

## **Chapter 1: INTRODUCTION**

### **1.1 Introduction: Energy conversion and storage devices**

The primary cause of the rise in CO<sub>2</sub> levels in atmosphere is the overconsumption of fossil fuels brought on by the exponential expansion in energy consumption in various spheres of human civilization. Research is focused on identifying renewable and eco-friendly energy sources as means of avoiding the depleting supplies of fossil fuels and the exponential increase in pollution. As the renewable energy resources like solar and wind are sporadic, there arises the need of efficient energy conversion and storage technologies.

### **1.2 Overview of fuel cell (FC)**

Fuel cells have been recognized as alternative energy conversion systems, particularly for low power consumption electronic devices and domestic transportation systems [1]. A fuel cell converts the chemical energy stored in the chemical bond of the fuel into electrical energy. Moreover, fuel cells have attained tremendous research interests because of their low pollutant emission, high power density, and superfast recharging [1].

#### **1.2.1 Working principle of fuel cell**

At the anode/electrolyte interface, the primary fuel gets oxidized to produce protons (H<sup>+</sup> ions) in an acidic medium, whereas in a basic medium, OH<sup>-</sup> ions (travel towards the anode from the cathode side) react with the fuel to oxidize it and the electrons generated move towards the cathode via the external circuit through a load. In acidic medium, the electron reacts with oxygen and proton at the cathode to form water. However, in basic medium the electron reduces oxygen in presence of water to form hydroxyl ions. This energy generated across the load is the useful electric energy output of the fuel cell. During the whole process, the heat energy generated at the interface of the electrode/contact, electrode/electrolyte interfaces, resistance caused by the migration of protons or hydroxides through the electrolyte, and electrons migrating through the external circuit is lost into the surroundings as waste [1, 2]. The schematic of direct alcohol fuel cell (DAFC) in acidic and basic medium are shown in fig. 1.1 and 1.2

respectively. The working principle of the simplest fuel cell, H<sub>2</sub>-O<sub>2</sub> fuel cell is explained by equations 1.1-1.3.

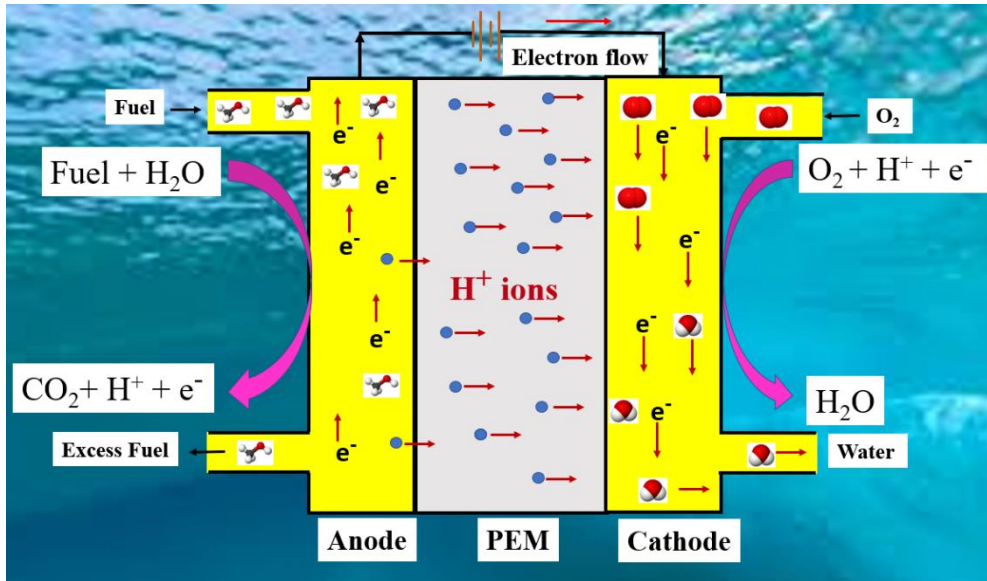


Figure 1.1: Schematic of the mechanism of DAFC in acidic medium

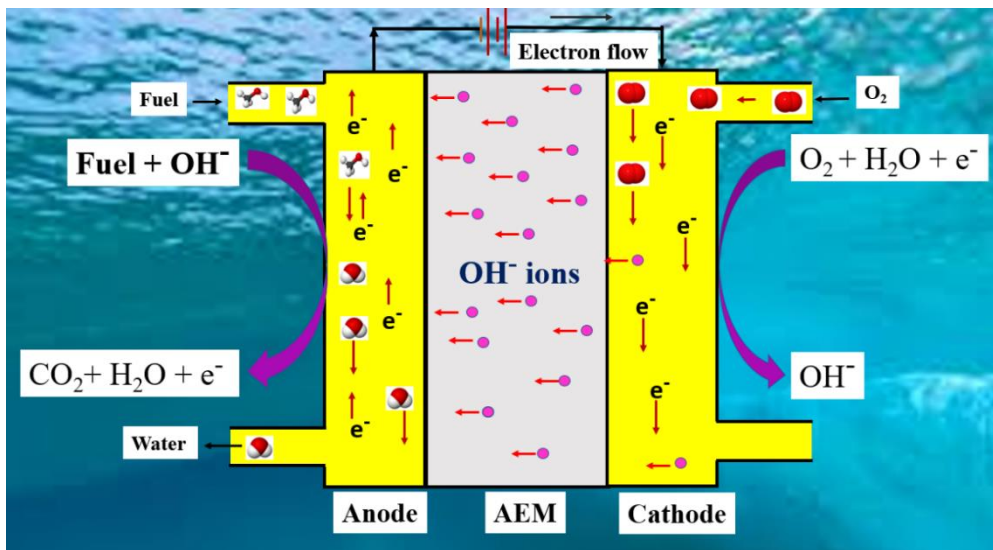
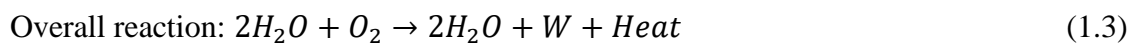
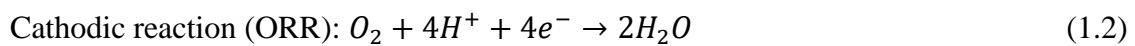
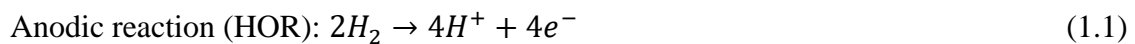


Figure 1.2: Schematic of the mechanism of DAFC in basic medium

The working principle of H<sub>2</sub>-O<sub>2</sub> fuel cell is explained by equations 1.1-1.3.



where W represents the useful electric energy supplied by the fuel cell.

### 1.2.2 Classification of fuel cells

Fuel cells are of different types depending on the fuel, operating temperature range, electrolyte, and types of ions transferring through the electrolyte. Classification of fuel cells is provided in Table 1.1 [1]. Fuel cells are further classified into direct and indirect fuel cells depending on the mode of fuel supplied to the anode. In the former, the fuel is supplied directly to the anode for electrooxidation. In the latter, the main fuel is first converted into a gas containing hydrogen (referred to as secondary fuel), and then the secondary fuel is fed to the anode for further oxidation to generate electricity [1, 3].

Table 1.1: Classification of Fuel Cells

<i>1. Classification by electrolyte</i>		
<i>Types of FCs</i>		<i>Description</i>
Alkaline Fuel Cell (AFC)		Aqueous Alkaline solution (generally KOH) as electrolyte
Proton exchange membrane fuel cell (PEMFC)/Solid Polymer Fuel Cell (SPFC)/Solid Polymer electrolyte Fuel Cell (SPEFC)/Polymer Electrolyte Fuel Cell (PEFC)/Polymer Electrolyte Membrane Fuel Cell (PEMFC)		Solid proton conducting membrane as electrolyte
Phosphoric Acid Fuel Cell (PAFC)		Phosphoric acid as electrolyte
Molten Carbon Fuel Cell (MCFC)		Molten Carbonate salt as electrolyte
Solid Oxide Fuel Cell (SOFC)		Solid oxide ion conducting ceramic as electrolyte
<i>2. Classification by type of ions passing through the electrolyte</i>		
Cation transfer fuel cell		Positively charged ions migrate through the electrolyte. Also known as Acid electrolyte fuel cell.
H <sup>+</sup> ion transfer PAFC	H <sup>+</sup> ion transfer PEMFC	
Anion transfer fuel cell		Negatively charged ions passing through the electrolyte. Also known as alkaline type fuel cell.
OH <sup>-</sup> (AFC)	CO <sub>3</sub> <sup>2-</sup> (MCFC)	
	O <sup>2-</sup> (SOFC)	
<i>3. Classification by operating temperature</i>		

Low temperature		60~80°C
AFC (60~80°C)	PEMFC (80°C)	
Intermediate temperature (PAFC)		~200°C
High temperature		High temperature range (~650°-1000°C)
MCFC (650°C)	SOFC (~1000°C)	
<i>4. Classification by type of fuels used</i>		
H <sub>2</sub> -O <sub>2</sub> fuel cell		H <sub>2</sub> as the fuel and O <sub>2</sub> as the oxidant
H <sub>2</sub> -air fuel cell, Ammonia-air fuel cell, Hydrazine-air fuel cell, Hydrocarbon-air fuel cell, Hydrogen-chlorine fuel cell, Hydrogen-bromine fuel cell, etc.		These fuel cells are named according to the fuel used and air as the oxidant
Direct Alcohol Fuel Cell, for instance Direct Methanol Fuel Cell (DMFC), Direct Ethanol Fuel Cell (DEFC), etc.		Different alcohols are used as the primary fuel

High temperature fuel cells, namely MCFCs and SOFCs show great promise in stationary power production units. The advantage of these fuel cells is that they do not get poisoned by carbon monoxide (CO) as they can use CO as fuel without any reforming. As no reforming stations or gas purifiers are required for these fuel cells, they are highly preferred as stationary or industrial power sources. However, they are not suitable in portable power applications like cars due to their high operating temperatures and lengthy startup periods. After the development of AFC by F. T. Bacon in late 1940s, NASA selected it as the power source for space missions in the 1960s [4]. Modern systems employ potassium hydroxide as the liquid electrolyte and run at relatively modest temperatures (~ 90°C) and pressures (~ 4 bars). The most challenging issue with an AFC is that, its electrolyte combines with carbon dioxide, to form potassium carbonate [5, 6, 7]. As the solubility of potassium carbonate is low at room temperature, precipitation of potassium carbonate occurs and it consumes the hydroxyl ions available at the anode, thereby lowering its concentration. Precipitation of carbonate may obstruct the pores of gas diffusion layer as well. Moreover, it alters the electrolyte's composition, which lowers its ionic conductivity [7]. Thus, AFC requires pure oxidant stream instead of air, to

reduce the amount of carbon dioxide. Several attempts have been made to address the CO<sub>2</sub> poisoning, such as use of liquid hydrogen or a circulating electrolyte to condense the CO<sub>2</sub> out of air, however, majority of these solutions are not suitable for commercialization. In contrast to the bulky liquid electrolytes used in PAFCs and AFCs, PEMFCs and DMFCs make use of solid polymer electrolyte. Unlike MCFCs and SOFCs, they run at low pressures and temperatures, which make them suitable for portable electronic appliances such as mobile phones, laptops, etc [8]. The main difference between PEMFCs and DMFCs is the nature of the fuel fed to the cell. In PEMFC, direct feed of hydrogen and oxygen/air is done to the anode and cathode, respectively. Whereas in DMFC, methanol and oxygen/air are fed to the anode and cathode, respectively. Although PEMFCs generate water as the sole byproduct of oxidation reaction, financial challenges are associated with transportation and storage of hydrogen. On the other hand, DMFCs use methanol which can be conveniently transported and stored. Moreover, methanol owns higher energy density and can be produced at low cost, which make DMFCs more promising than PEMFCs in tiny portable appliances [6]. After Cheng et al. [9] reported PEMFC and discussed the effectiveness of substituting the liquid electrolyte with a solid polymer electrolyte, studies have been concentrated on AFC based on anion-conducting polymer electrolytes [7]. Thus, the alkaline anion exchange membrane fuel cell (AAEMFC) is the technology, which mitigates the drawbacks of both PEMFCs and conventional AFCs and offers a more sophisticated, reliable, and affordable alternative approach [5, 7]. AAEMFC allows for nonprecious electrocatalysts with acceptable performance, durability, and reduced system-level complexity. Although catalysis in alkaline pH electrolytes has been of long interest, alkaline electrolyte-based fuel cells are triggering a rebirth due to the recent developments in highly conducting hydroxide anion-exchange membrane (AEM) electrolytes. The oxygen reduction reaction at the cathode produces hydroxide ions which leads to the production of water as end product on the anode side. The primary role of AAEM polymeric electrolyte is to separate the electrons and allow the selective transportation of -OH ions from the cathode to the anode and transfer of water from anode to the cathode side without any fuel/oxidant crossover [5]. It follows that the carbonate precipitation present in liquid electrolyte AFC is likewise significantly reduced when solid state AAEM electrolytes devoid of mobile alkali metal cations are used. AAEMFCs thus has the potential to seize the market of crucial backup

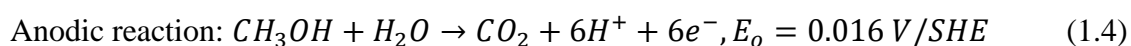
power, material handling equipment, auxiliary power sources for automobiles, etc [5]. The alkaline direct methanol fuel cell (ADMFC) is a subclass of AAEMFC [10].

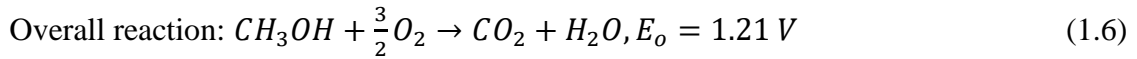
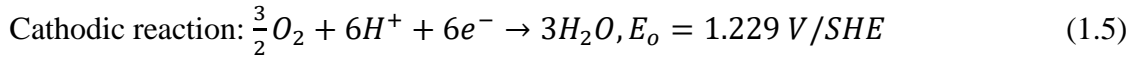
### 1.3 Direct methanol fuel cell (DMFC)

Alcohols like methanol, ethanol, and ethylene glycol have slower oxidation kinetics than hydrogen; however, they have drawn interest because of their higher energy density and facile storage and transportation. Among the direct alcohol fuel cells, direct methanol fuel cell (DMFC) is the simplest as the oxidation of methanol to carbon dioxide is a 6-step process, whereas ethanol oxidation process releases 12 electrons. There are four categories of DMFC technology viz. alkaline, passive, hybrid, and acidic. The alkaline DMFC was first developed by Kordesch and Marko in 1951, whereas, the acidic DMFC was operated in the 1960s. However, later in 1970s it was realized that alkaline DMFCs outperform their acidic counterparts.

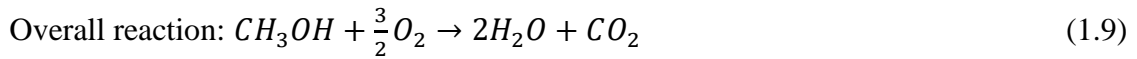
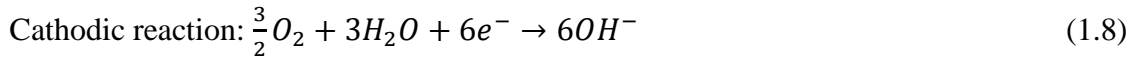
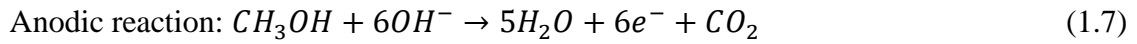
#### 1.3.1 Methanol oxidation reaction (MOR)

In DMFC, methanol is oxidised to carbon dioxide at the anode and oxygen is reduced at the cathode, which gives a theoretical cell potential of 1.2 V and energy density of 6094 Wh/kg. However, in practice CO poisoning, methanol crossover and many losses such as activation loss, concentration loss, and ohmic loss prevent this potential and energy density from being reached. In acidic DMFC, methanol reacts with water at the anode, to produce carbon dioxide, proton and electron. The proton reaches cathode by passing through the PEM and the electron travels through the external circuit to the cathode, where it reacts with oxygen and proton to form water molecules. Whereas, in alkaline DMFC methanol reacts with hydroxyl ions to form water, electron and carbon dioxide. The hydroxyl ions travel to cathode side by passing the AEM and the electron follows the external circuit. At the cathode these electrons react with oxygen and water to form hydroxyl ions [1]. The electrochemical reactions occurring in acidic medium are shown in equations (1.4) – (1.6), and that of the basic medium are explained in equations (1.7) – (1.9). These redox reactions are very sluggish and tend to produce intermediates such as carbon monoxide, formaldehyde, and formic acid, thereby reducing the conversion efficiency of the fuel cell. The methanol oxidation reaction (MOR) in acidic medium are as follows-





In basic medium, the MOR occurs as follows:



The acidic DMFC suffers from few drawbacks- i) Slow reaction kinetics of MOR, ii) substantial poisoning of the Pt based catalyst by the reaction intermediates, iii) methanol crossover across the PEM, iv) high cost of the Pt catalyst and the Nafion membrane. These significant disadvantages of acidic DMFCs have led researchers in focusing more on alkaline DMFCs. Thus, the search for an efficient, non-platinum metal based affordable anode catalyst is still ongoing.

### 1.3.2 Different components of DMFC

A single cell of DMFC consists of membrane electrode assembly (MEA), which is considered to be the primary part of the cell. On either side of the MEA, bipolar plates are attached. In between the MEA and bipolar plates, gaskets are placed on either side to prevent any leakage of methanol. The bipolar plates are then followed by current collectors, which are covered by end plates on either side [7]. The components are described briefly below and the schematic is shown in fig. 1.3.

#### 1.3.2.1 Membrane electrode assembly (MEA)

The membrane electrode assembly (MEA) is the heart of the DMFC. It comprises of a polymer electrolyte membrane, two gas diffusion layers (GDL), and two catalyst layers. The gas diffusion layers are placed on either side of the membrane and catalyst layers are coated on the GDLs towards the side facing the membrane.

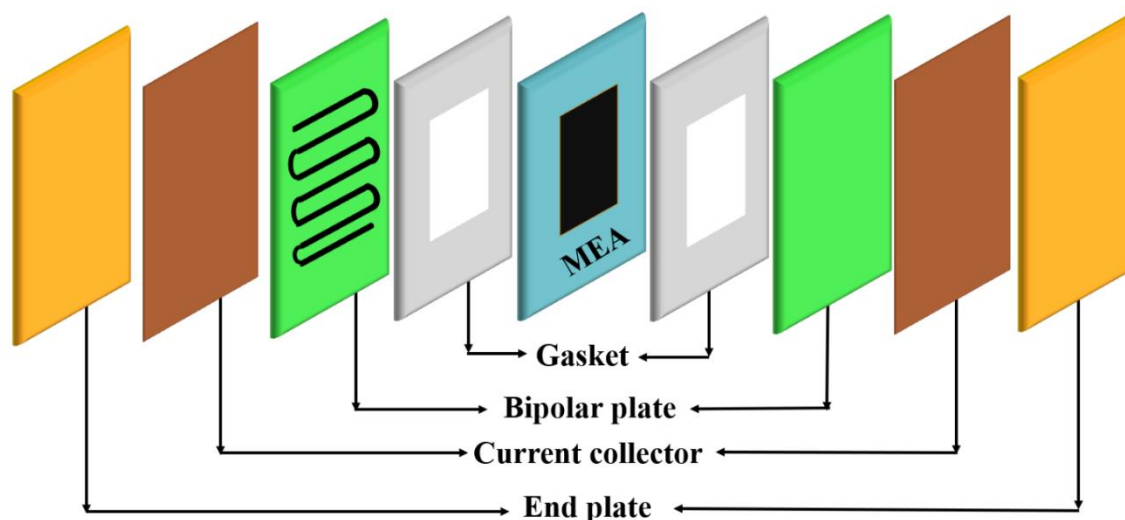


Figure 1.3: Schematic of DMFC setup

### 1.3.2.1.1 Polymer electrode membrane

The polymer electrolyte membrane allows spontaneous ion movement between cathode and anode by averting the electrons. It restricts the motion of fuel and oxidant to other side, and act as an insulation between the anode and cathode. As a result, the electrons reach the cathode side through the external circuit. In DMFC, the membrane plays an important role by lowering the methanol crossover, which is the greatest inhibitor of DMFC performance. An efficient membrane should be chemically, mechanically and thermally stable to prevent any type of structural changes during its use. Moreover, the membrane should be cost effective, environment friendly and must possess high ionic conductivity. Most commonly used membranes are polystyrene sulfonic acid membrane (PSSA) [11], Nafion with different grading 115, 117, 202, and 212 [5, 12], Tokuyama A201 anion-exchange membrane [5], Ionomr AEMION [13], Fumatech: FAA3 [13], etc. In PEMFC the membranes are basically made up of anion moieties to promote proton transport. The proton-conducting polymer (ionomer) phase is the primary component and it is a perfluorosulfonic acid (PFSA). These polymers have hydrophobic backbone which is joined to hydrophilic sulfonic acid groups, which function as strong acids with highly variable proton dissociation. Mobile proton carrying species such as hydronium ions are formed in the presence of water, which greatly increases the ionic conductivity of the membrane [14]. Nafion is one such perfluorosulfonic acid membrane having ionic



conductivity twice that of other membranes. Membranes with lesser thickness possess better proton conductivity. Membranes with lower equivalent weight are better than those with higher equivalent weight [8]. In AAEMFC, the AEM consists of cation moiety (e.g. quaternary ammonium groups) to promote hydroxyl ions transport. A hydrocarbon membrane backbone covalently functionalized with positively charged benzyltrimethyl quaternary ammonium cation headgroup side-chains for hydroxide-anion transport is the typical focus of most alkaline anion-exchange membrane (AAEM) polymer chemistry research [5, 15, 16]. The carbonate precipitation present in liquid electrolyte AFC is significantly reduced when solid state AAEM electrolyte devoid of mobile alkali metal cations are used. To allow moderate current density during fuel cell operation, typical AAEM solid electrolytes display hydroxide anion conductivity of around 20-40 mScm<sup>-1</sup> and ion exchange capacity of around 1.5-2 mmolg<sup>-1</sup> at ambient conditions [5]. In alkaline anion-exchange membrane, the hydroxide ions are moved through the membrane by means of hydrogen bond formed and dissociated along a chain of water molecules. When there is a gradient in electrical potential or concentration, diffusive transport takes place. Hydroxides passing through the membrane pull water molecules with them, creating a convective flow of water molecules within the membrane, which is why convective transport across the membrane occurs. Hydroxyl anions hop surface sites when they come into contact with quaternary ammonium groups present on the membrane. Due to the water in the system acting as a permanent dipole and interacting with other molecules, this sort of transport is believed to be secondary transport across the membrane [7].

#### **1.3.2.1.2 Electrode**

The catalyst layer coated on gas diffusion layers together comprise the electrode. The electrodes of the fuel cell are the place where electrochemical reactions occur. At the anode, methanol is fed where MOR takes place, whereas, at the cathode, air/oxygen is fed, where oxygen reduction reaction (ORR) occurs. The electrons produced in MOR are sent to the cathode side through the external circuit and the protons reach the cathode through the proton exchange membrane. At the cathode, these electrons react with oxygen and proton to form water in acidic medium (reactions are displayed in equations 1.4-1.6). In basic medium, the mechanism is somewhat different. Water and electrons are produced as a result of MOR at the anode. These electrons reach the cathode through the external circuit and the water molecules transfer to the cathode side via the anion

exchange membrane. At the cathode, the incoming electrons react with the water molecules and oxygen to form hydroxyl ions (reactions are explained in equations 1.7-1.9). The anion exchange membrane subsequently facilitates the transport of these hydroxyl ions to the anode. The properties of the material used as catalyst are important as they decide the performance and cost of the DMFC. High performance of the DMFC requires efficient transportation of reactants, products, electrons, protons, and anions inside the electrocatalyst. Good conductivity and porous active sites are among the fundamental requirements of an electrode to meet improved transport mechanism. The electrode's structure largely regulates the reaction kinetics of the DMFC. The state-of-the-art catalyst based on Pt-group metals (PGMs) are highly expensive with very low abundance in nature. As a result of which PGMs are finding it difficult to find ways in commercial market. Thus, the present focus of research effort has been the development of porous non-noble metal-based electrode materials with large surface area, good conductivity, high mechanical and electrochemical stability.

#### **1.3.2.1.3 Gas diffusion layer**

Gas diffusion layer (GDL) is one of the basic components of the MEA and is placed in between the catalyst layer (CL) and current collector. The GDLs are basically made of porous carbon paper/cloth, macroporous substrate, and a microporous layer (MPL) made of carbon black [17]. The GDL provide a conducting connection between the CL and the current collector. The GDLs are treated with polytetrafluoroethylene (PTFE) to make it hydrophobic so as to promote more efficient CO<sub>2</sub> transport at anode and O<sub>2</sub> transport at cathode [17]. The MPL provides effective mass transport and improved electrical contact. The basic functions of GDL include- a) Efficient transport of reactants to the CL and extraction of products from the CL, b) Provides support to the polymer membrane and the CL, c) Water management in DMFC, d) Heat management by removing the heat generated from the CL to the ambient environment during operation. Excessively wide pores make the cell readily flooded and results in a sharp decline in performance. Additionally, GDL performance is also influenced by the thickness and Teflon content of the GDL. Thinner GDLs are preferred since they often have better electrical conductivity and gas permeability. Nevertheless, extremely thin GDLs are unable to sufficiently establish a strong electrical connection between the catalyst layer and the current collecting plates [8, 17, 18]. Thus, an optimum thickness should be maintained

to obtain optimum performance of the DMFC. So, a GDL must have high porosity and permeability, hydrophobic/hydrophilic characteristics, strong mechanical, electrical, structural and thermal properties in order to support the complex transport process occurring in DMFC.

#### **1.3.2.1.4 Catalyst layer**

The catalyst layer is the area of the electrodes i.e. cathode and anode where the electrochemical reactions occur. It is called the “active layer” of the MEA. The catalyst layer (CL) can be coated directly onto the polymer electrolyte membrane or onto the gas diffusion layer. In order to obtain the redox reactions, the catalyst particles must be in close proximity with the electrolyte and current collector, and the byproducts must properly exit the system without preventing further incoming of fresh fuels. The point where the three phases namely, electronic conductor (catalyst particles), ionic conductor (electrolyte), and the pores for the passage of the fuel meet, is called the triple phase boundary (TPB) region. TPB area is the active sites of the catalyst accessible for the electrochemical reactions [19]. Large triple phase boundary of the catalyst layer is desirable for rapid charge transfer and better performance of the catalyst. Pt is the most frequently utilized catalyst in fuel cells. Furthermore, a variety of noble metals, transition metals, their oxides and metal alloys have been investigated as fuel cell catalysts [20, 21]. To achieve effective catalytic activity, catalysts particles are often synthesized on the surface of a carbon-based support materials. The support materials offer stability and enhanced activity to the catalysts and increase the TPB sites. The desirable properties of an efficient catalyst support are good electrical conductivity, high surface area and porosity, strong water management capacity, adequate interaction with the catalyst, good electrochemical stability and corrosion resistance. Thus, the right choice of catalyst support material is essential for achieving optimal catalytic performance.

#### **1.3.2.2 Gasket**

Gaskets are vital component of the DMFC which act as a sealant for the fuel and prevents leakage of fuels and crossover. They are utilized to isolate the fuels of anode and cathode. Gaskets are often composed of silicon or reinforced Teflon in a range of thickness depending on the MEA produced. A gasket should be made as thin as possible since a bulky gasket will increase the DMFC's internal resistance [22].

### **1.3.2.3 Bipolar plate**

Bipolar plate is a highly conductive material which is machined or casted with fuel flow passages that feed the MEA with fuel or oxidant to obtain uniform distribution of reactants within the cell. It also releases the unreacted fuel and reaction products, mostly water out of the cell. There are different types of flow field such as parallel flow field [23], serpentine flow field [24], interdigitated flow field [25], etc. each having their own advantages and disadvantages. The bipolar plates serve as a physical barrier separating the individual cells in a DMFC stack and provide mechanical support to the MEA. Moreover, these plates support the cell's cooling, gas humidification, and current collection [22]. In order to fulfil these purposes, a bipolar plate has to be mechanically strong, have high thermal and electrical conductivity and resistance towards alkalis and acids. Generally, stainless steel, titanium, and graphite-based composites are materials of choice for developing bipolar plates.

### **1.3.2.4 Current collector**

The current collector collects the electrical current produced inside the MEA. It should exhibit homogeneous area and excellent electrical conductivity. Materials such as copper, platinum-coated niobium, gold-plated copper, stainless steel and nickel are considered for preparing current collector [22].

### **1.3.2.5 End plate**

End plate is a support plate which ensures that the fuel cell system is properly compressed mechanically. It prevents leakage of current and restrict MEA shorting. The end plate should be insulating in nature, generally anodized materials are considered for the purpose [22]. The plates are designed in a way such that the weight of the stack remains minimum. Anodized aluminum 6061 is typically utilized as end plates due to its lightweight.

## **1.3.3 Applications of DMFC**

DMFCs have potential in the portable power market due to the high energy density of methanol. Theoretically, methanol has a far greater specific energy density than

sophisticated Li-ion batteries. However, a fair comparison of Li-ion batteries and entire DMFC systems reveals a much closer race. DMFCs have an advantage over Li-ion batteries at greater energy contents and for larger system sizes. Customers may have a completely "wireless" experience with miniature DMFCs that use methanol fuel cartridges in place of power cables and adapters, especially in places devoid of power grid [26]. A docking station including a DMFC was created by Samsung Advanced Institute of Technology, SAIT, South Korea in 2006. The DMFC could produce modest quantities of electricity for extended periods of time at low temperatures, with a maximum power output of 20 W. The first commercial DMFC named Smart Fuel Cell C25 for laptop computers was successfully introduced in 2003 by the Smart Fuel Cell AG Company, Germany [27]. This little 1.1 kg DMFC device provided a constant 25 W at 12 V power output. A few years later Smart Fuel Cell AG developed a portable DMFC hybrid system (SFC C20-MP) equipped with an exchangeable 1.5 Ah lithium polymer rechargeable battery [28]. The device was powered by 500 mL methanol fuel cartridges. Two such SFC C20-MP were created to work in moderate and high ambient temperature ranges. The US Army Communication-Electronics Research Development and Engineering center (CERDEC) conducted testing reports of these two devices. Comparing these systems to earlier DMFC systems that CERDEC examined, the former had better electrical characteristics and dependability. It was therefore determined that further effort is required to keep these systems getting better. A DMFC with a 10 L cartridge that weighs 18.5 lbs was created by SFC AG in 2008 with the goal of providing remote video surveillance applications with off-grid, unattended, round-the-clock electricity in any place [26]. The device was said to have the same energy content as 595 pounds of batteries. Without any assistance, this DMFC ran a security camera for up to eight weeks. Between 2002 and 2009, SFC AG produced and distributed 13,000 DMFC devices with 100,000 fuel cartridges for consumer electronics [26]. Neah Power Systems brought miniature DMFCs to market in 2005 by substituting silicon-based membranes for the normal polymer-based electrolyte. This move resolved problems with polymeric membranes, used normally in traditional DMFC systems [26]. A very small DMFC was created in 2004 by Toshiba Inc. (Japan) which was said to be the smallest DMFC at the time. With 25 cm<sup>3</sup> of methanol, the system could provide 1 W of continuous electricity for around 20 hours. Toshiba introduced its first market product Dynario™ in 2009. With a highly concentrated methanol solution, the Dynario™ generated 2.5 W, which

was adequate to charge a standard cell phone battery twice. Later in 2009, a company Sony introduced a cordless mobile phone charging system that used a hybrid Li-ion/DMFC battery setup. Each of the four DMFC single cells, which shared a 270 mL methanol tank, provided 550–600 mW of power to the cordless speaker system. A Li-ion secondary battery was added to the system to enable higher power outputs as needed. The greatest power output of the hybrid system was around 10 W. The wireless speaker system may run for a full year on a single charge, assuming three hours a week of use in a home theater setting [26]. For electric vehicles smaller than a car, the DMFC provides a significant additional value in serial hybrid operation. It enables the electric vehicles to remain independent of any power sources for weeks. Even in little cars, 20, 30, and even more kWh may be conveniently stored in methanol cartridges. There are 1,200 sales locations around Europe where one may purchase the EFOY fuel cell and cartridges [29]. The EFOY Pro performs admirably in a variety of applications, including monitoring systems, measurement stations, oil and gas, and many more, as an off-grid power source and as an on-board power supply in automobiles. EFOY fuel cells are designed for the recreational market and provide a completely automated battery recharge, whether in a cabin, boat, or camper. While there has been progress in the commercialization of micro DMFCs, more advancements in energy efficiency, power density, and packaging downsizing are utmost required. Increasing stack lifetime, improving heat and water management, developing the infrastructure for fuel cartridge and canister delivery, are some other factors that need to be taken into consideration.

#### **1.3.4 Challenges pertaining to DMFC and scope of improvement**

Lab-scale advancements in this area indicate that this anticipation will likely materialize quickly. This possibility has multiplied many times over, particularly with the invention of micro-DMFCs, which employ microelectromechanical system technologies that readily fit into portable electronic gadgets. The next expectation from DMFCs is that they will replace the currently utilized fossil-based power sources in tiny vehicles and aircrafts. It will however take a few years to meet this expectation. Another anticipation from DMFC is to provide electricity in isolated places. Unfortunately, given the current state of DMFC technology development, this is still a long way off and will require a significant amount of research and developmental work to be successful. Even though DMFCs are anticipated to eventually replace traditional batteries in portable electronic

devices, the anticipated result has not yet been achieved. It is true that DMFC technology is being marketed on a modest basis, but this commercialization is not at all widespread. This is due to a few significant shortcomings with this technology: 1) Excessive and uncontrollable methanol crossover via the membrane electrolyte, which leads to formation of cross-potential, leading to drop in cell performance, 2) extremely expensive and scarce noble metal Pt used as electrocatalysts, 3) poisoning of the catalyst by adsorbed intermediates of the methanol oxidation reaction which reduces the MOR kinetics, 4) the incapacity of the cell's constituent parts, particularly the membrane electrolyte, to tolerate low working humidity and high temperatures over 110°C [22]. Therefore, electroactive materials that are CO-resistant, extremely stable, and inexpensive are growing in demand. By running the fuel cell in an alkaline electrolyte, where the kinetics are enhanced and Pt-free catalysts may be utilized, this poisoning issue can be resolved. Therefore, there are several benefits of using alkaline electrolytes in fuel cells, including increased efficiency, better reaction environment, decreased risk of poisoning, less sensitivity to surface structure, and a wider selection of reasonably priced non-noble metal electrode materials. Co-based transition metal oxides ( $\text{MnCo}_2\text{O}_4$ ,  $\text{CoCo}_2\text{O}_4$ , or  $\text{NiCo}_2\text{O}_4$ ) and other mixed transition metal oxides are stable in alkaline electrolytes because  $\text{OH}^-$  ions continue to cover their surfaces [30]. These adsorbed  $\text{OH}^-$  ions dehydrate adsorbed alcohols and causes desorption of the poisoning intermediates during alcohol oxidation in an alkaline medium [31]. As the conductivity of the metal oxides are lesser than the Pt-based catalysts, the alcohol oxidation reaction can be compensated by making composites with other conducting 2D materials having large surface area [1].

#### **1.4 Energy storage device supercapacitor**

Among the various energy storage technologies available, electrochemical energy storage systems are sustainable, safe and efficient ways to store the renewable resources. Supercapacitors, as electrochemical energy storage devices, are becoming popular in the markets of electrical vehicles, portable electronic devices, and smart grids. Supercapacitors function as an immediate power source and, in contrast to batteries, have a wide operating temperature range, long cycle life, and short charging times [32, 33]. Capacitors store charge nonfaradaically and display specific energy less than 0.1 Wh/kg, but they offer higher power density than batteries. Batteries store charge faradaically and

have a high energy density of around 100 Wh/kg or even more, but their cycle stability is limited. Electrochemical supercapacitors have an exceptional cycle life of  $10^5$  cycles and a superior energy density of 10 Wh/kg as compared to regular capacitors [34, 35]. Supercapacitors, often referred to as ultracapacitors, are able to meet intermediate energy requirements and act as a transition between traditional capacitors and batteries.

#### 1.4.1 Working principle of supercapacitor

Based on its mechanism of charge storage, supercapacitors can be classified into three groups: (i) Electric double layer capacitors (EDLC), (ii) Pseudocapacitors, and (iii) Hybrid supercapacitors.

##### 1.4.1.1 Electric Double Layer Capacitor (EDLC)

In EDLC, electrostatic charge storage takes place by virtue of reversible adsorption of electrolyte ions onto the surface of the electrode material [32, 36]. At the electrode-electrolyte interface, polarization causes charge separation, and ions of opposite polarity accumulate on the electrode's surface, resulting in the formation of double layer at each electrode-electrolyte interface. Without any charge transfer taking place across the interface, the charge storage occurs at these double layers. The two double layers formed at cathode and anode-electrolyte interface denotes two capacitors connected in series. The thickness of double layer depends on concentration of the electrolyte, and size of the ions. For concentrated electrolytes, thickness of double layer is normally 5-10 Å [35]. The EDL capacitor comprises of cathode, anode, electrolyte and a separator as shown in fig. 1.4. During the charging process, the electrodes get polarized and attract the electrolyte ions of opposite polarity to pass through the separator and reach the electrode surface. The separator, which is a good ionic conductor, conducts only ions and prevents the electronic movement across it, thereby avoiding short circuit. On discharging, the electrolyte ions get desorbed and diffuse to their original positions and stored energy is released. If  $E_A$  and  $E_C$  represent respectively the positive and negative electrode surfaces,  $A^-$  and  $C^+$  are the anions and cations respectively and // represent the electrode-electrolyte interface [37], then the charging and discharging processes can be expressed as-

At positive electrode:





At negative electrode:



The overall charging/discharging of the cell can be expressed as-

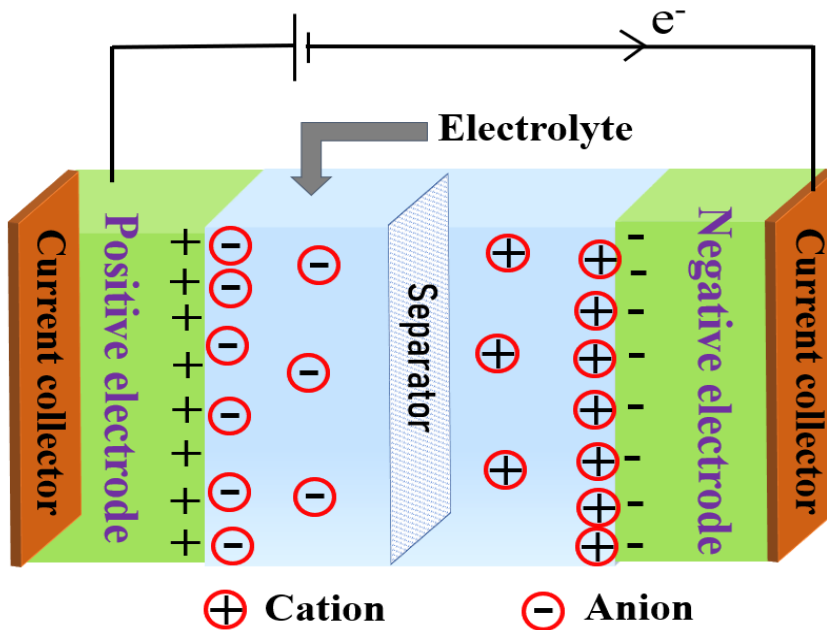
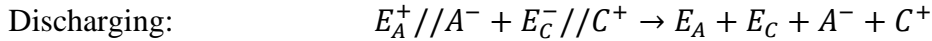
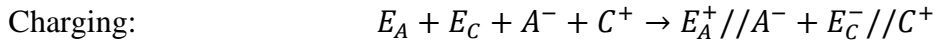


Figure 1.4: Schematic of charge storage mechanism in electric double layer capacitor

The short charge separation distance and large surface area of the electrodes, allow EDLC to attain higher capacitance than normal capacitors. As no chemical reactions are involved in EDLC charge storage mechanism, the charge/discharge process is fast and highly reversible. The charge/discharge speed depends on the speed of the ions within the electrolyte. Thus, electrolytes with high ionic conductivity exhibits faster charge/discharge. Therefore, EDL capacitors offer high power density and long cycle life ( $10^6$  cycle); however, their energy density is low (5-10 Wh/kg) as the charge storage is confined only to the surface of the electrode, and not the bulk [32, 38, 39]. Generally porous carbonaceous materials with large surface area are considered as EDL materials [36, 40].

### 1.4.1.2 Pseudocapacitor

In pseudocapacitor, besides electrostatic charge accumulation and intercalation, fast and reversible faradaic redox reactions between the electrode and electrolyte, are responsible for charge storage [32, 41, 42]. The application of a potential results in charge transfer across the electrode-electrolyte interface, leading to a change in the electrode's oxidation state. Such process is termed as faradaic reaction [43]. In contrast to EDLC, the amount of charge stored in pseudocapacitor is a function of the electrode's potential, which resembles to a capacitor, thereby the name 'pseudocapacitor' [44]. Thus, in a pseudocapacitor, the capacitance arises due to electrosorption and the redox reactions induced by the applied potential [32]. The faradaic reactions take place in the electroactive sites available both on the surface and in the bulk of the material, providing higher specific capacitance almost 10-100 times that of EDLC [45]. The faradaic reactions are sluggish than the ion adsorption in EDLC. Besides, the electrode encounters certain volumetric changes due to the continuous penetration of ions, causing degradation of the electrode with time. Hence, pseudocapacitor offers high energy density, but low power density and cycle life as compared to EDLC [39, 45]. Different conducting polymers [32, 37, 46, 47], nanostructured transition metal oxides [46, 48, 49], transition metal hydroxides [50], and transition metal oxide/hydroxide derivatives [50], etc. exhibit pseudocapacitive property.

### 1.4.1.3 Hybrid supercapacitor

In order to increase the energy density of EDLC without compromising its power density and cycle life, the concept of hybrid supercapacitor came into consideration. A hybrid supercapacitor is made of electrode materials which exhibit both EDL capacitance and pseudocapacitance [32, 51]. The hybrid supercapacitor is developed to mitigate the weaknesses of EDLC and pseudocapacitor by combining both to obtain a synergistic effect. As faradaic and non-faradaic processes appear in hybrid supercapacitor, a high energy density ( $20-30 \text{ Whkg}^{-1}$ ) is obtained along with high power density and cycle life [51, 52], thus outperforming the EDLC and pseudocapacitor performance. The hybrid supercapacitors are classified into three groups based on the electrode configuration [52], namely (i) Composite hybrid, (ii) Asymmetric hybrid and (iii) Battery-type hybrid supercapacitor.

(i) Composite hybrid supercapacitor: Composite hybrid electrode is developed by combining either metal oxide or conducting polymers with carbon-based materials to obtain a single electrode that integrate both faradaic and non-faradaic charge storage mechanisms into one [51, 52]. The carbon-based material besides providing EDL capacitance with high power density, also bestows large surface area to the pseudocapacitive material, thereby increasing its contact with the electrolyte. The pseudocapacitive material thus provides enhanced capacitance by benefiting from the advantages of the composite hybrid [53]. In this manner, composite hybrid provides good energy and power density by addressing the shortcomings of EDLC and pseudocapacitor charge storage mechanisms.

(ii) Asymmetric hybrid supercapacitor: Asymmetric hybrid supercapacitor is developed by combining an EDLC electrode with a pseudocapacitive electrode [51, 52]. The EDLC electrode is considered as the negative electrode and the pseudocapacitive one as the positive electrode. The asymmetric hybrid supercapacitor that couples these two mechanisms help mitigate the individual limitations and achieve higher energy density than ELDCs and higher power density and cycle life than pseudocapacitors [54].

(iii) Battery-type hybrid supercapacitor: Alike asymmetric hybrid supercapacitor, battery-type hybrid supercapacitor too integrates two electrodes; however; here it couples two different technologies; one electrode being supercapacitor and the other a battery electrode [51, 52]. This specialized coupling of technology benefits the energy density of batteries along with the power density, cycle life and fast charging times of supercapacitors [52]. Not much experimental data is available on battery-type hybrid supercapacitors; however, this hybrid category keeps immense potential in filling the gap between batteries and supercapacitors. Even with the encouraging outcomes, experts agree that further study is required to fully understand the potential of battery-type hybrids [55].

#### **1.4.2 Merits, demerits and scope of improvement**

As already discussed in the previous section, EDLC offers high power density and cycle life, however, its energy density is low as compared to pseudocapacitors. On the other hand, pseudocapacitor offers higher specific capacitance and energy density; however, it suffers from low power density and cycle life than the EDLC. Thus, both the

mechanisms, i.e., EDLC and pseudocapacitance have their own disadvantages, which can be mitigated by developing hybrid supercapacitors. Hybrid supercapacitor, as discussed in section 1.4.1.3, are composed of materials that combines both the mechanisms. Combining both the charge storage mechanisms help to compensate individual drawbacks and achieve desired energy density without compromising power density and cycle life. Thus, by making nanocomposites of pseudocapacitive material with EDLC exhibiting material, an efficient hybrid supercapacitor can be developed.

## **1.5 Electrode materials considered in the thesis**

For an efficient electrode material in methanol electrocatalysis and supercapacitor, electrochemically active material having multiple redox sites, large specific surface area, high electrical conductivity, tunable electronic properties, durability, good thermal and mechanical stability are required. In the present thesis nanocomposites of transition metal oxides with two-dimensional material namely, reduced graphene oxide and MXene are considered as the electrode materials. The materials are discussed briefly in the following sections.

### **1.5.1 Transition metal oxide**

Transition metal oxides (TMOs) have attracted interest in energy conversion [56, 57] and storage applications [58, 59] due to their low cost, controllable chemical and textural properties, environmental friendliness, rich electrochemical properties and high theoretical specific capacitance values. The cations in TMOs possess variable oxidation states due to the presence of unfilled d-orbitals, which offer different electronic properties to the TMOs. TMOs are evolving as potential alternatives to noble metal-based electrocatalysts because of their high stability in alkaline medium and their Lewis acid–base properties [1]. However, the electrochemical properties and specific capacitances of TMOs are significantly lower than their theoretical values due to limitations such as low ionic diffusion, low specific surface area, and weak intrinsic electrical conductivity [60]. Cobalt oxide ( $\text{Co}_3\text{O}_4$ ) is an intrinsic p-type semiconductor having normal spinel structure where  $\text{Co}^{2+}$  occupies tetrahedral sites and  $\text{Co}^{3+}$  occupies octahedral sites [61]. It is emerging as a promising material in various fields of energy storage, conversion, sensors, photocatalysis, solar selective absorber, etc. owing to its enriched electrochemistry, less toxicity, good reversibility, stability, and cost effectiveness [61, 62].

Nickel oxide (NiO) is also an intrinsic p-type semiconductor exhibiting strong pseudocapacitive properties and low oxidation potential, thereby attracting the attention in energy conversion and storage technologies [63]. It has been considered as one of the potential electrode materials due to its high theoretical capacitance ( $2584 \text{ F g}^{-1}$ ), natural abundance, cost effectiveness, and eco-friendliness. However, low electrical conductivity ( $< 10^{-13} \text{ Scm}^{-1}$ ) [64, 65] and low specific surface area limit its charge-discharge rates, due to which high specific capacitance cannot be achieved experimentally. Hence, to increase its conductivity and specific surface area, nanocomposites of NiO are explored with different carbon materials.

Poor electron transfer rate and slow kinetics of these monometallic TMOs restrain their further development. Mixed transition metal oxides can overcome these drawbacks due to the presence of multiple transition metal cations exhibiting variable redox couples. The different cations offer improved electrical conductivity than the monometallic TMOs [66]. Nickel cobaltite ( $\text{NiCo}_2\text{O}_4$ ) is a ternary TMO having inverse spinel structure, in which  $\text{Ni}^{2+}$  ion occupies octahedral sites,  $\text{Co}^{3+}$  ion occupies both tetrahedral and octahedral sites, and oxide ions occupy the fcc lattice points [67].  $\text{NiCo}_2\text{O}_4$  is obtained by substituting one of the Co atoms of  $\text{Co}_3\text{O}_4$  by Ni atom. The improved physicochemical characteristics of  $\text{NiCo}_2\text{O}_4$  is ascribed to the incoming Ni atom with ionic radius comparable to Co atom [67]. This replacement of Co by Ni affects the crystal structure, which impacts the electrochemical activity of  $\text{NiCo}_2\text{O}_4$  [66, 67].  $\text{NiCo}_2\text{O}_4$  has good electrical conductivity as a p-type semiconductor with a band gap of 2.1 eV [66]. It has conductivity in the range  $0.05\text{-}10^{-6} \text{ Scm}^{-1}$  [68].

### 1.5.2 Reduced Graphene Oxide

Graphene, a two-dimensional carbon material consisting of  $\text{sp}^2$ -bonded monolayers of carbon atoms, has been a topic of immense interest in material science and technologies since its initial synthesis in 2004 [69]. It owns outstanding properties which include excellent thermal ( $\sim 5000 \text{ Wm}^{-1}\text{K}^{-1}$ ) and electrical conductivity ( $10^6 \text{ S/cm}$ ), flexibility (Young's Modulus  $\sim 1100 \text{ GPa}$ ), ultrahigh specific surface area ( $2630 \text{ m}^2\text{g}^{-1}$ ), and outstanding chemical stability [70]. These exceptional properties make graphene a potential material for a wide range of applications, such as solar cells, sensors, transistors, energy storage devices, etc. [71]. Graphene is attracting attention in the field of energy

storage with promise for energy and power density enhancement. Consequently, great efforts are being undertaken to use materials based on graphene in advanced energy storage technologies. The most challenging part in successful application of graphene is high-yielding synthesis method. High quality graphene can be prepared using different primary techniques which include solution exfoliation, mechanical exfoliation, electrochemical exfoliation, chemical vapour deposition and epitaxial growth [71]. However, the yield of these techniques is relatively low. Conversely, reduction of graphene oxide has been extensively utilized to acquire graphene on large scale for basic and applied research. Graphite can be oxidized by using a number of chemical methods such as the Hummers method to yield graphite oxide, followed by exfoliation in suitable solvents to acquire a suspension of few layered graphene oxide [72]. Reduction process is employed to recover partially the parent graphite basal planes. Various kinds of reducing agents such as sodium borohydride, hydrazine hydrate, hydroiodic acid, vitamin C, etc. are used in the reduction process [73]. The chemically reduced graphene oxide (rGO) has poor graphene quality and low C/O ratio, as the oxide groups are not totally reduced [72, 44]. In the recent times, annealing at high temperature is practised to convert graphene oxide to pristine graphene [74, 75]. The oxygen functional groups contained in its structure offers hydrophilicity and enable tunable electrical and optical properties. The large specific surface area with conductivity, hydrophilicity and flexibility makes rGO an excellent graphene derivative, suitable for electrochemical energy storage/conversion applications. The rGO sheets tend to aggregate during the reduction process, which lowers its practical applications. These issues can be resolved by developing nanocomposites and heterostructures with nanostructures.

### 1.5.3 MXene

MXene is a new addition to the family of 2D materials after Naguib et al. exfoliated MXenes by selectively etching A layer from the MAX phase [76]. The MAX, a transition metal carbide and nitride, is typically represented by  $M_{n+1}AX_n$ , where n can be any number between 1 and 3, M is a transition metal, A can be any element from groups 13 to 16 of the periodic table, and X can be either carbon, nitrogen, or a combination of the two. The X atoms occupy the octahedral positions in the hexagonal layered structures of MAX phases, which are composed of  $M_{n+1}X_n$  layers joined together by A layers [76, 77]. Compared to the M–A bond, which is often metallic, the M–X bond is stronger as it is a

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blend of metallic, covalent, and ionic nature [78]. In contrast to its 2D inorganic counterparts, whereby the layers are held together by weak vander Waals forces, MAX exhibits significant interlayer bonding, which makes mechanical exfoliation challenging [48]. Nonetheless, it is feasible to exfoliate it by etching the A layer from  $M_{n+1}AX_n$  using various etchants (such as HF, LiF + HCl, and  $NH_4HF_2$ ) due to variations in the reactivity of M–X and M–A bonds [79]. Even though the etchant hydrofluoric acid (HF) has a high yield, concentrated HF is hazardous. A quicker and safer alternative exfoliation approach is required to prevent the use of corrosive HF and promote the industrial usage of MXenes. Ammonium bifluoride ( $NH_4HF_2$ ), was reported by Halim et al. in 2014 as a safer alternative to toxic HF [80]. Ghidui et al. [81] then suggested etching Al from  $Ti_3AlC_2$  by creating HF in situ via a reaction between HCl and LiF, in which intercalation and etching occur alongside. The transition metals on the surface bond with anions like  $OH^-$ ,  $F^-$ , and  $O^{2-}$  during the etching process. These anions are the terminations  $T_x$ , which are hydrophilic in nature [1]. As a result, the metallic bond M–A is replaced by a weaker hydrogen bond, which facilitates the intercalation of organic intercalants (dimethyl sulfoxide, urea, and water) between the layers. This allows a shearing force to delaminate the multilayers into a single or few layers [79]. MAX phases possess a combination of ceramic and metallic properties. They exhibit stiffness, thermal stability, brittleness, strength like ceramics, and good thermal and electronic conductivity like metals [82]. There are three potential lattice configurations of MXene corresponding to the value of n in MAX:  $M_2X$ ,  $M_3X_2$ , and  $M_4X_3$  [83]. Only 20 MXenes have been successfully exfoliated out of the 70 MAX phases reported so far [1]. MXenes have hexagonally close packed (hcp) structure in general. However, the crystal structure depends on the value of n, as the M atoms in  $M_2X$  have hcp structure, whilst  $M_3X_2$  and  $M_4X_3$  have fcc structure [1]. The intriguing characteristics of MXene include high metallic and electrical conductivity, which ranges from 6000 to 8000  $Scm^{-1}$ , as well as their hydrophilicity, large surface area, adjustable structure, and good thermal conductivity [84]. MXene is a fascinating candidate for many applications, including electrochemical energy storage devices, electromagnetic shielding, sensors, FETs, catalysis, and biological applications, due to its unique features. As an electrocatalyst and photocatalyst, MXene has recently acquired popularity in the fields of energy conversion and environmental applications [1, 61]. Titanium carbide MXene ( $Ti_3C_2T_x$ ) is the most studied MXene and its monolayer exhibits an electrical conductivity around 10,000  $Scm^{-1}$  and a very high Young's modulus

of  $0.33 \pm 0.03$  TPa. This value is nearly close to that of micro-mechanically exfoliated graphene ( $\sim 1$  TPa) [85].

### **1.6 Scope of the thesis and statement of thesis problem**

In light of the global energy challenges, researches are committed to develop efficient energy storage and conversion devices. Direct methanol fuel cell (DMFC) is a promising energy conversion technology due to its high-power density, low pollutant emission, and high conversion efficiency. Moreover, methanol has high energy density and is less toxic and biodegradable fuel that does not require the breaking of C-C bonds. Despite these advantages, the methanol oxidation reaction is sluggish, necessitating the use of anode catalysts to accelerate the electrooxidation process. State-of-the-art noble-metal based electrocatalysts suffer from scarcity, high price, CO poisoning effect and poor durability, which can be overcome by the non-noble metals electrocatalysts. Transition metal oxides (TMOs) have the potential to compete with noble-metal-based catalysts due to their easy availability, good stability in alkaline medium, and varied redox sites. As energy storage devices, supercapacitors are attracting attention in portable and electronic gadgets, electric vehicles, smart grids, etc. due to their high-power density, high cycle life and instantaneous power supply. However, supercapacitors still lag behind batteries in terms of energy density. Thus, efforts are poured in developing efficient supercapacitor electrode to achieve high specific capacitance and energy density. Materials exhibiting ELD capacitance offer high power density and cycling stability, but low energy density. In this regard, pseudocapacitive materials like transition metal oxides can offer high energy density due to the faradaic reactions taking place in the redox active sites. Thus, by developing nanocomposite of EDL and pseudocapacitive materials, one can obtain good capacitive performance without compromising the power and cycling performance.

Motivated by the above facts, in the present thesis, nanocomposites of transition metal oxides are developed with conducting 2D materials, reduced graphene oxide and MXene to design porous electrodes and achieve good interfacial interactions. Anode catalyst of DMFC and supercapacitor electrodes are designed by the synthesized nanocomposites. rGO and MXene could offer enlarged surface area for proper dispersion of the TMOs. The nanocomposites could resolve the aggregation, low surface area, and conductivity of TMOs. By the synergistic contribution of all the components, the



nanocomposites are expected to offer good electrocatalysis and supercapacitive performances. The objectives of the present thesis are mentioned below:

- 1) To synthesize 2D material based nanocomposites and develop
  - i) Non – noble metal electrocatalyst for electrooxidation of methanol
    - a)  $\text{Co}_3\text{O}_4$  nanoparticles decorated MXene.
    - b) Mixed metal oxide of  $\text{NiCo}_2\text{O}_4/\text{NiO}$  on reduced graphene oxide.
    - c) Mixed metal oxide of  $\text{NiCo}_2\text{O}_4/\text{NiO}$  on MXene.
- 2) To study the electrochemical performance of the developed Direct Methanol Fuel Cell anode catalysts.
- 3) To perform post methanol oxidation characterizations.
- 4) To study the supercapacitive property of the developed nanocomposites.

In order to achieve the above-mentioned objectives, the following methodologies are used.

- i. Surface morphology of the developed systems has been studied using Field Emission Scanning Electron Microscopy (FESEM).
- ii. Transmission Electron Microscopy (TEM) has been performed to study the size, shape, uniformity of materials, crystal structure and crystalline phases.
- iii. X-ray Diffraction (XRD) is performed to confirm the formation of crystalline samples.
- iv. Fourier-Transform Infrared Spectroscopy (FTIR) has been performed to identify the chemical bonds and the new compounds present in the samples.
- v. The elemental composition and different oxidation states of the samples have been studied using X-ray Photoelectron Spectroscopy (XPS).
- vi. The specific surface area and pore size distribution have been studied using nitrogen adsorption-desorption isotherms using Brunauer–Emmett–Teller method (BET).
- vii. Electrochemical performances and electron transfer mechanisms of the electrodes are studied using the Cyclic Voltammetry (CV) method.
- viii. Chronoamperometry (CA) is done to study the adsorption of intermediates on the electrodes, and stability of the electrodes.
- ix. Electrochemical impedance spectroscopy (EIS) is performed to evaluate the ion transport/diffusion on the surface of electrode, and different impedances involved in the electrode-electrolyte interactions.
- x. Galvanostatic charge-discharge (GCD) measurements are done to analyse the charge-

storage properties of the developed supercapacitor electrodes.

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