CHAPTER I

Introduction

1.1 Overview of fuel cell

Development of efficient and eco-friendly energy conversion and storage devices have become extensively researched area due to present energy crisis. Fuel cells are promising renewable energy conversion devices which convert chemical energy into electrical energy. Unlike batteries where reactants are stored inside the cell compartment, fuels (hydrocarbon, hydrogen, alcohol) are constantly fed from outside the cell compartment in fuel cells [1]. Moreover, recharging a battery takes much time than refueling of an external fuel. Therefore, fuel cells can be regarded as suitable alternative to conventional batteries. Fuel cells do not store charges but directly deliver electricity obtained from the chemical reaction of reactants. The main advantages of fuel cells over conventional batteries are increased operation time, extended durability, compact load and ease of recharging [2]. Fuel cells have been regarded as promising renewable energy source with immense applications in portable electronics such as cellular phones, laptop, notepad, battery chargers, electronic appliances, stationary items and electric vehicles [3, 4].

Table 1.1: *Types of fuel cells and their features.*

Fuel cell type	Operating temperature	Electrolyte used	Efficiency	Output power	Applications
Alkaline Fuel Cell (AFC)	90-100 °C	Aqueous solution of potassium hydroxide (KOH)	60%	10-100 kW	• Armed forces • Space vehicles
Solid Oxide Fuel Cell (SOFC)	500-1000 °C	Yttria added solid zirconium oxide	60%	1 kW-2 MW	• Decentralized electricity generation
Molten Carbonate Fuel Cell (MCFC)	600-700 °C	Molten mixture of lithium and potassium carbonates	50%	300 kW-3MW	• Electric utility • Distributed generation
Phosphoric Acid Fuel Cell (PAFC)	150-200 °C	Phosphoric acid soaked in matrix	40%	400 kW	• Stationary power • Transportation
Proton exchange membrane fuel cell (PEMFC)	50-80 °C	Perfluoro sulphonic acid	40-60%	1-100 kW	• Backup and portable power • Transportation

1.2 Direct methanol fuel cell (DMFC)

Hydrogen has been used in fuel cells with many advantages such as environment friendliness and high power density. Moreover, the fast reaction kinetics in hydrogen fuel cell results into excellent cell performance. However, the major limitations are difficulty in storage, transportation and handling of hydrogen. Therefore, to overcome these issues, liquid fuels including methanol, ethanol, propanol, ethylene glycol, formic acid have been used to draw hydrogen for fuel cell applications. In this process, liquid fuel is converted into hydrogen by using a fuel reformer and therefore overall cost of the cell increases [5]. However, in direct alcohol fuel cells, the liquid fuels can be directly fed into the fuel cell without using a reformer system [6-9]. Among different alcohols, methanol attracts much attention since it is liquid at room temperature having high energy density (5.04 kWh L^{-1}) and easy to store and transport and also it can be processed from various carbon based components including biomass, coal, wood and natural gas [10-13]. DMFC is based on proton exchange membrane (PEM) technology, where a polymer electrolyte membrane is used similar to proton exchange membrane fuel cell (PEMFC). DMFCs have gained much attention of the researchers due to simple design, low temperature (60-120 ^{o}C) operation, cost effective, easy portability and lightweight. Moreover, the lifetime of DMFC is also longer than that of conventional lithium ion batteries and also refuelling can be done by simply replacing cartridge of the fuel.

1.2.1 Operating principle of DMFC

Apart from supplied fuel, the main operating principle of DMFC is similar to PEMFC. The major components of DMFC are anode and cathode that are separated by a proton conducting electrolyte membrane. Figure 1.1 displays the schematic illustration of DMFC system showing basic operating principle of DMFC with reactant and exhaust components and directions of ions and electrons. In DMFC, methanol (CH_3OH) is oxidized into carbon dioxide (CO_2) and water (H_2O) and thus chemical energy is converted into electrical energy. At the anode side, methanol unit reacts with water molecule and generates carbon dioxide, six protons and six electrons. This half-cell reaction occurred at anode is known as methanol oxidation reaction (MOR) [14].

At anode: $\mathrm{CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-}$ E^0_{anode}=0.02 V (vs. SHE) (1.1)

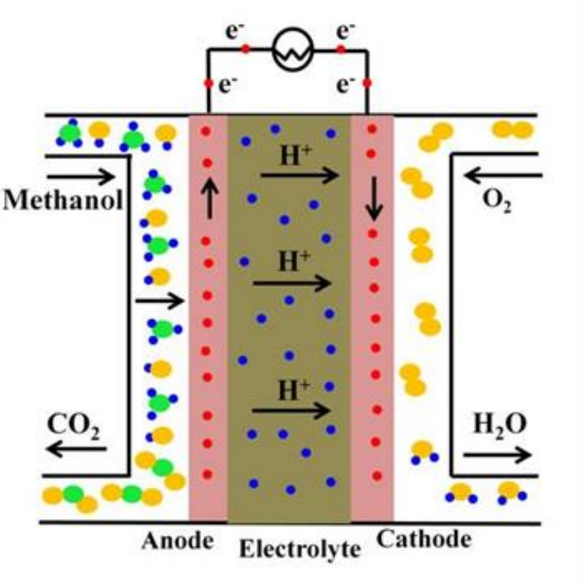

Figure 1.1: *Schematic representation of DMFC.*

The protons migrate via the electrolyte towards cathode while electrons flow towards cathode through the external circuit. The produced CO_2 gas is exhausted by the electrolyte. The protons flowing through electrolyte solution and the electrons migrating via external circuit reach at the cathode, and O_2 is reduced forming H_2O molecules [15]. This half-cell reaction is named as oxygen reduction reaction (ORR) [14]:

At cathode: $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ $E^0_{cathode}$=1.23 V (vs. SHE) (1.2)

The overall cell reaction in DMFC is shown below [14]:

Overall reaction: $CH_3OH + \frac{3}{2}O_2 \rightarrow 2H_2O + CO_2$ E_{cell}=1.21V (vs. SHE) (1.3)

The electric potential generated between the anode and cathode due to excess electrons produced at the anode, generates a current in external circuit and thus the fuel cell can act as a power source. The theoretical voltage of DMFC due to overall reaction is 1.21 V with maximum theoretical efficiency of 96.5%, but practically this voltage and efficiency are not attainable due to CO poisoning and different types of losses including activation loss, ohmic loss and concentration loss as well as methanol crossover in the electrolyte [16, 17].

1.2.2 Methanol oxidation reaction (MOR) mechanism

In 1988, MOR mechanism was reviewed by R. Parsons et al. [14], which can be briefly discussed as follows: (i) methanol molecules are adsorbed over the catalyst surface by dehydrogenation, (ii) adsorbed molecules are dissociated due to activation of C-H bond, (iii) water molecules are adsorbed and activated to release oxygen (O_2) molecule and (iv) CO_2 is generated upon addition of O_2 to the surface of adsorbed intermediates formed during methanol oxidation. Figure 1.2 illustrates the methanol oxidation mechanism over Pt surface [18, 19].

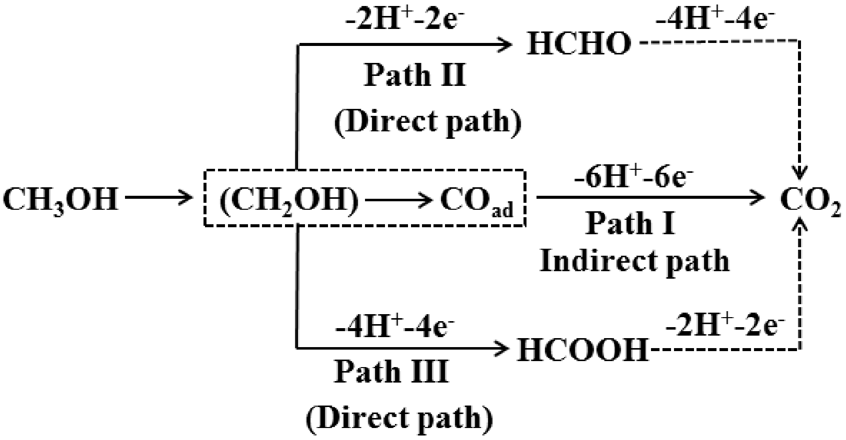

Figure 1.2: *Schematic of different pathways for MOR.*

Figure 1.2 shows that the carbonaceous intermediates formed during MOR are strongly adsorbed onto the Pt surface. Therefore, surface area of the catalyst decreases and thus the activity of DMFC. Bagotzky et al. [20] and Parsons et al [14] suggested that MOR can be explained by dual path mechanism. One is indirect mechanism in which methanol molecules are initially get oxidized into CO and then to CO_2 (path I in Figure 1.2), while the other (paths II and III as shown in Figure 1.2) is direct, where methanol units are directly get oxidized to CO_2 without forming toxic CO gas.

1.2.3 Applications of DMFC

Nowadays, much effort has been given on commercialization and applications of DMFC in different fields. The widespread uses of DMFC's are in automotive sectors i.e. cars, motorcycles, trucks, and portable electronic devices such as cellular phones, notepad, laptop etc.

1.2.3.1 Transport applications

There are some disadvantages related to internal combustion engine such as low efficiency and air-pollution. Therefore, the internal combustion engine can be replaced by DMFC having high efficiency, low cost, light weight and high-power densities [21]. In 2003, Yamaha (Japan) launched a motorcycle powered by the FC06 prototype of DMFC [22]. 25 kW DMFC is manufactured by Toyota (Japan), which can operate simultaneously with a battery pack [22]. A hybrid system of EFOY DMFC and Li-ion battery was developed by Smart Fuel Cell AG for electric vehicles of weight less than 500 kg [23]. An automatic control system is equipped with DMFC to constantly monitor the charge state of the battery. DMFC starts charging the battery whenever the charge state goes down below a certain level. Thus, the efficiency of the system is increased by eliminating unfavourable operation mode.

1.2.3.2 Portable applications

Recently, lots of efforts have been made to use DMFC in mobile phones, notebook computers, laptops, camera and electronic gadgets. Researchers are constantly trying to overcome the drawbacks of DMFC to replace lithium ion batteries, which are now being used in laptops and mobile phones. Solid State Research Centre of Motorola Labs in USA, in partnership with Los Alamos National Laboratory (LANL), USA, is trying to develop low power DMFCs (>300 mW) for mobile phone applications [24]. In 2006, Panasonic showed their prototype of a DMFC in laptops, which can supply power to a computer about 20 h in conjunction with laptop battery using 200 ml of methanol [25]. In the year 2009, a cordless mobile phone charger powered by DMFC and Li ion battery hybrid was launched by Sony [22]. Four DMFC single cells with each of power 550-600 mW and sharing a tank of 270 ml methanol was used to drive the cordless mobile phone. The Li-ion battery was used to supply higher power outputs when required. The maximum power output provided by the hybrid system is about 10 W without refuelling for one year considering 3h/week use.

1.2.4 Components of DMFC

DMFC is made up of proton exchange membrane (electrolyte) that is in contact with both the electrodes on each side. This basic unit is heart of DMFC named as membrane electrode assembly (MEA). A schematic diagram of MEA is presented in Figure 1.3.

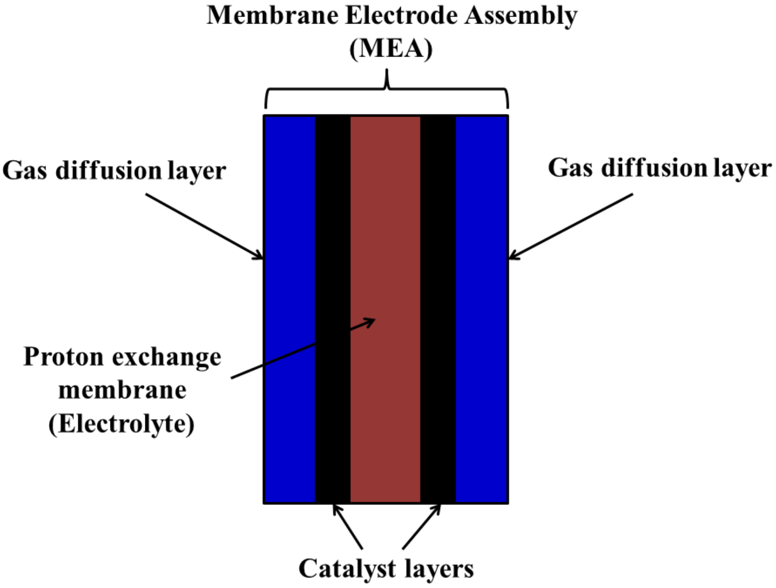

Figure 1.3: *Schematic diagram of membrane electrode assembly (MEA).*

The main parts of MEA are: (i) a proton exchange membrane (PEM) and (ii) the two electrodes as shown in Figure 1.3 [26]. The MEA plays a pivotal role for proper functioning of DMFC. The three transport mechanisms governed by MEA are: (i) the transfer of protons (H^+ ions) from PEM to catalyst layer, (ii) transfer of electrons to catalyst layer from current collector via gas diffusion layer and (iii) diffusion of reactant and exhaust gases to and from the catalyst layer. MEA is the core of DMFC where all the electrochemical reactions can occur that finally produce electric current [27]. All the components of MEA are discussed in detail:

1.2.4.1 Electrode

The major parts of an electrode in DMFC are comprised of catalyst layer and gas diffusion layer. PEM and catalyst surfaces are connected through the electrode. Moreover, the channels for passage of fuels and the current collectors are also linked via the electrodes. The electrodes have different functions that are discussed below [28]:

i. At anode, methanol is supplied and then distributed whereas at cathode, oxidant i.e. oxygen is supplied and distributed.
ii. Electron is conducted and catalysis occurs at both the electrodes.
iii. Protons are transported from the anode to the electrolyte and then from the electrolyte to the cathode.
iv. Transportation of water and heat energy.

Figure 1.4 shows the transport process of reactants in electrode [29]. For better transport mechanism, the electrode must fulfill some basic criteria such as presence of porous electroactive sites with high conductivity. The performance of DMFC basically depends upon the structure of electrodes that controls kinetics of the reaction. Much effort has been given by the researchers to develop porous electrode materials with large surface area, good conductivity, high electrochemical and mechanical stability [1]. Subdivisions of electrodes are: (a) gas diffusion layer and (b) catalyst layer.

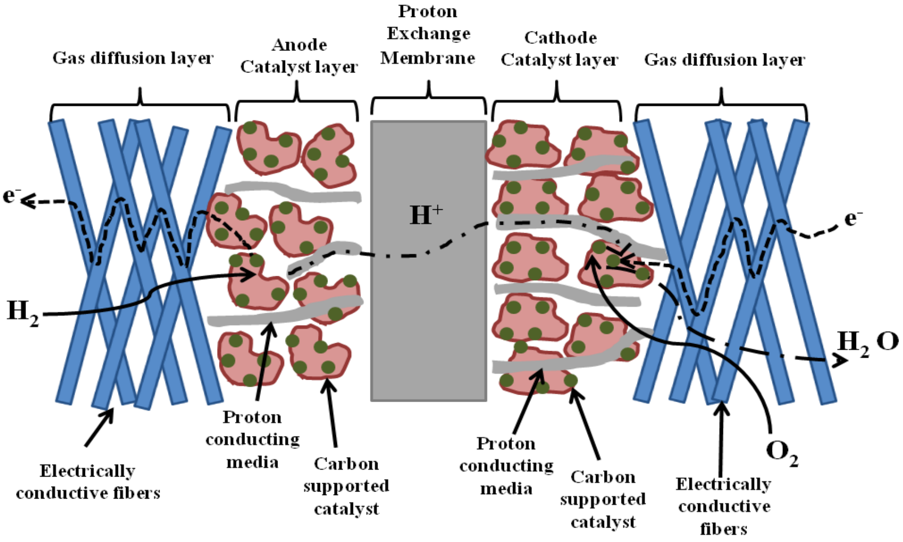

Figure 1.4: *Schematic for the transport phenomena of reactants in electrode.*

1.2.4.2 Gas diffusion layer

The gas diffusion layers are porous, electrically and thermally conductive medium that play important role for proper functioning of DMFC [30, 31]:

i. Controls diffusion of reactants.
ii. Allows removal of by-products from catalyst layer.
iii. Provides paths for transportation of electrons between the catalyst layer and current collector.
iv. Water management by ensuring the exact amount of water to reach the membrane and ejecting excess water and thus prevent flooding.
v. Provides mechanical support to hold the delicate membrane electrode assembly from expansion caused during absorption of water.
vi. Heat management during operation.

Two basic structural factors of diffusion layer influence the activity of DMFC [30]: one is tortuosity, which has an effect on passage of reactants and another is surface roughness and wettability behavior. Generally, gas diffusion layers are made up of carbon cloth and carbon paper within a thickness range from 100 to 400 μm and also pre-treated with PTFE (polytetrafluoroethylene) to avoid blocking of the pores by water [32].

1.2.4.3 Catalyst layer

Both the electrodes in a DMFC i.e. anode and cathode are consist of catalyst layer, where all the electrochemical reactions occur. The methanol molecules are dissociated into protons and electrons at anode while at cathode; oxygen molecules reduce and combine with protons to form water. Therefore, the catalyst layers are also known as active layers, where the electroactive sites are present for half-cell reactions. The catalyst layer must be in close contact with electrolyte, fuel methanol, and current collector; and simultaneously the unused fuel and by-products must go out from the system without restricting the supply of fresh fuels. The point, at which the three different phases i.e. ionic conductor (electrolyte), electronic conductor (carbon supported catalyst particles) and pores for the passage of gaseous and liquid fuels intersect, is referred as triple phase boundary (TPB) zone [33]. Figure 1.5 depicts the schematic diagram of electrode/electrolyte interface including the TPB zone.

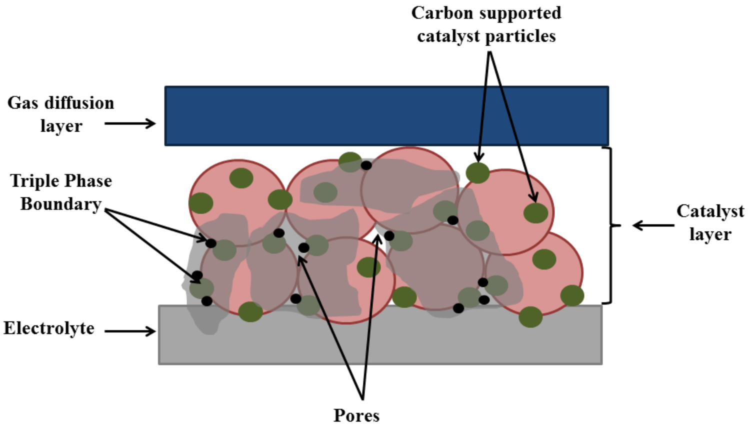

Figure 1.5: *Schematic overview of electrode/electrolyte interface including the triple phased boundary zone.*

The following points are to be considered to design catalyst layers that provide fast electron kinetics and high output power [34]: (i) large triple phase boundary zone in the catalyst layer, (ii) easy transport of ions, (iii) efficient passage of methanol and removal of exhaust gases, by-products and water molecules, and (iv) continuous flow of current between the reactive sites and the current collector. Platinum (Pt) catalysts have long been used in DMFC, however the high cost of Pt and CO poisoning over catalyst surface are the major drawbacks of platinum. Therefore, various non-precious catalysts including transition metals, metal oxides and carbides, perovskites have been developed [35-38]. Generally, catalyst particles supported on carbon have been used in DMFC to achieve good catalytic activity and high stability [39-41]. The reason behind the enhancement in catalytic performance is due to increase in triple phase boundary zone upon using the carbon support and fine dispersion of catalyst particles over the carbon support increasing electron transfer rate [33]. The strong interaction between the catalyst particles and carbon support reduces poisoning of catalyst surface and thereby increasing stability of the electrode.

1.2.4.4 Electrolyte membrane

The electrolyte membrane is another important component of DMFC that separates the anode and cathode and also behaves as a media for proton conduction between these two electrodes. Some of the main properties of electrolyte membrane are good electrical conductivity, low permeability to fuels and oxidants, thermally and chemically stable, resistant to corrosion and cost-effective [33]. Nafion, a copolymer of perfluorosulfonic acid (PFSA) and polytetrafluorethylene (PTFE) made by DuPont is the most common solid electrolyte membrane used in DMFC [33]. The leakage of electrolyte can be avoided by using solid electrolyte. The basic chemical structure of Nafion is presented in Figure 1.6. It comprises of fluorocarbon at the main chain of polymer and sulfonic acid groups as side chains. The sulfonic group is strongly bonded to the main chain whereas the proton is weakly bonded and takes part in ionic transport [33]. The membrane can absorb huge amount of water due to presence of sulfonic groups resulting in hydrated zones that form channels for movement of protons towards the cathode from anode.

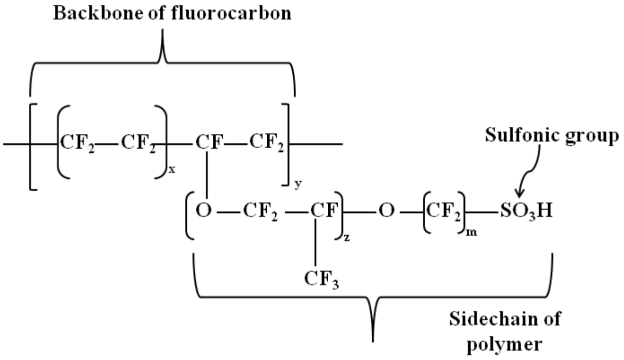

Figure 1.6: *Chemical structure of Nafion.*

1.2.5 Challenges related to DMFC

DMFCs have lots of applications in portable electronics and electric vehicles; however the commercialization of DMFC is still difficult due to some unavoidable issues [42]. Details of all the prime challenges such as sluggish electrooxidation kinetics, methanol crossover and high cost of platinum (Pt) are discussed below [17, 33].

1.2.5.1 Methanol crossover

In DMFC, the hydrophilicity and presence of hydroxyl groups in the membrane induce interactions between the substrate and membrane facilitating diffusion of methanol molecules from anode to cathode across the electrolyte and directly react with oxygen on the cathode surface causing a mixed potential due to interference of oxidation of methanol with oxygen reduction reaction [43]. This also causes increase in oxygen reduction overpotential due to decrease in concentration of oxygen at the cathode and poisoning over the cathode surface that finally decreases the cell performance and efficiency of DMFC [44]. Methanol can be transported across the membrane by three processes [44]: (i) electro-osmosis (methanol molecules are adhered to H^+ ions in ionomer phase), (ii) diffusion (driving force generated due to dissolution of concentrated methanol in ionomer phase) and (iii) Convection (due to difference of pressure within the membrane). Dilute methanol solution can be used as fuel to reduce crossover; however this also lowers the power density of DMFC. Therefore, appropriate structure of the electrodes, proper thickness of membrane, design of novel membranes and highly active electrocatalysts and optimum concentration of methanol are the major research interests to lower the methanol crossover effects. Crossover of methanol is also reduced by maintaining the concentration of electrolyte and pressure across the membrane.

1.2.5.2 Sluggish electrooxidation kinetics

The sluggish reaction kinetics involved with oxidation of methanol is another major obstacle for commercialization of DMFC. During methanol oxidation, methanol is converted into CO and finally oxidized into CO_2. However, numerous intermediates such as aldehyde (COH_{ads}), bicarbonate (HCO_{ads}) and formic acid ($HCOO_{ads}$) are formed during methanol oxidation [45, 46]. Some of the intermediates can’t be oxidized and are strongly adsorbed over the surface of Pt. Therefore, the rate of adsorption of new methanol molecule slows down and thus the reaction rate. Thus, fuel cell performance is reduced due to catalyst poisoning. Therefore, main aim of the researchers is to develop novel electrocatalysts to reduce catalyst poisoning and also to enhance the reaction rate.

1.2.5.3 Use of platinum as electrocatalyst

Many Pt based catalysts supported on carbon or Pt alloyed with other metals are usually used as catalyst for both MOR and ORR in DMFC owing to excellent electrocatalytic activity [47-50]. However, the high price and global scarcity of Pt hinder the practical application of DMFC. Therefore, much effort has been given to find alternative to Pt. Moreover, CO poisoning over the Pt catalyst is another reason to find alternative Pt free catalyst. Hence, these drawbacks can be overcome by reducing Pt loading in the catalyst material and also exploring non-platinum catalysts including transition metal oxides, transition metal chalcogenides, carbon nanomaterials, perovskites and their composites [39, 51-53].

1.2.6 Non-noble metal based anode materials for DMFC

In DMFC technology, the methanol oxidation is a six electron process that occurs at an anodic voltage of 0.02 V. However, MOR produces carbonaceous intermediates, which block the electrode surface causing poisoning of Pt-based electrodes. Transition metal oxides have been reported as active electrocatalyst towards methanol oxidation, which can improve reaction rate in MOR by increasing resistance to the poisoning [39, 54, 55]. Although, due to low electrical conductivity, their application is limited as anode catalyst in DMFC. To overcome this issue, metal oxide structures have been composited with carbon materials to develop effective anode catalysts with good electrocatalytic activity and enhanced stability. Moreover, the presence of conducting polymer in electrocatalyst enhances electrochemical stability that prevents the catalyst from dissolution in the electrolyte [56]. Therefore, constant efforts have been made by the researchers for the development of non-noble metal-based anode catalyst using transition metal oxide, carbon materials and conducting polymer that can decrease the adsorption of CO over electrode surface and also increase the kinetics of methanol oxidation by lowering the anodic overvoltage.

1.2.6.1 Transition metal oxide

Transition metals are the elements in block d of periodic table including groups 3 to 12 with partially filled d orbital. They can share their electrons by accepting or losing to other atoms which is enabled by partially filled d orbitals [57]. Transition metals have several oxidation states that correspond to the unpaired electrons in d orbital. Transition metals are bonded to oxygen atom to form transition metal oxides (TMOs). Depending on the metallic components, transition metal oxides (TMOs) have a wide range of electronic properties and oxidation states owing to the contribution from d-orbital electrons in formation of bond, which are useful in catalytic reactions including methanol oxidation, water splitting, and oxygen reduction and dye degradations [54, 58-60]. Nanostructured TMOs have significant impact on their catalytic activity such as increase in surface to volume ratio increases the specific surface area and therefore a greater number of available active sites leading to enhancement in catalytic activity. TMOs are generally formed through calcination from their corresponding hydroxides [61]. The surface of oxides plays main role in heterogeneous catalysis, where the molecules initially interact with surface, and then dissociate and react with other adsorbed molecules over the surface. In oxidation process, the dissociated molecules are adsorbed, and then react with lattice oxygen. Missing of oxygen lattice from the structure causes reduction of surface by changing its oxidation state. The electrocatalytic activity of TMOs is associated with presence of $M^{n+}/M^{(n+1)+}$ redox couples related to oxygen vacancies, which are necessary for adsorption or splitting of the reactant molecules and for activation of O_2 molecule [62]. The mixed transition metal oxides (MTMO) such as spinel oxides exhibit superior electrocatalytic performance due to coexistence of $M_1^{n+}/M_2^{(n+1)+}$ redox couples in the crystal structure [62]. Moreover, the high stability and good electrical conductivity of spinel oxides with formula AB_2O_4 are due to cubic close-packed structure of O^{2-} ions, where tetrahedral and octahedral coordinations have been occupied by A^{2+} and B^{3+} cations, respectively [63]. In normal spinel oxide, A^{2+} ions occupy one-eighth of the tetrahedral interstices and B^{3+} ions occupy half of the octahedral interstices. An example of normal spinel oxide is $MgAl_2O_4$. In inverse spinel A^+ ions are in the octahedral interstices, whereas half of the B^{3+} ions occupy octahedral interstices and other half of B^{3+} ions occupy tetrahedral holes. An example of inverse spinel is $MgFe_2O_4$. Although, having many advantages of TMOs and MTMOs such as low cost, environment friendliness and high redox activity still, some limitations exist including poor conductivity, agglomeration and poor regeneration. Therefore, major research interests have grown on incorporation of various conductive materials to TMOs and MTMOs such as carbon materials, conducting polymers, 2D materials etc. to increase the dispersion, electrical conductivity and regeneration ability [36, 39, 54-56].

1.2.6.2 Carbon material

Carbon materials are usually used as catalyst support owing to good electrical conductivity and large specific surface area. The carbon materials can improve conductivity, transportation of mass and stability of the catalyst. Therefore, several carbon-based materials have been developed in various structural forms such as dots, tubes, fibres, sheets etc. [64-67]. The commonly used carbon materials as electrocatalyst in DMFC are summarised below:

1.2.6.2.1 Carbon quantum dot

Carbon quantum dots (CQDs) are zero-dimensional form of carbon with size less than 10 nm. Recently, CQDs have attracted much attention owing to fast electron transfer ability, low toxicity, high surface area, facile preparation methods and significant stability. The use of lignin-based carbon dots support to Pt catalysts (Pt/Lg-CDs) in DMFC shows a rise in oxidation peak current density from 0.65 mA cm^{-2} Pt to 0.76 mA cm^{-2} Pt compared to PtRu/C [68]. The enhancement in catalytic activity of Pt/Lg-CDs-800 catalyst can be attributed to lignin based carbon dots and summarized as follows: (i) abundance of oxygenated functional groups on carbon dot offers excellent water solubility, hence synthesis of Pt occurs in homogenous system; (ii) the presence of large number of functional groups enriches the interaction between Pt catalysts and carbon dots and (iii) incorporation of carbon dots increases the number of -C-OH- groups, which can promote conversion of oxidation intermediates into CO_2. The comparison of methanol oxidation activity between Pd-NPs/RCQDs/GCE and Pd-NPs/GCE reveals a more negative oxidation peak potential and five folds larger oxidation peak current density of the Pd-NPs/RCQD/GCE [69]. The presence of CQDs in catalyst improves conductivity of the electrodes and also offers large surface area for catalysis. Thus, there is considerable increase in CO tolerance of Pd-NPs/RCQD/GCE than that of Pd-NPs/GCE. Ni nanoparticles decorated CQDs modified glassy carbon electrode (Ni-NPs/RCQD/GCE) produce higher methanol oxidation peak current density of 32 mA cm^{-2} at a lower voltage of 0.56 V (vs. Ag/AgCl) compared to Ni-NPs/GCE [70]. The enhanced activity of Ni-NPs/RCQD/GCE is due to increased electroactive area offered by CQDs and strong interaction between Ni-NPs and CQDs, favouring rapid methanol oxidation process and enhanced electron transfer kinetics. The confinement effect of CQDs prevents agglomeration of Ni-NPs that result into uniform morphology and thus increasing the stability of catalyst during oxidation process.

1.2.6.2.2 Carbon black

Carbon black comprises of graphite particles having diameter less than 50 nm, combine to form aggregates of particle with diameter around 250 nm [71]. The carbon particles possess para-crystallite structure, where each crystallite contains many turbostratic layers having interplanar distance of 0.35-0.38 nm [71]. The large specific surface area (e.g. surface area of Vulcan XC-72 is 250 $m^2 g^{-1}$); abundance and low price of carbon blacks make DMFC cost effective [72]. Pd nanoparticles supported on graphitic carbon nitride and carbon black (g-C_3N_4 /carbon black) shows a high peak current density of 1720 mA mg_{Pd}^{-1} towards methanol oxidation [73]. The high electrocatalytic activity of the catalyst is due to large surface area provided by carbon black in the hybrid catalyst, strong interaction between Pd and the substrate and good dispersion of small-sized Pd particles over g-C_3N_4/carbon black. Pd/Ni catalysts supported on chemically treated carbon black have been demonstrated for methanol oxidation [74]. High dispersion and decrease in size of the particles on chemically modified carbon black improve electrocatalytic activity of the catalyst particles in comparison to individual components.

1.2.6.2.3 Mesoporous carbon

Mesoporous carbon (MC) has large specific surface area with pore size within 2-50 nm and monodispersed mesosphere that are connected three-dimensionally and can facilitate the transport of reactant molecules to electroactive sites. MCs can be classified into two kinds based on the synthesis process and structure: (i) ordered MC (OMC) and (ii) disordered MC [72]. Huajun Zheng et al. [75] reported that the electrocatalytic activity of ordered mesoporous carbon/tungsten carbide (OMC/WC) with pore size 3.86 nm is almost comparable to that of platinum disk electrode. OMC present in the catalyst acts both as the support and source of carbon. CMK-3 is one of the mesoporous carbon materials that has drawn much attention of researchers, which can be obtained by the replication of mesoporous silica, SBA-15. CMK-3 has highly ordered two-dimensional structures with outstanding textural properties. The electrocatalytic activity of PdNi nanoparticles supported on defective CMK-3 carbon (CMK-3-D) with different molar ratios of Pd and Ni for both MOR and ORR has been studied [76]. The optimized PdNi/CMK-3-D displays improved performance for the oxidation of methanol with a larger peak current of methanol oxidation, a more negative onset voltage, and higher I_f/I_b ratio due to the presence of greater number of reactive sites for MOR and synergetic contributions of Pd and Ni. The electronic structure of catalysts for improved catalytic activity is influenced by the presence of defects. The carbon defects provide numerous electroactive sites for anchoring of metals.

1.2.6.2.4 Carbon nanofibres

Carbon nanofibres (CNFs) are one dimensional (1D) material that possess a smaller number of defects, low density and high electrical conductivity. Metal catalysts supported on CNFs are synthesized by electrospinning of a solution containing transition metal acetate precursors with a polymer, which is thermally less stable such as poly(vinyl alcohol) (PVA) or polyvinylpyrrolidone (PVP), followed by calcination under an inert atmosphere. In this process, the metal atoms are formed due to decomposition of transition metal precursors and enclosed within CNF. In addition, adsorption of fuel increases over the surface of catalyst due to presence of carbon layer [77]. In a recent study, the synthesis of carbon nanofibers/poly(para-phenylenediamine) hybrid on carbon paste electrode (CPE/CNF/PpPD), followed by electrodeposition of nickel particles (NiPs) has been reported [78]. The CPE/CNF/PpPD/NiPs electrode exhibits superior electrocatalytic activity toward MOR with a peak current density of 38.1 mA cm^{-2}, better stability and durability than that of CPE/CNF/NiPs. The presence of hybrid structure CNF/PpPD in the catalyst increases electroactive surface area that in turn promotes methanol adsorption rate over the surface of electrode. A significant decrease in charge transfer resistance and increment in electron transfer rate is attributed to the synergetic effects of CNFs and PpPD contributing to superior conductivity and large surface area. The influence of amount of nitrogen on MOR activity at Ni/N-CNFs catalyst supported on a graphite disk has been investigated [79]. The incorporation of nanofibers on graphite disk shows significant improvement in electrocatalytic activity since the underneath nanofibers merge with graphite support that lowers the interfacial resistance. Ni/N (5.0 wt%)-CNFs/graphite catalyst exhibits a current density of 270.4 mA cm^{-2}, while unsupported fibers reveal a current density of 80.5 mA cm^{-2} in 0.5 M methanol. The current density of methanol oxidation increases with an increase in nitrogen content owing to the presence of lone pair of electrons in nitrogen. N doping boosts the immobilization of Ni NPs onto CNFs and also improves binding between the catalyst and graphite disk without using Nafion.

1.2.6.2.5 Carbon nanotubes

Discovery of carbon nanotubes (CNTs) in 1991 by Iijima was a breakthrough in the science of nanomaterials [80]. The cylindrical structured CNTs are usually formed by rolled-up sheets of graphene. Among the several carbon nanomaterials that developed in recent years, CNTs exhibit promising results as catalyst support because of their remarkable mechanical, electrical and structural properties [81]. These can be classified into single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). The merits of MWCNTs are highly graphitized wall, sp^2 hybridized carbon constructed surface and nanostructured channels [82, 83] that resulting into rapid transfer of mass and electrons and thus improving the electrical conductivity [84]. CNTs are extensively used as anode catalyst in DMFC owing to their excellent properties. A ternary alloy copper-cobalt-nickel is electrodeposited over CNT modified GCE (CuCoNi@CNTs/GCE) for electrooxidation of methanol [85]. The electro activity towards methanol oxidation is increased by 2.5 times at $CuCoNiO_x$@CNT/GCE in comparison to Cu, Co, or Ni mono electrocatalysts. The improved electrocatalytic activity and stability of $CuCoNiO_x$@CNT/GCE are mainly due to contribution from three metal oxides present in the same alloy. Moreover, CNTs offer large specific surface area for deposition of ternary metal oxides and prevent agglomeration and sintering of the metal oxides. However, the high cost and small-scale production of CNT, difficulty in metal loading and preparation of CNT based electrodes face serious issues that limit their applications. The amount of CNTs (15, 25, 35, and 45 wt%) in NiCo/C-N catalyst on the catalytic activities of methanol and ethanol oxidation, has been demonstrated [86]. Ni_3Co_1/C-N/CNT catalyst with 35 wt% of CNT content exhibits high electrocatalytic activity with peak current densities of 213 mA cm^{-2} and 181 mA cm^{-2} towards 1 M methanol and 1 M ethanol, respectively. The incorporation of 35 wt% CNTs increases the charge transfer rate between the catalyst and electrolyte solution, and also assists in good dispersion of Ni_3Co_1/C-N nanoparticles, however, a further increase in the amount of CNT (45 wt%) reduces the number of electroactive sites and thereby decreasing electrocatalytic activity of the catalyst.

1.2.6.2.6 Graphene

Graphene, a one atom thick planar sheet of sp^2-hybridized carbon atoms with a thickness of 0.34 nm was a ground-breaking discovery by Geim and Novoselov in 2004 [87]. They were awarded with the Noble Prize in Physics in the year 2010 because of successful mechanical exfoliation of a single layer of graphite using ‘scotch-tape’ method. The carbon atoms of graphene are tightly packed into a 2D lattice as shown in Figure 1.7.

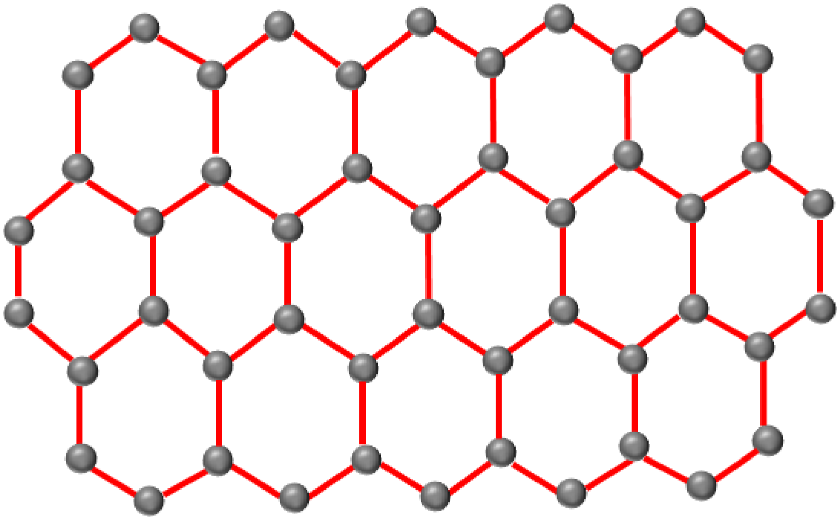

Figure 1.7: *Graphene: a two-dimensional crystalline allotrope of carbon.*

The extraordinary properties of graphene with excellent electrical conductivity around 6000 S cm^{-1}, large specific surface area of 2630 m^2 g^{-1}, high electrochemical activity and mechanical stability make it suitable for electrochemical applications [88-90]. Large numbers of electroactive sites present on the surface of graphene facilitate electrocatalytic reactions and can be used as catalyst support in fuel cells [91, 92]. The two-dimensional structure of graphene nanosheet, allows both the edge and basal planes for interaction with catalyst nanostructures. Graphite powder is oxidized to form graphite oxide (GO) according to Hummers′ method or modified Hummers′ method or Improved Hummers′ method [93]. Then reduction is done using reducing agents such as hydrazine hydrate [94], ammonia [95], ascorbic acid [96], sodium borohydride [97] etc. to form reduced graphene oxide (rGO) nanosheets. The presence of defects such as vacancies, edges, distortions and oxygen containing functional groups in rGO makes it suitable for attachment and growth of the catalyst [98]. In comparison to Ni-Co/CPE, the Ni-Co/rGO/CPE electrode shows high electrocatalytic activity since large number of nanoparticles can be deposited over rGO modified electrodes due to the high specific surface area and fast electron transfer rate of rGO nanosheets [99]. Two-dimensional quadrilateral shaped CO_3S_4 nanosheets over graphene-decorated nickel foam (2DQ-CO_3S_4-NSs/3DGr) exhibit high electrocatalytic activity with an anodic current density of

134.1 mA cm^{-2} at an onset potential of 0.28 V (vs. SCE) in 0.5 M methanol [100]. The highly porous structure of 3DGr provides enough open space and multi-channel paths to increase the rate of diffusion and thus enhancing the electrode and electrolyte interaction that finally leads to a rapid transfer of ions. In addition, the fast electron transfer kinetics is also attributed to the continuous interconnected structure of 3DGr. $NiCo_2O_4$ hexagonal nanoplates grown over rGO nanosheets exhibit a peak oxidation current density of 16.6 mA cm^{-2} at an onset potential of 1.324 V, while pristine $NiCo_2O_4$ electrode shows a peak oxidation current density of 12 mA cm^{-2} at an onset potential of 1.382 V [101]. The higher catalytic activity of $NiCo_2O_4$- rGO nanohybrid than that of pristine $NiCo_2O_4$ is due to the presence of rGO nanosheet that controls aggregation of $NiCo_2O_4$ nanocrystals during the formation of $NiCo_2O_4$ hexagonal nanoplates.

1.2.6.3 Conducting polymers

The plastics that we use in our daily life are basically polymers, which are macromolecules with repeating structural units. Traditionally, polymers have been used as insulating materials in the form of plastic coating in electrical wires, packaging, textiles and plastic bags etc. Until 1977, electrical conduction in polymers was not considered as a desirable phenomenon. The breakthrough occurred in the year 1977, when Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa discovered that under certain conditions, polymers which are regarded as insulators can exhibit electrical conductivity [102]. Their path breaking discovery was the increase in conductivity of polyacetylene by nine orders upon doping with iodine [103]. They received the Nobel Prize in Chemistry in the year 2000 “for the discovery and development of electronically conductive polymers” [104-106]. Polyacetylene is highly sensitive to air and also insoluble in many solvents, which limit its processability and applicability in different fields. Therefore, researchers have shifted their interest towards another class of conducting polymers and their derivatives. Most commonly used conducting polymers (CPs) and their chemical structures are shown in Figure 1.8 [107].

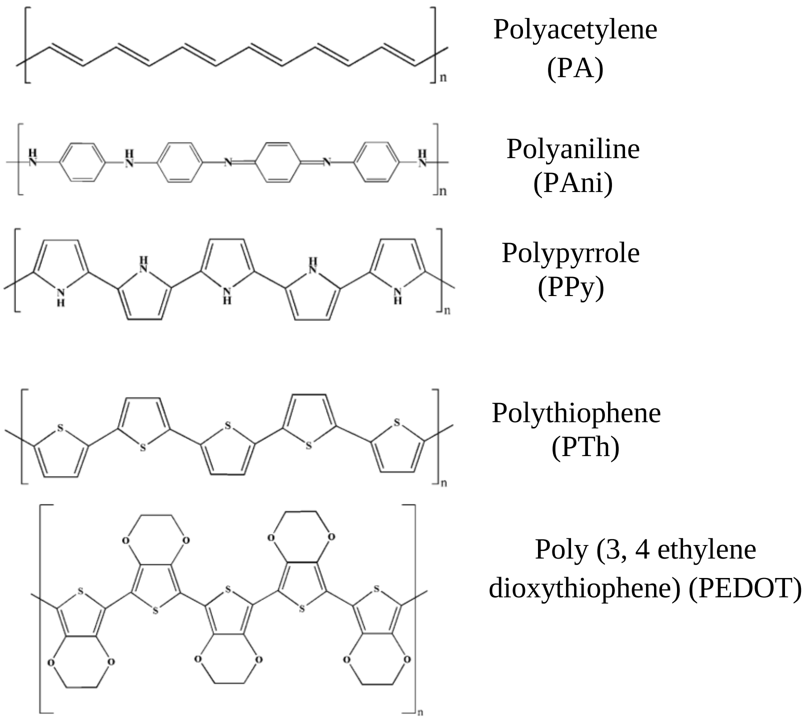

Figure 1.8: *Chemical representations of few of the commonly used conducting polymers.*

The polymers can be synthesized either chemically or electrochemically. In chemical synthesis, oxidizing agents such as ammonium peroxydisulfate (APS), ferric chloride ($FeCl_3$) are incorporated into the monomer. The oxidants initiate polymerization reaction to yield the polymer. In electrochemical synthesis, a standard three electrode system is used, where the electrodes are dipped into a solution containing both supporting electrolyte and monomer. Upon application of an oxidation potential to the working electrode, monomer gets oxidized leading to deposition of polymeric film onto the surface of working electrode [108]. Compared to pristine CPs, their composites with carbon materials and metal-based compounds exhibit remarkable electrocatalytic activity, which arise from their large specific surface area, superior conductivity, enhanced electrochemical activity and excellent mechanical properties [109, 110]. Moreover, CP composites show advantages due to their synergetic performance obtained from individual component. For instance, transition metal oxides possess redox states and graphene exhibits excellent conductivity but lack the cycling stability needed for commercial applications. Therefore, CPs are incorporated with transition metal oxide and graphene to increase cycling stability of the composite by synergetic interaction among all the materials present in the composite [111, 112]. In these composites, CPs can also inhibit the aggregation and restacking of metal oxide particles through the electrostatic effect and space steric hindrance, and thereby causing uniform dispersion of the metal oxide particles over CP matrix [113].

1.2.6.3.1 PEDOT:PSS as promising conducting polymer

PEDOT, an interesting derivative of PTh, was synthesized in the second half of 1980s at the Bayer AG research laboratories in Germany. PEDOT is a p-type CP having significant characteristics such as moderate band gap (1.5 eV), high conductivity (300 S cm^{-1}), low redox potential (-0.6 V) and electrochemical stability [114]. In PEDOT, the absence of undesired α-β and β-β couplings with polymer backbone due to the blockage of β-β bonds of thiophene ring by an ethylenedioxy group makes it highly stable in comparison to other CPs such as PPy, PAni etc. [115, 116]. However, PEDOT is poorly soluble in any solvent, therefore during 1990s; the Bayer AG research laboratories incorporated poly(styrenesulfonic acid) (PSS) to the positively charged PEDOT to form a stable suspension, known as PEDOT:PSS (shown in Figure 1.9). The polymerization of PEDOT has been done in presence of PSS, using peroxydisulfate with monovalent cations (Na^+, K^+, NH_3^+) and iron (III) salt as the initiator [117]. PSS plays two roles, as a counter ion for charge neutralization and as a surfactant for stabilization of the positively charged PEDOT [118]. The electrical conductivity of PEDOT:PSS decreases on increasing the amount of PSS [114]. Moreover, the electrical conductivity also depends on particle size as larger the size of the particles, higher the conductivity of PEDOT:PSS film [117].

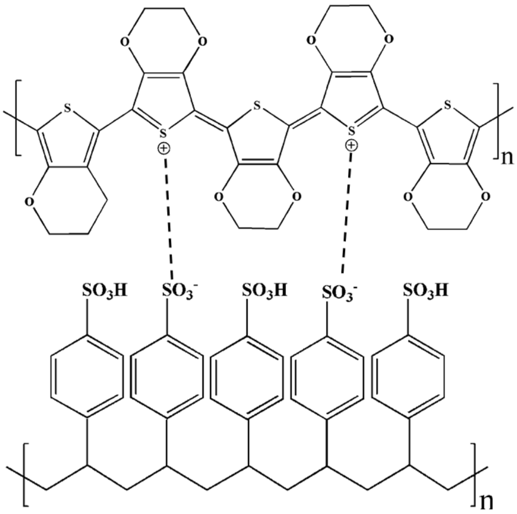

Figure 1.9: *Chemical structure of PEDOT:PSS.*

Lengths of PSS chains are much longer than that of PEDOT chain. These long PSS chains and short PEDOT chains are attached to each other due to strong Coulombic interaction between PEDOT and PSS [119]. PSS segments exhibit two types of conformations based on the strength of Coulombic interactions between PEDOT and PSS chains and the interactions among polymer segments [120]. When the Coulombic interaction between PEDOT and PSS surpasses the repulsions among PSS, it results into a coil conformation (Figure 1.10 (i)) and thus forming a core shell structured blob [121]. Although, the PSSH segments that do not attach to PEDOT, dissociate into negatively charged PSS ions and protons in water. A linear conformation (Figure 1.10 (ii)) is adopted by PSS anions to have the largest distance and minimum potential energy [119]. Linear conformation favours the charge transport in PEDOT:PSS.

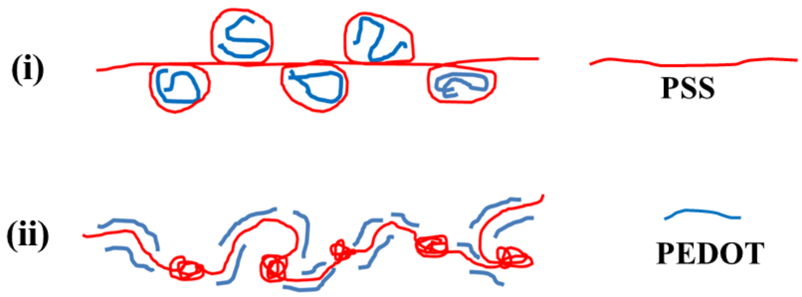

Figure 1.10: *Conformations of PEDOT:PSS (i) coiled and (ii) linear structures.*

1.2.6.4 Nanocomposite anode catalysts for methanol oxidation

Significant efforts have been made to integrate carbon materials and conducting polymers with transition metal oxides as anode catalyst for the replacement of costly platinum in DMFC. The contribution from individual components in the nanocomposite improves electrocatalytic activity towards methanol oxidation and also enhances stability of the resulting nanocomposite.

In the following sections, a brief literature review of platinum free anode catalysts for DMFC based on binary and ternary nanocomposites is presented.

1.2.6.4.1 Binary nanocomposites

CeO_2/rGO nanocomposite exhibits higher electrocatalytic activity toward methanol oxidation than that of CeO_2 with an anodic peak current density of 23 mA cm^{-2} at an overpotential of 0.55 V (vs. Ag/AgCl) in a solution of 0.3 M methanol due to strong interaction between CeO_2 and rGO and excellent electrical conductivity of rGO [54].

Mesoporous $NiCo_2O_4$ nanoneedles synthesized over 3D graphene-nickel foam (NCO/GNF) shows excellent electrocatalytic activity with a peak current density of 93.3 A g^{-1} at an onset potential of 0.4 V (vs. Hg/HgO) in 0.5 M methanol and 94.2% current retention after 500 cycles due to the presence of two redox active sites Ni and Co and macroporous and highly conductive 3D GNF [122]. The large contact area between $NiCo_2O_4$ nanoneedles and electrolyte provides short path for transport of ions and electrons. Moreover, the growth of $NiCo_2O_4$ nanoneedles on GNF without using binder possesses good electrical contact between $NiCo_2O_4$ and graphene. Core-shell PPy/Co_3O_4 nanospheres/GC electrode exhibits a current density of 111 mA cm^{-2} at 0.5 V (vs. Ag/AgCl), which was about three-fold higher than that of Co_3O_4 nanospheres/GC electrode. Moreover, the onset potential of hybrid PPy/Co_3O_4/GC electrode (0.34 V vs. Ag/AgCl) was negative shifted by 33 mV in comparison to bare Co_3O_4/GC for methanol oxidation. The presence of PPy shell can increase transport of electrons, thereby improving the catalytic performance. Moreover, the formation of highly electroactive Co-Nx sites due to bonding between oxidized Co_3O_4 with nitrogen functionalities of PPy enhances the methanol oxidation activity [123].

1.2.6.4.2 Ternary nanocomposites

Deposition of Cu_2O NPs into PPy-GO matrices leads to a current density of 155 mA cm^{-2} toward methanol oxidation and a power density of 31 mW cm^{-2} at 0.2 V with a higher stability than that of Pt-Ru/C [56]. The good electrocatalytic activity is due to the presence of enhanced surface area, improved electric conductivity and higher stability than that of pure PPy. GO supported PPy in the composite prevents leaking of Cu_2O nanostructure into the electrode, thus enhancing the catalytic activity. Moreover, uniform deposition, homogeneous distribution and dispersion of Cu_2O nanoparticles onto PPy-GO sheets and synergetic effect of GO, PPy and Cu_2O catalyst nanoparticles improve DMFC performance. Chokkiah Bavatharani et al. [124] fabricated FTO/GR-PDPA-SiO_2 electrode that attains a maximum peak current density of 190 mA cm^{-2} in a solution of 1 M methanol. The excellent elelectrocatalytic activity of modified FTO/GR-PDPA-SiO_2 nanohybrid electrode is due to the presence of SiO_2 network as well as synergetic connection between PDPA and GR nanosheets that confirms rapid electron transfer process between the electrode and electrolyte. Although, the above-mentioned literatures reveal superior electrocatalytic activity of the ternary nanocomposites based on graphene derivatives, conducting polymer and metal and semiconductor oxides toward methanol oxidation, still limited amount of works have been reported till now and yet to be explored further.

1.3 Scope of the thesis and statement of thesis problem

In recent years, lots of efforts have been made by the researchers to develop environmentally benign technologies for energy conversion and storage devices such as supercapacitors, lithium ion batteries and fuel cells etc. Recently, DMFC is mainly focused due to easy handling and transportation, low cost and high energy density of methanol (5.04 $kWhL^{-1}$) [125]. Moreover, the use of low cost and non-noble metal-based catalyst in DMFC including transition metal oxides, carbides, perovskite helps it to attain much attention of the scientists [36-38]. Activity of a catalyst for methanol oxidation depends on the size, morphology and dispersion of the metal nanostructure. Platinum and other noble metal-based materials are the promising catalyst for methanol oxidation. Although, the high price, scarcity, poor durability and formation of poisonous intermediates are the major drawbacks of platinum and other noble metal-based catalysts [17]. The sluggish methanol oxidation kinetics at the noble metal-based electrodes decreases the performance of DMFC for practical applications. Therefore, oxides of highly abundant 3d transition elements including Ni [55], Co [122], Cu [56], Ti [126], Mn [55], and Zn [127] have been developed as catalyst materials for DMFCs. The presence of various redox states in transition metals assists the charge transfer mechanism and thus leading to enhancement in electrocatalytic activity. Moreover, the mixed transition metal oxides (MTMOs), particularly spinel oxides, have large applications in electronics, magnetic devices and electrochemical systems such as batteries, supercapacitors, biosensors and fuel cells [128-133]. However, some common issues such as low conductivity and agglomeration of metal nanostructures can be solved by making composites of transition metal oxides with conducting polymers such as polypyrrole (PPy) [112], polyaniline (PANI) [109], poly(3,4-ethylenedioxythiophene) (PEDOT) [110] and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) [134]. Among the conducting polymers, PEDOT:PSS shows relatively high electron transfer rate, film forming capability and good stability due to the presence of ethylenedioxy group at third and fourth positions of thiophene ring [115]. Further the limited charge transfer, low specific surface area and poor cycle life can be overcome by incorporating carbon materials such as carbon dot [70], carbon black [73], carbon nanofibre [79], carbon nanotube [84] and graphene [99]. Among these the chemically prepared derivative of graphene, reduced graphene oxide (rGO) draws much attention due to its unique features such as large surface area, high electrical conductivity and good mechanical stability [90]. Recently, ternary nanocomposites have been investigated as electrocatalyst materials for oxidation of methanol to obtain improved electrocatalytic performance. By synthesizing ternary nanocomposite, maximum utilization of each component can be done and also drawbacks of all the components present in the nanocomposite can be overcome. In ternary nanocomposites of transition metal oxide, conducting polymer and rGO; the polymer coated metal oxide nanostructures are uniformly dispersed over rGO nanosheet and thus the redox material is protected from dissolution into the electrolyte as reported in literatures [135]. However, till now few works have been reported on the development of ternary nanocomposite based on rGO, PEDOT:PSS and mixed transition metal oxide and metal oxide with coexistence of two types of morphology as anode catalyst for methanol oxidation.

Considering the above-mentioned facts, the main objectives of the present thesis have been presented below:

1. The primary goal of this thesis is to develop non-noble metal based anode catalyst with ternary nanocomposites of transition metal oxides, conducting polymer PEDOT:PSS and rGO nanosheets, which is almost comparable to platinum based catalyst in terms of oxidation current density and onset voltage.
2. The ternary nanocomposite catalyst must also possess good cyclic stability, long term durability and high current retention factor.
3. To study the electrode behaviour and electron transfer kinetics of the modified electrodes is another important objective of the present thesis.

The following ternary nanocomposite systems have been studied to fulfill the aforementioned objectives in the present work:

a) Synthesis of MnO_2 incorporated PEDOT:PSS and rGO nanosheets based nanocomposite for electrooxidation of methanol.
b) Anode catalyst based on NiO, PEDOT:PSS and rGO nanosheets for methanol oxidation with a purpose to obtain enhanced electrocatalytic activity and cyclic stability.
c) Ternary nanocomposite of $NiMn_2O_4$, PEDOT:PSS and rGO nanosheets for electro-oxidation of methanol with good electrocatalytic performance.

The physical and electrochemical characterization techniques used to study the nanocomposite systems have been mentioned below:

i. Surface morphology of the synthesized systems have been studied by scanning electron microscopy (SEM).
ii. Transmission electron microscopy (TEM) measurements have been done to know the size, shape and distribution of nanostructures.
iii. The formation of samples has been confirmed by X-ray diffraction (XRD).
iv. The presence of defects in the samples has been analysed using Raman spectroscopy.
v. The electronic state and chemical environment of the materials have been investigated using X-ray photoelectron spectroscopy (XPS).
vi. Nitrogen adsorption-desorption isotherms have been employed to determine specific surface area and pore size distribution of the materials.
vii. The electrochemical performance and electrocatalytic behaviour of the modified electrodes toward methanol oxidation have been investigated using cyclic voltammetry (CV) technique using a three-electrode setup.
viii. The methanol oxidation activities have also been studied using linear sweep voltammetry (LSV).
ix. Electrochemical impedance spectroscopy (EIS) is used to analyse different types of internal resistances appeared at the electrode-electrolyte interface during transfer of charges.
x. The stability of the electrodes with time has been studied using chronoamperometry (CA).

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