidal route, the polyol reduction process etc. have been developed in recent years based on using various organic stabilizers, reducing agents or shell removing approaches.

In recent years, the polyol reduction process/method (PLM) using ethylene glycol as both solvent and reducing agent of metallic precursors has been extensively investigated for synthesis of Pt-based electrocatalysts (Shen et al., 2015 and Hu et al., 2016). In this process, the reflux of alcohol ethylene glycol containing the metallic ions and a stabilizing agent provides homogeneous colloidal metal solutions of the corresponding metal nanoparticles. The reduced colloidal metal nanoparticles are then deposited on the carbon support. Glycolate produced in situ from ethylene glycol oxidation in alkaline medium serves as stabilizer for metal colloids and the size of the resulting colloids is controlled via the pH of the solution. This method provides precise size control, adequate distribution of metal nanoparticles on the support surface without the need for additional stabilizers (Wang et al., 2009, Lee et al., 2010 and Lee et al., 2012).

The microemulsion method, a new route for Pt-based electrocatalyst synthesis in fuel cell applications, has also been studied in recent years (Godoi et al., 2010 and Li et al., 2011). This method involves following synthesizing steps. First, the required metal precursors are dissolved in the aqueous phase and the resulting aqueous solutions are mixed with surfactant, cosurfactant and oil to obtain microemulsion. The obtained microemulsion was reduced by the addition of reductant directly into the system or by solubilizing it with another microemulsion system containing the reducing agent. In this process, the nanosized water droplets containing the metal precursor are engulfed by surfactant and cosurfactant molecules and uniformly dispersed in an immiscibly continuous organic

phase. Consequently, these water droplets serve as microreactors for synthesis reaction take place and inhibit nanoparticle agglomeration (Liu et al., 2006 and Li et al., 2011). This method offers ease in controlling metallic composition along with good control of particle shape and size within a narrow distribution by varying the synthesis conditions. Li et al., (2011) have adopted water-in-oil microemulsion methodology to synthesize Pt_xSn/C nanoparticles homogeneously deposited on carbon support with particle sizes ranging from 2 nm to 4 nm (mean particle size 2.9 nm) and the EDX composition quite close to nominal value. However, this method is not appropriate for large-scale production as it involves a considerable number of separation and washing steps and uses expensive surfactant molecules.

Thus, in the present work low cost, simple and efficient electrocatalyst synthesis methods such as the formic acid method (FAM) and the polyol reduction method (PLM) are adopted to synthesize highly dispersed electrocatalyst nanoparticles supported on acetylene carbon black or multi-walled carbon nanotubes.

2.1.1.2.2 Cathode electrocatalysts

The cathode is also an essential fuel cell compartment that determines the performance of DEFC. A good anode electrocatalyst that quickly oxidizes ethanol however, when it is combined with a sluggish cathode electrocatalyst that slowly reduces oxygen leads to reduced cell performance. Thus, to increase the efficiency of DEFC, both electrodes of the fuel cell must perform effectively. In addition, some consideration must be given to the potential ethanol crossover through the polymeric membrane of Nafion[®], which severely affects the performance of the cathode. Thus cathode electrocatalyst materials for DEFC in acidic medium must have a high ethanol tolerance and a high electrocatalytic

oxygen-reduction reaction (ORR) activity. Currently, monometallic platinum supported on high surface carbon i.e., Pt/C with 20-40 wt. % Pt loading is the most widely investigated cathode electrocatalyst in acidic media due to its excellent electrocatalytic properties for ORR (Lopes et al., 2008, Pramanik and Basu, 2011 and Akhairi and Kamarudin, 2016). However, the slow kinetics of the ORR process with Pt due to the formation of oxygenated intermediates (-OH species at +0.8 V) hinders the further reduction of O_2 molecules and hence the loss of performance. So, researchers concentrated on the development of Pt-based alloys or composite electrocatalysts that inhibit the adsorption of oxy/hydroxy species and enhance the ORR activity. It has been identified that the incorporation of transition metal atoms in the Pt structure enhances electrocatalytic activity by disrupting both the Pt-Pt configuration and the inter-atomic gap (Beyhan et al., 2015 and Akhairi and Kamarudin, 2016), reducing Pt-O formation during inhibition of molecular oxygen reduction (Murthi et al., 2004), more active exposure of the vicinal plane to dispersed platinum particles (Beard and Ross, 1990), increased Pt 5d-electron vacancy resulting in increased O_2 adsorption and a weakening of the O-O bond in the oxygen structure (Toda et al., 1999). Lopes et al., (2007) investigated the activity of commercial Pt/C and Pt-Co/C (Pt:Co atomic ratio 3:1, E-TEK) electrocatalysts for ORR and ethanol tolerance in a temperature range of 60-100 °C. Cell performance of DEFC with Pt-Co/C as a cathode electrocatalyst was found to be higher than that of Pt/C electrocatalyst due to increased electrocatalytic activity of the Pt-Co/C alloy electrocatalyst for ORR. However, the addition of Co to Pt does not increase the tolerance of ethanol, because Pt/C and Pt-Co/C exhibit the same behaviour for crossover ethanol electrooxidation in the cathodic potential region.

There are only a few studies in the literature regarding the cathode electrocatalyst development for DEFC application in acidic medium. However quite satisfactory results have been reported in most studies using Pt/C (Pramanik and Basu, 2007, Tayal et al., 2011, Tayal et al., 2012 and Goel and Basu, 2014). Thus, in the present work commercially procured Pt/C (40 wt. %) from Alfa Aesar was used as cathode electrocatalyst.

It is important to evaluate the electrocatalytic activity of the anode using laboratory synthesized electrocatalysts and cathode of commercial electrocatalysts before it is applied in a single cell. The electrochemical analysis for anode and cathode is discussed in the section 2.1.1.2.4 (Page no. 48).

2.1.1.2.3 Physical characterization of anode electrocatalysts

The physical characterizations of anode electrocatalysts are very much essential to know the crystallite size, particle size, binding energy and oxidation state of elements, and surface morphology/surface composition etc. There are various characterization techniques of the electrocatalysts are reported in literature like X-ray diffraction (XRD) (Zhou et al., 2003, Zhou et al., 2004, Tayal et al., 2012 and Shen et al., 2015), Transmission electron microscopy (TEM) (Zhou et al., 2003, Zhou et al., 2004 and Lee et al., 2011), X-ray photoelectron spectroscopy (XPS) (Lee et al., 2011, Shen et al., 2015 and Jacob et al., 2015) and Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analyses (Tayal et al., 2012, Shen et al., 2015 and Ribadeneira and Hoyos, 2008) which are discussed below.

The X-Ray diffraction analysis are carried out to identify the phases present in the electrocatalyst and evaluate crystallite size of the dispersed metal crystallites onto the

surface of support material. It is one of widely used technique to study the crystallography of materials. Zhou et al., (2003) and Zhou et al., (2004) studied XRD patterns of the various carbon supported Pt and Pt-based bi-metallic and tri-metallic electrocatalysts synthesized using the modified polyol method in 2θ scan range from $20º$ to $90º$. The characteristic diffraction peaks observed at 2θ of $20º$-$25º$ in all electrocatalysts were assigned to the (002) plane of support material Vulcan XC-72 carbon with hexagonal structure. The other four diffraction peaks observed at about $39º$, $46º$, $68º$ and $81º$ were attributed to the Pt (111), Pt (200), Pt (220) and Pt (311) planes, respectively, which approved the typical characteristics of face centered cubic (fcc) crystalline structure of Pt. They reported that all the supported Pt-based electrocatalysts prevailed Pt (fcc) crystal structure without indicating other distinct reflection peaks of Ru, Sn, Pd and W metals or oxides in the XRD spectra. From the results of XRD analysis, they observed that addition of Ru and Pd to Pt/C decreases the lattice parameter of Pt (fcc) crystal with peak shift to higher angles, while the addition of Sn and W results opposite effect i.e., an increase in lattice parameter. The decrease in lattice parameter of the Pt_1Ru_1/C (0.38830 nm) compared to pure Pt/C (0.39156 nm), demonstrate incorporation of Ru atoms in the Pt fcc structure and formation of PtRu alloy nanoparticles. Whereas, the additions Mo and W to Pt_1Ru_1/C showed no obvious effect on its XRD pattern and suggesting no change was detected in their crystal structure. The average crystallite sizes calculated from the XRD (220) peak were in the range of 1.8 nm to 3.2 nm. The lattice contraction of PtRu/C alloy electrocatalyst and lattice expansion of PtSn/C alloy electrocatalyst compared to Pt/C are in agreement with the observations reported by Colmati et al., (2006) and Li et al., (2007). Tayal et al., (2012) investigated the XRD patterns of $Pt_{20}Re_{20}$/C, $Pt_{20}Sn_{20}$/C, $Pt_{20}Re_{10}Sn_{10}$/C and $Pt_{20}Re_5Sn_{15}$/C (by wt. %) electrocatalysts with 40 wt. % metal loading synthesized by impregnation reduction method. The XRD patterns of electrocatalysts

showed diffraction peaks of typical Pt fcc crystalline structure and the formation of Pt and Sn alloys to some extent. The addition of Re to Pt/C or PtSn/C does not introduce much affect to the Pt crystal structure due to its atomic radius (r_{Re} = 0.137 nm) very close to Pt atomic radius (r_{Pt} = 0.139 nm). In case of PtSn/C electrocatalyst, the XRD analysis showed presence of Pt, Re metals and the formation of Pt-Sn alloy. Shen et al., (2015) studied XRD pattern of Pt/few-layered graphene (FLG), $Pt_{75}Ru_{25}$/FLG, $Pt_{75}Ni_{25}$/FLG and $Pt_{75}Ru_{15}Ni_{10}$/FLG) electrocatalysts synthesized via the polyol reduction method. It was observed that with the addition of Ru and Ni to the Pt matrix, XRD fcc peaks shifted to higher angles. No other distinct diffraction peaks of metallic Ru and Ni metals or oxides were detected, manifesting the formation of alloy in electrocatalysts. The average crystallite sizes of the Pt/FLG, PtRu/FLG, PtNi/C and PtRuNi/FLG electrocatalysts determined from XRD analysis were 1.6 nm, 1.9 nm, 1.0 nm and 1.2 nm, respectively.

The TEM analyses of electrocatalysts are performed to observe the morphology, average particle size and particle size distribution of the electrocatalysts nanoparticles. Zhou et al., (2003) and Zhou et al., (2004) investigated TEM analysis of several carbon supported Pt-based bi-metallic and tri-metallic electrocatalysts synthesized using modified polyol method. TEM results revealed that all the electrocatalyst are consisting of uniform nanosized particles and homogeneous distribution on the carbon support without agglomerations. The particle size of Pt_1Ru_1/C was ranged between 1 nm and 4 nm with an average particle size of 1.9 nm. The average particle size of the tri-metallic $Pt_1Ru_1W_1$/C, $Pt_1Ru_1Mo_1$/C and $Pt_1Ru_1Sn_1$/C were about 2.4 nm with sharp particle size distribution. The average particle sizes of the electrocatalysts obtained by TEM results were in good agreement with the crystallite size calculated the XRD data. Lee et al., (2011) studied size distribution and dispersion morphology of polyol method synthesized Pt_1Sn_1/C,

$Pt_1Sn_1Mo_{0.4}/C$ and $Pt_1Sn_1Mo_{0.6}/C$ electrocatalysts by TEM analysis. TEM images showed both dispersed nanoparticles as well as agglomerated nanoparticles onto the carbon support. They observed that average particle size and size dispersion decreases as the Mo content increase in the electrocatalysts. The average particle sizes calculated for Pt_1Sn_1/C, $Pt_1Sn_1Mo_{0.4}/C$, and $Pt_1Sn_1Mo_{0.6}/C$ electrocatalysts were 3.62 nm, 3.57 nm and 3.16 nm, respectively.

The XPS measurements are generally conducted to identify oxidation states of elements and their quantification. The XPS test is considered to be the best way to identify the presence of metal oxides or hydroxides in electrocatalysts. As metal oxides and hydroxides exist in the form of amorphous states and/or small quantities and/or small particles and thus it is difficult to detect them by XRD measurement (Antolini, 2007b). Lee et al., (2011) studied XPS analysis of Pt_1Sn_1/C and $Pt_1Sn_1Mo_{0.4}/C$ electrocatalysts synthesized by polyol method. XPS results of Pt_1Sn_1/C showed the presence of Pt^o (metallic Pt), PtO or $Pt(OH)_2$, PtO_2, Sn^o (metallic Sn) and SnO_2. The XPS measurements on $Pt_1Sn_1Mo_{0.4}/C$ indicated the presence of Pt^o (metallic Pt), PtO or $Pt(OH)_2$, PtO_2, SnO_2 and MoO_3. The addition of Mo induces negligible shift (0.1 eV change) in the binding energy (BE) of Pt and Sn and suggests no significant electronic modification on Pt and Sn in $Pt_1Sn_1Mo_{0.4}/C$. Shen et al., (2015) investigated surface composition and electronic properties of Pt/few-layered graphene (FLG), $Pt_{75}Ru_{25}/FLG$, $Pt_{75}Ni_{25}/FLG$ and $Pt_{75}Ru_{15}Ni_{10}/FLG$ electrocatalysts by XPS tests. It was observed that the BE of Pt in bi-metallic and tri-metallic electrocatalysts shifted to higher energies compared to Pt/FLG due to incorporation of Ru and Ni atoms. Pt was observed in the form of metallic Pt and PtO or $Pt(OH)_2$ in all the electrocatalysts. The XPS measurements indicate Ru existence in metallic Ru (Ru^o) and RuO_2 in both PtRu/FLG and PtRuNi/FLG electrocatalysts.

Whereas, Ni was found to exist in four different species such as metallic Ni, NiO, $Ni(OH)_2$ and NiOOH in PtRuNi/FLG electrocatalyst. Jacob et al., 2015 analyzed XPS spectra of the Pt 4f, Sn 3d and Ce 3d for each of the $Pt_{75}Sn_{25}$/C, $Pt_{50}Ce_{50}$/C, $Pt_{70}Sn_{20}Ce_{10}$/C, $Pt_{60}Sn_{20}Ce_{20}$/C and $Pt_{50}Sn_{20}Ce_{30}$/C electrocatalysts. XPS measurements indicated presence of Pt^o, PtO, PtO_2, Sn^o, SnO_x, Ce_2O_3 and CeO_2 oxides. The electrocatalysts contained bulk of non alloyed Pt and SnO_x, while electrocatalyst surface is formed by Pt-rich PtSn alloy (25-40%).

The surface morphology and porous structure of electrocatalysts are visualized by SEM measurements. The synthesized carbon supported electrocatalysts must have porous structure to ensure the transport of reactants from the bulk phase to the active electrocatalysts sites. The chemical compositions and the content of metals in synthesized electrocatalysts could be determined using EDX analysis. Tayal et al., (2012) observed the porous structure of bi-metallic $Pt_{20}Re_{20}$/C and $Pt_{20}Sn_{20}$/C, and tri-metallic $Pt_{20}Re_{10}Sn_{10}$/C and $Pt_{20}Re_5Sn_{15}$/C (by wt. %) electrocatalysts nanoparticles with uniform surface morphology by SEM analysis. The EDX measurements revealed the presence of desired elements with some variation in composition. In some cases, common impurities such as sodium, chlorine and oxygen were also detected containing less than 1 wt. %. Similar observations were observed by Tayal et al., (2011) for bi-metallic and tri-metallic Pt-Sn/C, Pt-Ir/C and Pt-Ir-Sn/C electrocatalysts synthesized by impregnation-reduction method. Shen et al., (2015) analyzed the elemental composition of the polyol method synthesized Pt/few-layered graphene (FLG), $Pt_{75}Ru_{25}$/FLG, $Pt_{75}Ni_{25}$/FLG and $Pt_{75}Ru_{15}Ni_{10}$/FLG electrocatalysts by EDX spectra analysis. The EDX elemental composition of electrocatalysts was observed close to the nominal composition. The small discrepancies in actual metal loadings of synthesized electrocatalysts with nominal weight

of 40 wt. % were also noted**.** Ribadeneira and Hoyos, (2008) analyzed EDX analysis of 10 different Pt-based bi-metallic and tri-metallic electrocatalysts synthesized using the polyol reduction method. They observed that EDX composition of bi-metallic electrocatalysts were very close to nominal composition, while for the tri-metallic electrocatalysts EDX composition were less accordant with nominal composition. They reported the polyol reduction method as a versatile and efficient technique for the synthesis of multi-metallic supported electrocatalysts.

2.1.1.2.4 Electrochemical characterization of electrodes

Methods of electrochemical calculation such as cyclic voltammetry (CV), chronoamperometry (CA) are most widely used to test the electrochemical activities of working electrodes produced from electrocatalyst ink/slurry. These electrochemical characterization techniques are sensitive, selective convenient, and less expensive (Baghbamidi et al., 2013). The electrochemical characterization of the working electrode helps to predict the formation of intermediates, poisoning species, and reaction mechanisms at fuel cell electrodes (Pramanik and Basu, 2011). Among them, cyclic voltammetry (CV) is the technique most widely used to test the electrooxidation and reduction processes of anode fuels and cathode oxidants on a suitable electrocatalyst material. The electrochemical characterization of anode and cathode are discussed in the following section.

2.1.1.2.4.1 Electrochemical characterization of anode

The electrochemical test methods used for electrooxidation of ethanol at anode using Pt-based alloy electrocatalysts in half cells are summarized in Table (2.2). The literature shows that cyclic voltammetry (CV) and chronoamperometry (CA) are the most common

techniques in electrochemical studies. The electrocatalytic oxidation of ethanol at different Pt-based electrodes, Pt-X (X = Ru, Sn, Mo) were investigated by Lamy et al., (2001) and Lamy et al., (2002). Detailed study of the reaction mechanism for ethanol electrooxidation using various techniques such as chromatographic techniques (HPLC, GC) (Hitmi et al., 1994), differential electrochemical mass spectrometry (DEMS) (Iwasita and Pastor, 1994, Schmidt et al., 1996 and Fujiwara et al., 1999) and in situ Fourier transform infrared spectroscopy (FTIRS) (Iwasita and Pastor, 1994), the following parallel and consecutive oxidation reactions on Pt electrodes in acidic medium has been proposed.

$$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^- \qquad (2.2)$$

$$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^- \qquad (2.3)$$
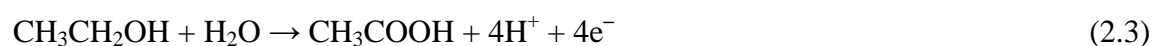
The reaction (Equation 2.2) primarily occurs at lower potentials (E < 0.6 V vs. RHE reversible hydrogen electrode) (Hitmi et al., 1994). The reaction (Equation 2.3) occurs at higher electrode potential (E > 0.8 V vs. RHE) where the water molecule is stimulated at the surface of the platinum to form oxygenated species. Dissociative adsorption of water occurs at the intermediate potential (0.6 V versus RHE < E < 0.8 V versus RHE) (Lamy et al., 2001, Lamy et al., 2002, and Hitmi et al., 1994):

$$Pt + H_2O \rightarrow Pt\text{-}OH_{ads} + H^+ + e^- \qquad (2.4)$$

In order to generate acetic acid, the oxidation of adsorbed CH_3CHO may be as follows:

$$(CH_3CHO)_{ads} + Pt\text{-}OH_{ads} \rightarrow (CH_3COOH)_{ads} + H^+ + e^- + Pt \qquad (2.5)$$
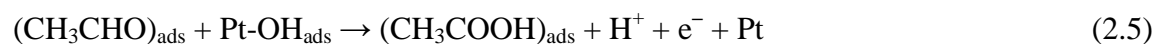
On pure Pt electrodes at room temperature, further oxidation of intermediate species into carbon dioxide is typically difficult. Infrared reflectance spectroscopy (Perez et al., 1989) and gas chromatography (Hitmi et al., 1994) clearly detected carbon monoxide, acting as

a poisoning species, and CO_2. This may be expressed by the following reactions (Equations 2.6 to 2.8):

$$Pt + CH_3CHO \rightarrow Pt\ (CO\text{-}CH_3)_{ads} + H^+ + e^- \tag{2.6}$$

$$Pt + Pt\ (CO\text{-}CH_3)_{ads} \rightarrow Pt\text{-}(CO)_{ads} + Pt\text{-}(CH_3)_{ads} \tag{2.7}$$

$$Pt\text{-}(CO)_{ads} + Pt\text{-}OH_{ads} \rightarrow 2Pt + CO_2 + H^+ + e^- \tag{2.8}$$
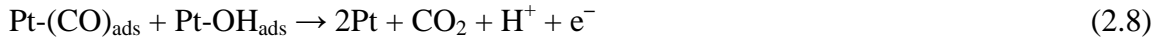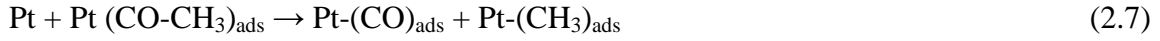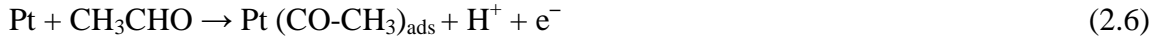
Some traces of methane were also found at low potential (E < 0.4 V versus RHE), which is represented by the mechanism of the following reaction:

$$2Pt + H_2O \rightarrow Pt\text{-}H_{ads} + Pt\text{-}OH_{ads} \tag{2.9}$$

$$Pt\text{-}(CH_3)_{ads} + Pt\text{-}H_{ads} \rightarrow CH_4 + 2Pt \tag{2.10}$$

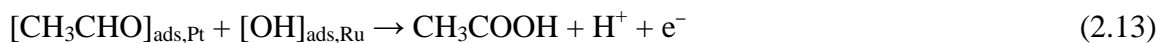The presence of poisoning species (adsorbed CO) and other two-C intermediate reaction products reduces the correspondingly the energy density and efficiency of fuel. Thus, it is important to develop new electrocatalyst materials capable of breaking ethanol molecule C-C bonds at low temperatures and CO adsorbed oxides at lower potential levels.

Pramanik and Basu, (2010) and Goel and Basu, (2015) have proposed a three-step reaction scheme for ethanol electrooxidation on PtRu/C electrocatalyst in acidic medium at moderate temperatures (< 100 ºC), as follows:

$$CH_3CH_2OH + Pt \rightarrow [CH_3CH_2OH]_{ads,Pt} \rightarrow [CH_3CHO]_{ads,Pt}, + 2H^+ + 2e^- \tag{2.11}$$

$$H_2O + Ru \rightarrow [OH]_{ads,Ru} + H^+ + e^- \tag{2.12}$$

$$[CH_3CHO]_{ads,Pt} + [OH]_{ads,Ru} \rightarrow CH_3COOH + H^+ + e^- \tag{2.13}$$

Ethanol oxidation in DEFC using bi-metallic Pt-Ru/C electrocatalyst due to the bifunctional mechanism (Garcı'a et al., 2012) of ethanol molecules is first adsorbed to the surface of Pt electrocatalyst to form acetaldehyde and then releases proton and electrons

(Equation 2.11). The dissociative adsorption of water occurs on the surface of the Ru metal of the bi-metallic Pt-Ru/C electrocatalyst, according to the second reaction stage (Equation 2.12). The adsorbed species associate with each other (e.g., $[CH_3CHO]_{ads,\ Pt}$ and $[OH]_{ads,\ Ru}$) and form acetic acid (Equation 2.13). At high potential region (Antolini, 2013) the mechanism is already given by reactions (Equation 2.5) and (Equation 2.8). Where, the activation H_2O to form the OH^- species is the rate-determining step.

Goel and Basu, (2014) investigated ethanol electrooxidation on Pt-Ru/ mesoporous carbon nitride (MCN), Pt-Ru/treated-MWCNT (t-MWCNT), Pt-Ru/MWCNT and Pt-Ru/Vulcan XC electrocatalysts in acidic medium (Fig 2.4).
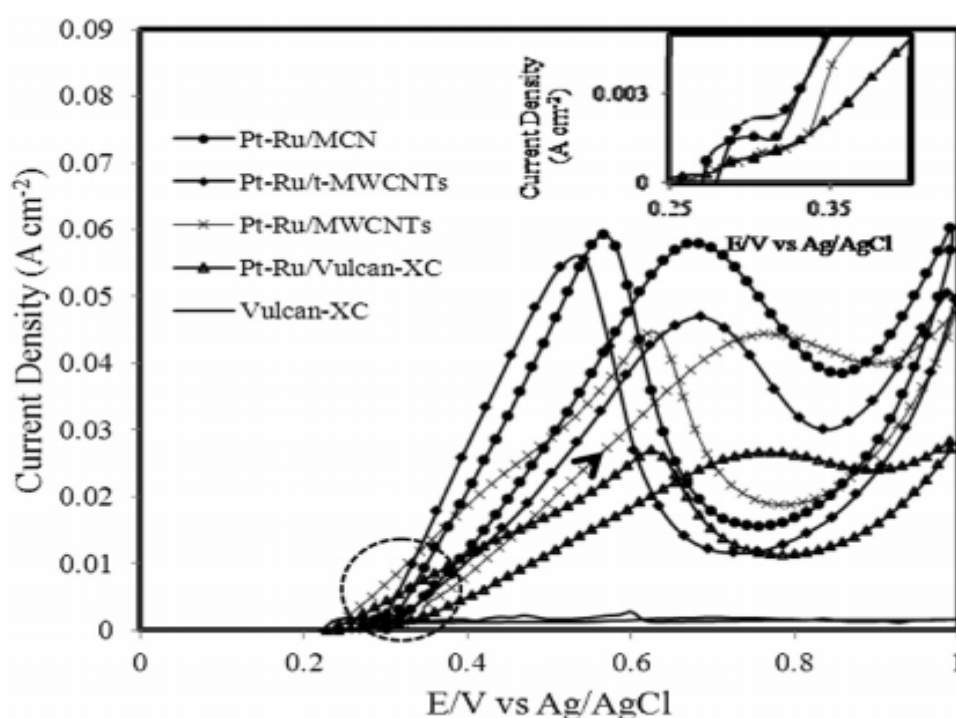

Figure 2.4 Cyclic voltammograms (CVs) of Pt-Ru/MCN, Pt-Ru/t-MWCNT, Pt-Ru/MWCNT and Pt-Ru/Vulcan XC electrocatalysts in 0.5 M H_2SO_4 and 1 M ethanol solution with a scan rate 20 mV/s and at room temperature of 25 ℃ (Goel and Basu, 2014).

The cyclic voltammetry studies reveal that activity of Pt-Ru electrocatalysts supported on MCN and t-MWCNT show higher electrocatalytic activity for ethanol electrooxidation than that of MWCNT and Vulcan XC supported Pt-Ru electrocatalysts. They claimed that Ru-t-MWCNT helps to break H_2O to OH_{ads} which favors the further oxidation of adsorbed intermediates such as CO_{ads} and CH_3CO_{ads} to CO_2 and CH_3COOH. The use MCN support extends the lattice distance as confirmed by XRD results, which facilitates the dissociative adsorption of ethanol molecule at lower potential with enhanced electrocatalytic activity.

Table 2.2 Fabrication of electrocatalyst employed for ethanol electrooxidation at the anode in acidic conditions and techniques used for the analysis of the system.

References	Electro-catalyst	Fuel/ethanol and electrolyte concentration	Subject of investigation/Major electrochemical investigation technique	Electrocatalyst and electrode preparation technique	Remarks
Spinace et al., (2004)	Pt_1Ru_3/C, Pt_1Ru_1/C and Pt_3Ru_1/C	**Fuel:** Ethanol (1 M) **Electrolyte:** H_2SO_4 (0.5 M)	Ethanol electrooxidation/cyclic voltammetry; chronoamperometry	The Pt-Ru/C electrocatalysts were prepared by the alcohol reduction process. The working electrode was prepared by a thin porous coating technique.	The electrocatalyst synthesized by co-reduction of mixed ions showed the best performance for ethanol electro-oxidation and the performance increased with the increase of Ru content.
Wang et al., (2006)	Pt_1Ru_1/C and $Pt_6Ru_3Ni_1/C$	**Fuel:** Ethanol (0.5 M) **Electrolyte:** H_2SO_4 (0.5 M)	Ethanol electrooxidation/cyclic voltammetry; chronoamperometry	The electrocatalysts were synthesized using the $NaBH_4$ reduction method. By depositing the electrocatalyst slurry on the glassy carbon substrate, the working electrode was prepared.	$Pt_6Ru_3Ni_1/C$ showed higher electrocatalytic activity than Pt_1Ru_1/C due to the promoting effect of Ni. Both of them, however, had almost the same exact electrochemically active field.

References	Electro-catalyst	Fuel/ethanol and electrolyte concentration	Subject of investigation/Major electrochemical investigation technique	Electrocatalyst and electrode preparation technique	Remarks
Wang et al., (2007)	Pt_1Ru_1/C and $Pt_6Ru_3Mo_1/C$	**Fuel:** Ethanol (0.5 M) **Electrolyte:** H_2SO_4 (0.5 M)	Ethanol electrooxidation/cyclic voltammetry; chronoamperometry	The electrocatalysts were synthesized using the $NaBH_4$ reduction method. The working electrode was prepared by pipetting the electrocatalyst suspension onto the glassy carbon substrate.	$Pt_6Ru_3Mo_1/C$ demonstrated superior performance to PtRu/C in terms of catalytic activity, durability and CO-tolerance.
Antolini et al., (2009)	Pt_1Sn_1/C, Pt_3Pd_1/C, $Pt_1Sn_1Pd_1/C$ and $Pt_1Sn_1Pd_{0.3}/C$	**Fuel:** Ethanol (1 M) **Electrolyte:** H_2SO_4 (0.5 M)	Ethanol electrooxidation/ chronoamperometry; Tests in DEFCs	The electrocatalysts were prepared by the formic acid method. The working electrode was prepared by applying the electrocatalytic ink over a carbon cloth.	PtSnPd/C displayed lower ethanol electrooxidation activity with respect to bimetallic PtSn/C. It was concluded that the only way to boost the EOR of PtSn/C was to add the third metal in the oxide form.

References	Electro-catalyst	Fuel/ethanol and electrolyte concentration	Subject of investigation/Major electrochemical investigation technique	Electrocatalyst and electrode preparation technique	Remarks
Bonesi et al., (2010)	PtSn/C PtSnNi/C	**Fuel:** Ethanol (1 M) **Electrolyte:** H_2SO_4 (0.5 M)	Ethanol electrooxidation/cyclic voltammetry; chronoamperometry; Electrochemical impedance spectroscopy (EIS)	The electrocatalysts were prepared by a modified ethylene glycol reduction method. The working electrode was prepared by applying the electrocatalytic ink over a glassy carbon disk.	The catalytic activity of the PtSnNi/C electro-catalyst for ethanol electrooxidation was higher than that of the Pt-Sn/C catalyst. The addition of Ni to PtSn/C improves the performance of ethanol electrooxidation.
Beyhan et al., (2014)	$Pt_{80}Sn_{10}M_{10}/C$ (M = Ni, Co, Rh, Pd)	**Fuel:** Ethanol (0.1 M) **Electrolyte:** $HClO_4$ (0.1 M)	Ethanol/In situ Fourier transform infrared (FTIR) spectroscopy measurements	The electrocatalysts were synthesized using the Bönnemann's colloidal method. The working electrodes were fabricated by pipetting electrocatalyst ink onto a glassy carbon/gold disk electrode using a micro syringe.	The addition of Ni or Pd to PtSn/C at low potential greatly favors the formation of acetic acid, while the incorporation of Ni or Rh contributes to the cleavage of the C-C bond in ethanol and favors the pathway of CO_2 formation.

References	Electro-catalyst	Fuel/ethanol and electrolyte concentration	Subject of investigation/Major electrochemical investigation technique	Electrocatalyst and electrode preparation technique	Remarks
Jacob et al., (2015)	$Pt_{75}Sn_{25}/C$, $Pt_{50}Ce_{50}/C$, $Pt_{70}Sn_{20}Ce_{10}/C$ $Pt_{60}Sn_{20}Ce_{20}/C$ and $Pt_{50}Sn_{20}Ce_{30}/C$	**Fuel:** Ethanol (0.5 M) **Electrolyte:** H_2SO_4 (0.5 M)	Ethanol electrooxidation/ linear sweep voltammetry (LSV); chronoamperometry (CA) measurements; single cell DEFC experiments	The electrocatalysts were synthesized by a modified formic acid method. The working electrodes were fabricated by depositing an ultra-thin layer of electrocatalyst ink on a glassy carbon disk electrode.	The higher Sn/Pt atomic content on the electrocatalyst ($Pt_{75}Sn_{25}/C$ and $Pt_{60}Sn_{20}Ce_{20}/C$) surface is more effective than the addition of Ce to PtSn/C for ethanol electrooxidation.
Corradini et al., (2015)	$Pt_{75}Pr_{25}/C$, $Pt_{70}Sn_{10}Pr_{20}/C$, $Pt_{70}Sn_{15}Pr_{15}/C$, and $Pt_{45}Sn_{45}Pr_{10}/C$	**Fuel:** Ethanol (0.5 M) **Electrolyte:** H_2SO_4 (0.5 M)	Ethanol electrooxidation/ linear sweep voltammetry (LSV); chronoamperometry (CA) measurements	The modified formic acid method was used to prepare the electrocatalysts. The working electrodes were manufactured on a glassy carbon disc electrode by depositing an ultra-thin film of electrocatalyst ink.	The $Pt_{45}Sn_{45}Pr_{10}/C$ electrocatalyst exhibited both the highest mass activity and the highest specific activity and found to be more tolerant of CO-containing intermediate species poisoning.

Spinace et al., (2004) synthesized PtRu/C electrocatalysts by alcohol reduction process for analyzing the electrochemical behavior of ethanol in acidic medium via cyclic voltammetry and chronoamperometry tests. Superior electrocatalytic activity for ethanol electrooxidation was exhibited by the PtRu/C electrocatalysts prepared by co-reduction of mixed ions than that of electrocatalysts (PtRu/C) synthesized by successive reduction of metal ions. The Pt_1Ru_3/C electrocatalyst revealed the best activity for ethanol electrooxidation among bi-metallic electrocatalysts of Pt_1Ru_3/C, Pt_1Ru_1/C and Pt_3Ru_1/C. This may be due to the presence of more species of ruthenium oxide on the surface of nanoparticle. Wang et al., (2006) studied ethanol electrooxidation on Pt-based bi-metallic and tri-metallic electrocatalysts synthesized using the $NaBH_4$ reduction process. Electrochemical studies have shown that the electrocatalytic operation of $Pt_6Ru_3Ni_1$/C electrocatalyst for ethanol electrooxidation is superior to that of Pt_1Ru_1/C electrocatalyst due to the promotion of Ni feature. Wang et al., (2007) investigated ethanol electrooxidation with Pt/C, Pt_1Ru_1/C and $Pt_6Ru_3Mo_1$/C electrocatalysts prepared by the $NaBH_4$ reduction method. The performance of the electrocatalyst $Pt_6Ru_3Mo_1$/C was found to be better than that of Pt_1Ru_1/C in terms of catalytic activity, durability and CO-tolerance. The promotional effect of Mo in the PtRuMo/C nanoparticle electrocatalyst was due to the bi-functional mechanism, the hydrogen spillover effect and the change to the Pt electronic states. Antolini et al., (2009) evaluated the effect of alloy phase characteristics of tri-metallic $Pt_1Sn_1Pd_{0.3}$/C and $Pt_1Sn_1Pd_1$/C for ethanol electrooxidation synthesized by a formic acid reduction method. They found that the electrocatalytic activity of tri-metallic PtSnPd/C electrocatalysts for ethanol oxidation was lower than that of binary PtSn/C, supported by chronoamperometry measurements and DEFC tests. It was believed that the only way to improve the ethanol electrooxidation activity of $(PtSn)_{alloy}/SnO_2$ is by adding a third metal in the oxide form. Bonesi et al., (2010) studied

ethanol electrooxidation on PtSn and PtSnNi nanoparticles supported on functionalized support such as Vulcan XC-72R synthesized by chemical reduction method. They concluded that the addition of Ni to bi-metallic PtSn/C significantly improves the catalytic performance in ethanol electrooxidation. Beyhan et al., (2014) examined the reaction mechanism of ethanol electrooxidation on PtSn-based trimetallic electrocatalysts by in situ FTIR spectroscopy. They concluded that the catalytic activity of $Pt_{80}Sn_{10}Ni_{10}/C$ and $Pt_{80}Sn_{10}Pd_{10}/C$ favored the formation of acetic acid potential at about 0.25 and 0.3 V vs. RHE, respectively. However, $Pt_{80}Sn_{10}Ni_{10}/C$ and $Pt_{80}Sn_{10}Rh_{10}/C$ showed superior performance than $Pt_{90}Sn_{10}/C$, $Pt_{80}Sn_{10}Co_{10}/C$, and $Pt_{80}Sn_{10}Pd_{10}/C$ for the formation of CO_2 during ethanol electrooxidation. Jacob et al., (2015) investigated the effect of Ce addition to PtSn/C electrocatalysts on ethanol electrooxidation behaviour and stability of tri-metallic PtSnCe/C electrocatalysts. They found that ternary PtSnCe/C electrocatalyst had significantly higher ethanol electrooxidation activity than PtCe/C and Pt/C, primarily due to the presence of Sn in electrocatalysts. It was also found that the onset potential for ethanol electrooxidation decreased with an increase in the Sn content of the electrocatalyst surface. They proposed that ethanol electrooxidation on PtSnCe/C electrocatalysts could take place through two key pathways with different potentials (0.44 and 0.55 V vs. RHE) which are highly dependent on the Ce/Sn atomic ratio. Single cell DEFC findings indicate that a higher Sn/Pt atomic content is more efficient for ethanol electrooxidation than the introduction of cerium (Ce) to PtSn/C. Corradini et al., (2015) studied the ethanol electrooxidation activity and stability on tri-metallic PtSnPr/C electrocatalysts in acidic medium by cyclic voltammetry (CV) and chronoamperometry (CA) measurements, synthesized via a modified formic acid method. It was found that the electrocatalyst $Pt_{45}Sn_{45}Pr_{10}/C$ displayed both the highest mass activity and the highest specific activity. They also argued that the stability of tri-metallic PtSnPr/C

electrocatalysts increases with the surface Sn/Pt atomic ratio. It was suggested that the dissolution of Sn and Pr oxide from PtSnPr/C electrocatalysts surface could occur through repetitive potential cycling (RPC) under the Ar atmosphere, increasing their ethanol electrooxidation catalytic activity.

It is seen from the above literature review on the electrochemical characterization of anode for ethanol electrooxidation that the types of electrocatalysts using different synthesis methods and metal composition are controlling factors which affects the activity of electrocatalysts. It is also seen that various types of electrocatalysts are giving different reaction routes/mechanism for the electrochemical oxidation of ethanol fuel in acidic medium. Thus in the present thesis work cyclic voltammetry (CV) and chronoamperometry (CA) studies were adopted for the electrochemical characterization of the synthesized electrocatalysts. The CV and CA results are discussed in chapter 5 (Page no. 136-141, 162-167, 192-197).

2.1.1.2.4.2 Electrochemical characterization of cathode

As reported in the literature that the oxygen (O_2) is converted to water at the cathode electrode via the oxygen reduction reaction (ORR) generally proceeds by two possible reaction pathways in acidic medium (i) single step four electron ($4e^-$) pathway and (ii) two step 2+2 electron pathways (Pramanik and Basu, 2011 and Martínez-Huerta and Lázaro, 2016). In direct four electrons ($4e^-$) pathway, O_2 is directly reduced to water is given by Equation (2.14):

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{2.14}$$
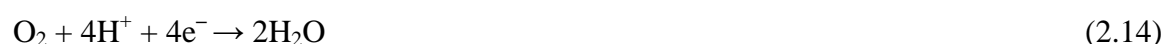
The two step pathways with two electrons ($2e^-$) transferred in each case and peroxide intermediate, are expressed by Equations (2.15) and (2.16).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad\qquad\qquad\qquad (2.15)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad\qquad\qquad\qquad (2.16)$$

In two step pathway involving two electrons, O-O bond in adsorbed O_2 molecule is not broken thereby resulting H_2O_2 formation which electrode surface and activity (Equation 2.15). Thus, obtain maximum energy capacity, the electroreduction of O_2 must follow four electron ($4e^-$) pathway.

Pramanik and Basu, (2011) studied the electroreduction beahaviour of O_2 on commercial electrocatalysts Pt-black high surface area (HAS), Pt/C and PtRu/C in acid medium (0.5 M $HClO_4$). Fig (2.5 (a)) shows cyclic voltammetry of Pt/C in O_2 and N_2 saturated electrolyte solution. The presence of oxygen influences the electroreduction behaviour Pt electrode surface with an increase in reduction current. The oxygen reduction peaks of Pt-black HAS, Pt/C and PtRu/C electrocatalysts were observed at electrode potentials of 0.47 V, 0.526 V and -0.02 V, respectively (Fig 2.5 (b)). Moreover, a well pronounced peak in the hydrogen adsorption-desorption region was also observed for Pt-black HAS and Pt/C electrocatalysts. All the test electrocatalysts showed higher current density peak for oxygen-saturated electrolyte compared to nitrogen saturated. The authors argued that oxygen reduction reaction on Pt-black HAS and Pt/C electrocatalysts followed a four-electron pathway mechanism (Equation 2.14) as confirmed by the single reduction peak observed in CV results (Fig 2.5 (a) and (b)).
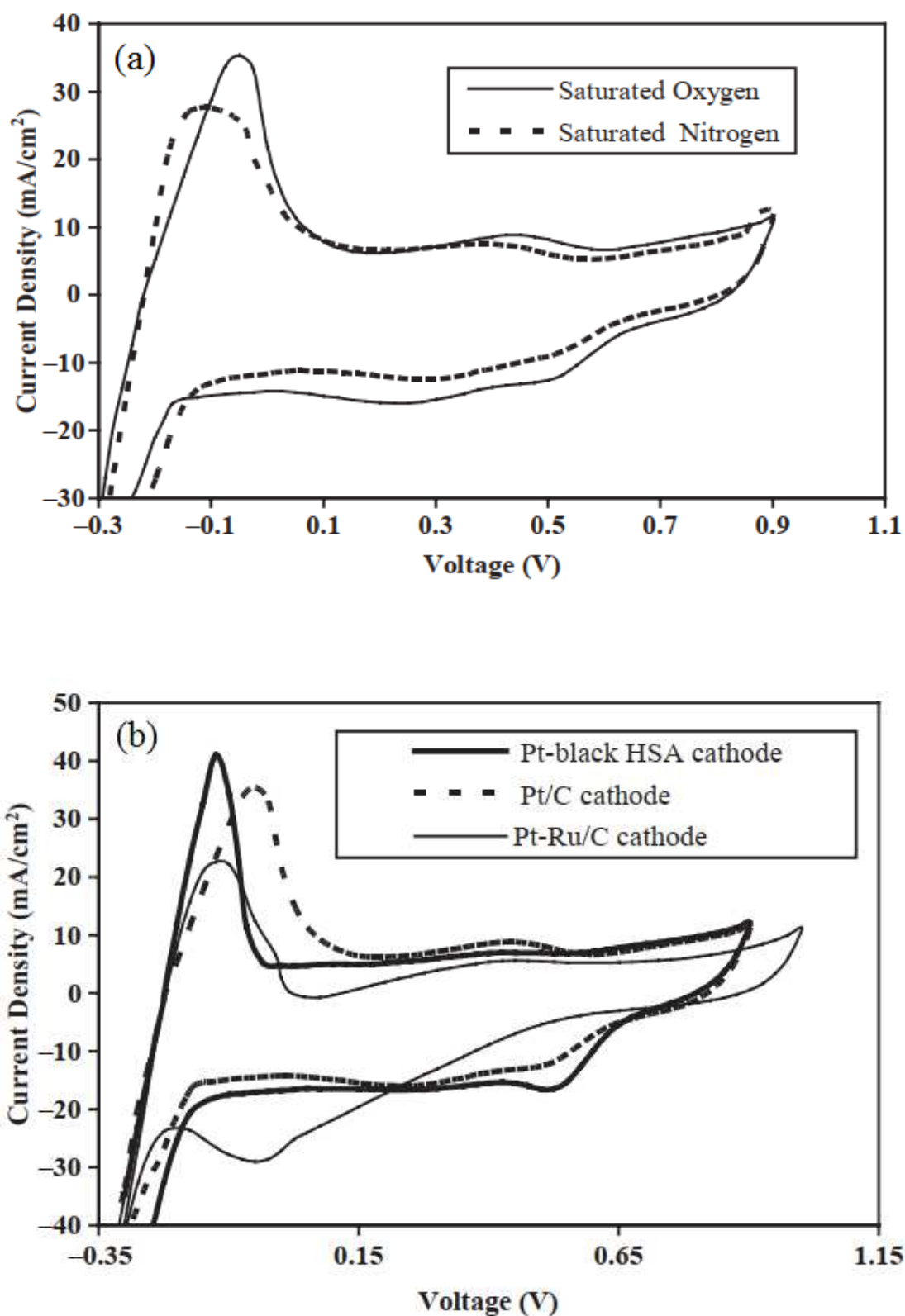
Figure 2.5 Cyclic voltammograms (CVs) of (a) Pt/C cathode in 0.5 M $HClO_4$ saturated with oxygen and nitrogen gas and (b) PtRu/C, Pt-black HSA and Pt/C cathode in the presence of oxygen in 0.5 M HClO4 solution with scan rate of 10 mV/s at a temperature of 42 ºC (Pramanik and Basu, 2011).

Rao and Viswanathan, (2010) investigated oxygen reduction behaviour on Pd/C and Pd-Co-Mo/C electrocatalyst using rotating disk electrode (RDE) measurements. Moreover, the addition of alloying elements Co and Mo to Pd suppress the formation of (hydr)oxy species on Pd surface. The authors observed comparable ORR activity of heat treated Pd-Co-Mo/C at 973 K with that of commercial Pt/C (E-TEK). In addition, Pd-Co-Mo/C showed higher ethanol tolerance than Pt/C and followed the four-electron pathway leading to water. Single cell DEFC tests and stability test under DEFC operation for 50 h demonstrated also comparable performance of Pd-Co-Mo/C with that of commercial Pt/C. Meenakshi et al., (2014) synthesized Pt-TiO_2/C (Pt:Ti atomic ratio of 1:1, 2:1 and 3:1) by alcohol reduction reaction and its electrochemical studies were evaluated using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques. The Pt-TiO_2/C shows significant improvement in ORR than Pt/C. The DEFC employing Pt-TiO_2/C as cathode electrocatalyst shows enhanced performance compared to Pt/C. Wang et al., 2021 fabricated ternary $Pt_{22}Pd_{27}Cu_{51}$ ultrathin (~5 nm) NWs via a facile surfactant free strategy and performed CV and LSV tests for ORR electrochemical evaluation. The authors reported that $Pt_{22}Pd_{27}Cu_{51}$ ultrathin exhibited enhanced electrocatalytic activity towards ORR. The enhanced electrocatalytic performance of $Pt_{22}Pd_{27}Cu_{51}$ ultrathin could be attributed to the synergistic effect between Pt, Pd and Cu, modified electronic structure with anti CO-poison ability.

Thus, in this thesis work, cyclic voltammetry (CV) and chronoamperometry (CA) have been used as electrochemical techniques to evaluate the electrocatalytic activity of anode and cathode electrocatalysts. From the literature survey, it is clear that Pt-based electrocatalyst is highly effective for ORR in acidic medium. Thus, in this thesis work, commercial electrocatalyst Pt/C (40 wt. %, Alfa Aesar) was used for cathode fabrication

and the electrochemical performance of cathode was evaluated by CV analysis. The CV results are discussed in chapter 5 (Page no. 141-142).

2.1.2 Performance of Pt-based anode electrocatalysts in single DEFC study

The majority of work were performed using Pt-based bimetallic and trimetallic electrocatalysts is limited to electrocatalyst synthesis and electrochemical characterization. Very few research studies have been conducted in detail on a single cell DEFC studies using synthesized anode electrocatalysts in an acidic medium. Table (2.3) shows the process parameters and single cell DEFC output data using Pt-based bi-metallic and tri-metallic electrocatalysts. Zhou et al., (2003) formulated the bi-metallic Pt_1Ru_1/C electrocatalyst and evaluated its performance in acidic medium for ethanol fuel using commercial Nafion® 115 membranes. The anode electrocatalyst loading was 1.33 mg Pt/cm^2 of Pt_1Ru_1/C. The maximum open circuit voltage (OCV) and maximum power density (P_{max}) of 0.667 V and 28.54 mW/cm^2 were obtained at a cell temperature of 90 ℃, respectively. Liu et al., (2005) reported cell performance of bi-metallic alloyed Pt_1Ru_1/C electrocatalyst synthesized by a microwave-assisted polyol process. A maximum OCV of ~0.85 V with a power density of ~60 mW/cm^2 was achieved at a cell temperature of 80 ℃. However, anode and cathode electrocatalysts had a very high loading of Pt_1-Ru_1/C of 3 mg Pt/cm^2 and Pt/C (40 wt. %, E-TEK) of 2 mg Pt/cm^2, respectively. Similarly, Rousseau et al., (2006) obtained the maximum OCV and power density of 0.75 V and 50.0 mW/cm^2, respectively using tri-metallic $Pt_{86}Sn_{10}Ru_4/C$ as anode electrocatalyst at a cell temperature of 80 ℃. Very high loading of anode $Pt_{86}Sn_{10}Ru_4/C$ (3 mg/cm^2) and cathode of Pt/C (40 wt. %, E-TEK) of 2 mg Pt/cm^2 were used. Antolini et al., (2007) reported the formic acid reduction method for tri-metallic $Pt_1Sn_1Ru_{0.3}/C$ electrocatalyst synthesis to improve the presence of Sn and Ru oxides in

the PtSnRu with crystallite size of 2.7 nm. The maximum power density of 32 mW/cm^2 was obtained at a cell temperature of 90 ℃. The anode and cathode electrocatalyst was at a low loading of $Pt_1Sn_1Ru_{0.3}$/C of 1 mg/cm^2 and Pt/C (20 wt. %, E-TEK) (1 mg/cm^2), respectively. Ribadeneira and Hoyos, (2008) reported single cell DEFC experiments using 10 different catalytic mixtures as anode and Pt/C (40 wt. %, E-Tek) as cathode electrocatalyst. The maximum power density of 3.8 mW/cm^2 was achieved using $Pt_{75}Ru_{15}Ni_{10}$/C (20 wt. %) as an electrocatalyst at a cell temperature of 80 ℃. It has been observed that the addition of Ni to the anode improves the cell efficiency of DEFC. Tayal et al., (2012) reported the addition of Re to Pt-Sn/C electrocatalyst, which contributes to the breakup of C-C bond during DEFC ethanol electrooxidation. The maximum OCV of 0.64 V and a power density of 30.5 mW/cm^2 were obtained, respectively, at a cell temperature of 100 ℃. They used higher cell temperature (100 ℃) and high loading of both anode and cathode (2 mg/cm^2). A maximum OCV of 0.64 V and a power density of 30.5 mW/cm^2 were obtained at a cell temperature of 100 ℃, respectively. They used higher cell temperature (100 ℃) and high loading of both anode and cathode (2 mg/cm^2). Chu and Shul, (2010) applied combinatorial chemistry to determine the optimum composition of tri-metallic PtRuSn/C electrocatalysts for the low-temperature direct alcohol fuel cells fed with methanol, ethanol, and 2-propanol. It was observed that the $Pt_{80}Ru_{20}Sn_0$/C had the highest power density and OCV for methanol electro-oxidation, $Pt_{50}Ru_0Sn_{50}$/C for ethanol, and $Pt_{20}Ru_{70}Sn_{10}$/C for 2-propanol in single cell DEFC results, respectively. The maximum OCV of 0.722 V and a power density of 35.3 mW/cm^2 were obtained, respectively, at a cell temperature of 88 ℃. However, a high loading of anode $Pt_{50}Ru_0Sn_{50}$/C (4 mg/cm^2) and cathode of Pt/C (60 wt. %, JM) of 4 mg/cm^2 was used. Goel and Basu, (2014) studied the effect of support material for ethanol electrooxidation including mesoporous carbon nitride (MCN), multiwall carbon nanotubes (MWCNTs),

functionalized MWCNTs (f-MWCNT) and Vulcan-XC on the catalytic activity of on bi-metallic Pt-Ru for ethanol electrooxidation. The Pt-Ru/f-MWCNT electrocatalyst was used as an anode at a cell temperature of 100 ℃ to achieve a maximum OCV of 0.77 V and a power density of 50.8 mW/cm^2. The anode and cathode electrocatalyst were of Pt-Ru/f-MWCNT of 2 mg/cm^2 loading and Pt/C (40 wt. %, JM) (1 mg/cm^2), respectively. It was claimed that the high electrocatalytic activity of Pt-Ru/f-MWCNT electrocatalyst might be ascribed to the unique structural characteristics and a small number of organic impurities in f-MWCNT. Pramanik et al., (2008) investigated ethanol electrooxidation using commercial Pt-Ru/C (40%:20% by wt., JM) electrocatalyst in the anode and synthesized Nafion$^®$ 117 membrane at 90 ℃ for the anode and 60 ℃ for the cathode. The maximum OCV of 0.815 V and a power density of 10.30 mW/cm^2 were obtained using 2 M ethanol as anode fuel. The anode and cathode electrocatalyst were of Pt-Ru/C (40%:20% by wt., JM) of 1 mg/cm^2 and Pt-black high surface area (HAS, JM) (1 mg/cm^2), respectively.

Table 2.3 Synthesis methods of carbon supported Pt-based electrocatalysts as potential anode materials for direct alcohol fuel cell (DEFC).

References	Synthesis method	Process parameters and electrolyte used	Cell performance
Zhou et al., (2003)	Polyol reduction method	Electrolyte: Nafion® 115 Cell temperature: 90 °C Anode: Pt_1-Ru_1/C (Pt 20 wt. %) Loading: 1.33 mg Pt/cm^2 Cathode: Pt /C (20 wt. %, JM[#]) Loading: 1 mg/cm^2) Fuel: ethanol (1 M) (1.0 ml/min) Oxidant: unhumidified O_2 (120 ml/min)	P^*_{max}: 28.54 mW/cm^2 OCV[**]: 0.677 V
Liu et al., (2005)	Microwave-assisted polyol process	Electrolyte: Nafion® 117 Cell temperature: 80 °C Anode: Pt_1-Ru_1/C (20 wt. %) Loading: 3 mg Pt/cm^2 Cathode: Pt/C (40 wt. %, E-TEK) Loading: 2 mg Pt/cm^2 Fuel: ethanol (2 M) (2 ml/min) Oxidant: humidified O_2 (500 cm^3/min)	P_{max}: ~ 60 mW/cm^2 OCV: ~ 0.85 V
Rousseau et al., (2006)	Bonnemann method/Collo-idal method	Electrolyte: Nafion® 117 Cell temperature: 80 °C Anode: $Pt_{86}Sn_{10}Ru_4$/C (60 wt. %) Loading: 3 mg/cm^2 Cathode: Pt/C (40 wt. %, E-TEK) Loading: 2 mg Pt/cm^2 Fuel: ethanol (2 M) (10 ml/min) Oxidant: oxygen (300 ml/min)	P_{max}: 50 mW/cm^2 OCV: 0.75 V

[*]P_{max} - maximum power density (mW/cm^2)

[**]OCV- Open circuit voltage (V)

[#]JM - Johnson Matthey

References	Synthesis method	Process parameters and electrolyte used	Cell performance
Antolini et al., (2007)	Formic acid reduction method	Electrolyte: Nafion® 115 Cell temperature: 90 °C Anode: Pt_1-Sn_1-$Ru_{0.3}$/C (20 wt. %) Loading: 1 mg /cm^2 Cathode: Pt /C (20 wt. %, E-TEK) Loading: 1 mg /cm^2 Fuel: ethanol (1 M) (1.0 ml/min) Oxidant: unhumidified O_2 (120 ml/min)	P_{max}: 32 mW/cm^2 OCV: 0.72 V
Ribadeneira and Hoyos, (2008)	Polyol reduction method	Electrolyte: Nafion® 117 Cell temperature: 80 °C Anode: $Pt_{75}Ru_{15}Ni_{10}$/C (20 wt. %) Loading: 2 mg Pt/cm^2 Cathode: Pt/C (40 wt. %, E-TEK) Loading: 1 mg Pt/cm^2 Fuel: ethanol (1 M) (2 ml/min) Oxidant: humidified O_2 (20 cm^3/min)	P_{max}: 3.8 mW/cm^2 OCV: ~ 0.53 V
Tayal et al., (2012)	Impregnation reduction method using H_2 as reducing agent	Electrolyte: Nafion® 117 Cell temperature:100 °C Anode: $Pt_{20}Re_5Sn_{15}$ (wt. %)/C (40 wt. %) Loading: 2 mg/cm^2 Cathode: Pt/C (40 wt. %, JM) Loading: 2 mg/cm^2 Fuel : ethanol (5 M) (1 ml/min) Oxidant: oxygen (300 ml/min)	P_{max}: 30.5 mW/cm^2 OCV: 0.64 V

References	Synthesis method	Process parameters and electrolyte used	Cell performance
Chu and Shul, (2010)	Impregnation reduction method using $NaBH_4$ as reducing agent	Electrolyte: Nafion$^®$ 117 Cell temperature: 88 ℃ Anode: $Pt_{50}Ru_0Sn_{50}$/C (40 wt. %) Loading: 4 mg/cm^2 Cathode: Pt /C (60 wt. %, JM) Loading: 4 mg/cm^2 Fuel: ethanol (2 M) (1.8 ml/min) Oxidant: humidified O_2 (300 ml/min)	P_{max}: 35.3 mW/cm^2 OCV: 0.722 V
Goel and Basu, (2014)	Impregnation reduction method using H_2 as reducing agent	Electrolyte: Nafion$^®$ 117 Cell temperature:100 ℃ Anode: Pt_1-Ru_1/f-MWCNT (40 wt. %) Loading: 2 mg /cm^2) Cathode: Pt /C (40 wt. %, JM) Loading: 1 mg/cm^2) Fuel: ethanol (2 M) (1.0 ml/min) Oxidant: humidified O_2 (60 ml/min)	P_{max}: 50.8 mW/cm^2 OCV: 0.77 V
Pramanik et al., (2008)	Commercial	Electrolyte: Synthesized Nafion$^®$ 117 Cell temperature: 90 ℃ Anode: Pt-Ru /C (40%:20% by wt., JM) Loading: 1 mg/cm^2 Cathode: Pt black-HSA (JM) Loading: 1 mg/cm^2 Fuel : ethanol (2 M) (1.2 ml/min) Oxidant: oxygen	P_{max}: 10.3 mW/cm^2 OCV: 0.815 V

It is evident from the above-mentioned comprehensive literature survey that several research studies have been performed on Pt-based bi-metallic and tri-metallic electrocatalysts for single-cell DEFC applications. Almost no work on Pt-based bi-

metallic and tri-metallic electrocatalysts supported on functionalized acetylene black (C_{AB}) and functionalized multi-walled carbon nanotubes (f-MWCNT) 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. In addition, the comprehensive studies on bi-metallic Pt-Ru/C_{AB} electrocatalysts synthesized by different chemical synthesis routes and thorough physicochemical characterization of the electrocatalysts have not been reported in the published literature till date. Thus, a thorough analysis of the synthesized carbon supported Pt-based bi-metallic and tri-metallic electrocatalysts of different weight/atomic ratio followed by physicochemical characterization and evaluation of their electrocatalytic activity in half cells and single cell DEFC have been performed and reported in the thesis. The synthesized electrocatalyst was further tested in a single cell DEFC tests to determine optimum conditions for different cell parameters, e.g. ethanol concentration, anode electrocatalyst loading, cathode electrocatalyst loading and cell temperature to achieve maximum cell performance.

2.2 Objectives

The comprehensive literature review reveals that development work on Pt-based bimetallic and tri-metallic anode electrocatalysts for the electrooxidation of ethanol in direct ethanol fuel cell is needed as half-cell and single-cell studies show promising results in terms of power density and cell voltage. A thorough study is needed to fully understand the effect of various parameters on electrocatalyst synthesis and single cell performance using commercial Nafion$^{®}$ 117 membrane. The thesis has the following the objectives for fulfilling these requirements:

1. To synthesize carbon supported Pt-based bi-metallic and tri-metallic electrocatalysts of different combinations by the polyol reduction method (PLM) and the formic acid method (FAM).

2. To study the physicochemical properties of synthesized electrocatalysts.

3. To study the electrochemical properties of fabricated electrodes made of synthesized electrocatalysts.

4. To study the performances of various synthesized anode electrocatalysts in PEM based DEFC and determine the optimum values of different parameters like electrocatalysts types, electrocatalyst loading at the anode, ethanol concentration and cell temperature to achieve the highest cell performance in terms of power density.

5. To study the stability of fabricated proton exchange membrane (PEM)-based DEFC.

6. Optimization and validation of process parameters using response surface methodology (RSM) for effective power generation from a PEM based DEFC.

The next chapter describes the experimental detail related to the development of PEM-based DEFC using laboratory synthesized anode electrocatalysts for ethanol fuel, synthesis of carbon supported Pt-based anode electrocatalysts and their physicochemical properties, anode and cathode preparation and properties, electrochemical analysis of fabricated electrodes through cyclic voltammetry and chronoamperometry tests, single cell performance and stability test of single cell.