1. INTRODUCTION

1.1. FUEL CELL

1.1.1. HISTORY

It was as early as in 1839 that William R. Grove discovered the basic operating principle of fuel cell technology by reversing water (H$_2$O) electrolysis to generate electricity from hydrogen (H$_2$) and oxygen (O$_2$) [1]. This technology has attracted increased attention during the last couple of decades both from scientists and technologists all over the world [2-13]. A fuel cell is defined as an electrochemical energy conversion device that combines a fuel (H$_2$, natural gas, methanol (CH$_3$OH), gasoline etc.) and an oxidant (air or O$_2$), and converts a fraction of their chemical energy into useful electrical power. Unlike a battery, a fuel cell does not store energy, it works in a continuous manner whenever fuel is delivered, and is devoid of charge-discharge cycles. Moreover, fuel cells practically avoid the emission of toxic gases, such as sulfur dioxide and nitrogen oxides [14-17]. At present scenario, when protecting global environment has become a serious issue, research on fuel cells has gained more acceptance as a highly promising technology to solve problems associated with energy resources, atmospheric pollution, green house effects and global warming because they provide high efficiency and low emissions [18].

1.1.2. CLASSIFICATION OF FUEL CELL

Fuel cell systems can be classified on the basis of various parameters, which include the nature and type of fuel used, whether the fuel is processed externally (external reforming) or internally (internal reforming), operating temperature, pressure of operation and type of electrolyte. However, for practical reasons, they are simply distinguished by the type of electrolyte used. The six generic fuel cells in various stages of development are: (a) proton exchange membrane fuel cells (PEMFCs) [19], (b) direct methanol fuel cells (DMFCs), (c) alkaline fuel cells (AFCs), (d) phosphoric acid fuel cells (PAFCs), (e) molten carbonate fuel cells (MCFCs), and (f) solid oxide fuel cells (SOFCs). Among
these, the polymer electrolyte H₂/air and DMFCs are most promising systems for providing power to portable devices and in transportation sectors [20,21].

1.1.3. SELECTION OF FUELS: METANOL (CH₃OH)

The selection of organic fuels lies with size, weight, cost and finally their efficiencies. As compared in Table 1.1 [22], although hydrogen has proved to be the best fuel in terms of energy conversion (chemical to electrical); its production, storage and distribution have several associated problems [23,24]. Compared to hydrogen, methanol as a liquid fuel offers many advantages, such as higher energy density (6100 Wh Kg⁻¹ at 25° C), relatively cheap, easy storage and handling, readily available and soluble in aqueous electrolytes [25,26]. Since it can be readily derived from oil, natural gas, coal or biomass there is ample scope for its availability as a fuel. In addition, methanol needs no cryogenic storage container. Methanol can be completely electro-oxidized to carbon dioxide (CO₂) at temperatures well below 100° C at a fuel cell anode either directly or indirectly.

Table 1.1: Chemical and electrochemical data of various fuels [22].

<table>
<thead>
<tr>
<th>Fuel</th>
<th>( G^\circ ) (Kcal/mol)</th>
<th>( E_{\text{theo}}^\circ ) (V)</th>
<th>( E_{\text{max}}^\circ ) (V)</th>
<th>Energy density (kWh/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>-56.69</td>
<td>1.23</td>
<td>1.15</td>
<td>32.67</td>
</tr>
<tr>
<td>Methanol</td>
<td>-166.80</td>
<td>1.21</td>
<td>0.98</td>
<td>6.13</td>
</tr>
<tr>
<td>Ammonia</td>
<td>-80.80</td>
<td>1.17</td>
<td>0.62</td>
<td>5.52</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>-143.90</td>
<td>1.56</td>
<td>1.28</td>
<td>5.22</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>-124.70</td>
<td>1.35</td>
<td>1.15</td>
<td>4.82</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>-68.20</td>
<td>1.48</td>
<td>1.14</td>
<td>1.72</td>
</tr>
<tr>
<td>Methane</td>
<td>-195.50</td>
<td>1.06</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>Propane</td>
<td>-503.20</td>
<td>1.08</td>
<td>0.65</td>
<td>-</td>
</tr>
</tbody>
</table>

Overall, DMFC technology provides the following advantages: (a) elimination of need for fuel storage, (b) high energy density of the fuel, (c) modularity, vibration free and silent operation. Moreover, since CH₃OH is fed directly as diluted aqueous solution, it also avoids complex humidification and thermal management problems associated with
hydrogen in fuel cells. These advantages led the researchers to the conclusion that DMFC operating at low/medium temperatures of up to 130°C is the most favorable option for mobile and portable applications.

1.2. DIRECT METHANOL FUEL CELL (DMFC)

1.2.1. BASIC PRINCIPLE

DMFC uses methanol in the form of vapor or liquid as fuel and consists of a solid polymer electrolyte. A schematic illustration of a DMFC is shown in Figure 1.1. It consists of an anode at which methanol is electro-oxidized to CO₂ represented by the reaction:

At anode: \( CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \) \( (E^o = 0.02 \text{ V/ SHE}) \) \( (1.1) \)

At Cathode: \( 3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \) \( (E^o = 1.229 \text{ V/ SHE}) \) \( (1.2) \)

Overall reaction: \( CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \) \( (E_{cell} = 1.213 \text{ V}) \) \( (1.3) \)

Where, SHE stands for standard hydrogen electrode and a cathode, at which oxygen (usually air) is reduced to form water or steam,
resulting in release of electrons (e\(^{-}\)) and protons (H\(^{+}\)) as detailed in Reaction (1.1). The released electrons get conducted through the metal catalyst and carbon grains, and arrive at the cathode side of the cell via the external circuit. On the other hand, protons get transported through the polymer electrolyte membrane (PEM) to the cathode catalyst layer. Simultaneously, oxygen or air is fed into the cathode flow channel, where it diffuses through the diffusion layer and reaches the catalyst layer. Here it reacts with the generated protons and electrons to produce water according to the Reaction (1.2). The Gibbs free energy of methanol and oxygen is much higher than those of water and carbon dioxide. Consequently, the combustion of methanol is a spontaneous reaction under standard conditions of 298.15 K temperature and 1 atm. pressure. This energy difference facilitates the production of electrical energy.

1.2.2. COMPONENTS AND THEIR FUNCTIONS IN DMFCs

Typically, a DMFC is composed of a membrane electrode assembly (MEA), bipolar plates, gaskets, current collector and end plates.

Fig. 1.2 DMFC single cell (Left) and Schematic representation of the cell components (Right) [1 & 10 End plates, 2&9 Heaters, 3&8 Current collector plates, 4&7 bipolar plates and 5&6 Gasket].

(a) Membrane Electrode Assembly (MEA)

The MEA is the heart of a DMFC and consists of a proton exchange membrane, catalyst layers and gas diffusion layers (GDLs). Usually these components are fabricated
individually and then pressed together at high temperatures and pressures [27,28]. On the other hand, GDLs facilitate the transport of CH$_3$OH and Air/O$_2$ to the anode and cathode catalyst layers, respectively. In addition, GDL also allows the conduction of electrical current out of the cell and provides the MEA with mechanical stability by holding the porous film-like catalyst structure [29].

(b) Bipolar plates

Bipolar plates are generally used to distribute the fuel and the oxidant within the cell and separate the individual cells in the stack. They also contribute in collecting and distributing current, humidifying gases and keeping the cells cool. The commonly used materials for bipolar plates include nonporous graphite, a variety of coated metals and a number of composite materials [30-35].

(c) Gaskets, Current collector plates and End plates

In a DMFC system, a gasket prevents leaking of reactants [36,37] and isolates current between the current collector and end plates. The current collectors carry current generated in the MEA, and end plates maintain the compactness of the system. Copper, gold-plated copper, stainless steel, gold plated nickel and so on are used for the fabrication of the current collector [38,39]. On the other hand, materials that are mechanically strong and electrically nonconductive are used for making the end plates [40].

1.2.3. ADVANTAGES AND APPLICATIONS

Methanol releases six protons and electrons per molecule during its oxidation. Its high energy density makes methanol a suitable fuel for fuel cells. It can work at low and intermediate temperatures (up to 150º C) and are fed as a dilute aqueous solution of methanol.

Overall, DMFC technology is associated with several advantages like simple liquid fuel handling, simple system structure, reduced size and weight, high power generation efficiency and improved safety. Recently, DMFC has shown to work efficiently as a main power source in stationary, transportation and other portable devices [20, 21].
1.3. CHALLENGES OF DMFC AND PROSPECTIVE RESEARCH

In spite of several years of active research involved in the development of DMFC technology, their chemical-to-electrical energy conversion efficiencies are still lower compared with other alternative power sources traditionally used. These deficiencies associated with DMFC cell performance is due to (a) Electrode kinetic limitations, (b) Methanol crossover and (c) Gas and water management.

However, the use of acids as supporting electrolyte have resulted in enhanced solution conductivity and thereby improved electrode kinetics [41-43]. On the other hand, bipolar plates integrated with serpentine flow channel furnished high mass transfer, fast removal of gas and slightly lower methanol crossover than the use of conventional bipolar plates integrated with straight channel design [44-46]. On the other hand, utilization of sulfonated/non-sulfonated PVdF and its copolymer as a blend/composite, coating and/or laminate material with Nafion and other polymers has stepped in to conquer the methanol crossover hurdle up to an acceptable limit [47-50]. In addition, due to the similar fluorinated-carbon backbone chain as Nafion, PVdF and its co-polymer exhibits satisfactory mechanical strength, dimension stability and chemical resistance [51-53].