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Advances in Materials for Fuel Cell Technologies- A Review

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Abstract: The primary objective of this review paper is to highlight the advances in Fuel Cell with the newly developed fuel cell materials and membranes as well as their potential applications. The major disadvantage that limits the commercialisation of conventional Platinum (Pt)/Palladium (Pd) electrode based fuel cells is the expense and hence restricts the use of fuel cells, though being more an environment friendly energy production method. With recent development and the newly emerging materials, these conventional technologies can be replaced with advanced materials and membranes. The synthesis, process chemistry, physical, electrical and chemical properties, output characteristics, workability and performance of recently developed electrode materials: Nitrogen doped Graphene electrode, Carbon Nanotube based electrodes for applications in conventional proton exchange membrane and microbial fuel cells; newly emerging polymer electrolyte membranes; Synthesis of new materials i.e. quantum dots (graphene and polyvinyl alcohol) as catalysts or support for catalysts, electron mediators and advanced electrolyte solutions have been studied in the paper. Recent advancements in the synthesis of porous materials called Metal Organic Framework for fuel cell applications have also been reviewed.

Keywords: Fuel Cells, Nitrogen-doped Graphene, Carbon Nanotubes, Graphene and Polyvinyl Quantum Dots, electron mediators, Metal Organic Frameworks.

I. INTRODUCTION

Throughout the world, the need of the hour is power generation with environment protection. Fuel cells represent an alternative to the current conventional technologies. The advantages of Fuel Cells over other devices are higher efficiency in energy conversion, very low consumption of fossil fuel, low pollution level, low noise and low maintenance costs. The newly developed fuel cell materials and membranes have high proton conductivity, low water permeability and good thermal and mechanical stability[1]. The use of Fuel Cells has gained momentum over the past few years as they are a portable source of power for light duty vehicles, household and aeronautical applications and offer an excellent replacement for rechargeable batteries[2].

A fuel cell is a device that generates electric power due to chemical reactions taking place at the two electrodes as shown in Fig 1 [3]. Each fuel cell contains a negative electrode; Anode where oxidation reaction or loss of electrons take place and a positive electrode; Cathode where reduction reaction or gain of electrons occurs. Thus the electrons flow from negative to the positive terminal and the electric current gets generated, which flows from Cathode to Anode of the fuel cell. This is an Oxidation Reduction Reaction (ORR)[4]. It also contains an electrolyte solution or a selectively permeable membrane that allows only appropriate ions to pass between the cathode and anode chamber.

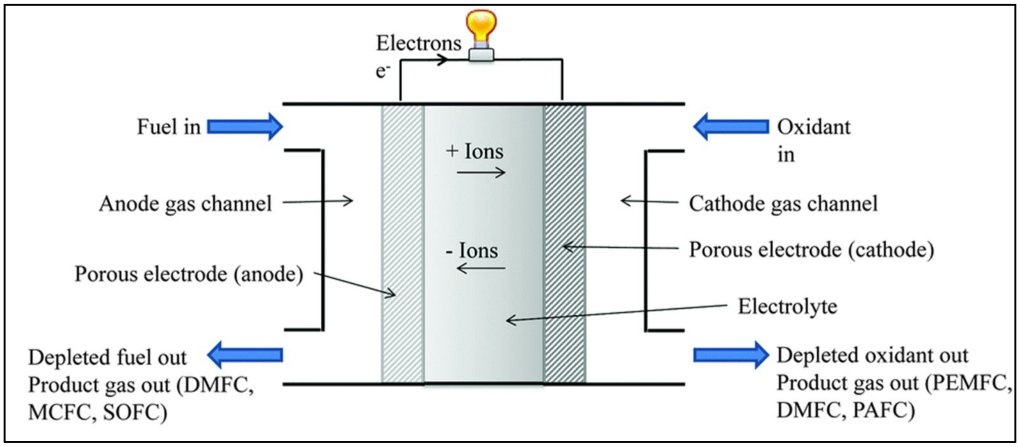

Figure 1: General Representation of Fuel Cells [5].

The output of the fuel cell is in the form of Direct Current (D.C.), which can be converted to alternating current (A.C.) if needed, by an inverter. Fuel cells generate electricity chemically rather than by combustion of fuel in a power plant. Hence it is a more environment friendly and efficient process. The different types of fuel cells were reviewed in Table 1.

Type	Temperature °C	Fuel	Electrolyte Mobile	Ion
PEM: polymer electrolyte membrane	70–110	H_2 CH_3OH	Sulfonated polymers (Nafion®)	$(H_2O)_nH^+$
AFC: alkali fuel cell	100–250	H_2	Aqueous KOH	OH^-
PAFC: phosphoric acid fuel cell	150–250	H_2	H_3PO_4	H^+
MCFC: molten carbonate fuel cell	500–700	Hydrocarbons CO	$(Na,K)_2CO_3$	CO_3^{2-}
SOFC: solid oxide fuel cell	700–1000	Hydrocarbons CO	$(Zr,Y)O_{2-\delta}$	O^{2-}

Table 1: Fuel cell types and selected features [6]

The major disadvantage of fuel cell is the cost. However, recent developments of cost-effective materials and advanced membranes have been successful to turn down this limitation too [7].

II. RECENT ADVANCES IN FUEL CELL TECHNOLOGIES

A. *Nitrogen Doped Graphene Fuel Cell*

1) *Oxidation-Reduction Reaction Pathways:* Electro catalytic ORR can be carried out in three pathways A: 1-electron transfer pathway: Reduction pathway from O_2 to O_2^-. Proceeds to producing superoxide ion. It can be observed in a non- aqueous aprotic solvent system, a room-temperature ionic liquid system, on specific transition-metal, macrocyclic-compounds-coated graphite electrodes in alkaline solutions.

   B: 2-electron transfer pathway: Reduction Pathway from O_2 to H_2O_2. It involves production of hydrogen peroxide. Carbon materials, Quinone and derivatives, mono-nuclear cobalt macrocyclic compounds and some chalcogenides can only catalyze 2-electron ORR.

   C: 4-electron transfer pathway: Reduction Pathway from O_2 to H_2O. It ends in producing water. Noble metal, noble metal alloy materials, iron-macrocyclic complexes, di-nuclear cobalt macrocyclic complexes, some chalcogenides, and transition-metal carbide-promoted Pt catalysts can catalyze 4-electron reduction. It is the most highly preferred pathway [8].

2) *Electro-catalyst Materials:* An electro-catalyst plays a crucial role for the ORR pathway in fuel cells. ORR requires de-bottlenecking because of the complex reaction pathways and sluggish electron transfer kinetics. Therefore, there has been a shift in interest towards catalysts that can produce high density current for practical purposes[4]. Nanoparticles (NPs) have emerged as good alternatives due to their versatile nature and large surface area. However, they require some support to avoid nanoparticle aggregation. The most commonly used materials for this are Platinum, Graphene sheets, Copper etc. Debe reported that Platinum NPs supported on carbon black shows good results. However, the high cost and dearth of Platinum has led to the look for further alternatives[9]. Shin-ya Ohno et al. studied the dissociation of oxygen molecules on copper surfaces. It consisted of a heterogeneous copper surface where some nitrogen adsorbed patches were separated from the clean copper patches[10]. The dissociation of O_2 molecules occurs selectively on the clean areas only via a two-step hydrogenation reaction to form water[11]. The same was corroborated by D.Kolovos-Vellianitis and co-workers who built on similar work performed on Nickel and Ruthenium surface and concluded that the hydrogenation of water occurs in two pre-dominant steps that have complicated temperature dependence[12]. Further modifications were made on Copper surfaces by supporting the Copper oxide NPs on Reduced Graphene Oxide (RGO) sheets by Conchi O. Ania et al. that increased the efficacy of the ORR pathway[13]. However, due to wrinkling effects and irregularity, these RGO sheets have reduced surface area[14]. Such obstacles can be overcome by the utilisation of nano-sized graphene particles termed as Graphene Quantum Dots (GQDs). GQDs have larger surface area to volume ratio and consequently better binding interactions that can be used for our benefit efficiently. Copper-GQD composites show higher electro catalytic performance over Platinum-GQD due to the greater affinity for oxygen of copper[8].

3) *Nitrogen Doped Graphene Mechanism:* Despite the novel innovations, they too have their own drawbacks. In order to overcome the disadvantages associated with metal based catalysts (nondurable and expensive); they must be replaced by economically beneficial and commercially available materials. Therefore, creating entirely metal free catalysts is of greater importance to the fuel cells[15].

Due to the novel properties exhibited by virtue of its two-dimensional structure Graphene has emerged as an exciting material. Single layer graphene is a one-atom thick sheet of carbon atoms densely packed into a two-dimensional honeycomb lattice. Graphene is doped through molecular charge transfer caused by electron-donor and acceptor molecules which generates significant changes in the electronic, chemical and molecular structure of graphene. In order to facilitate the application of graphene in electronics, opening the band gap in graphene is essential and for this, graphene bilayers are targeted. Arc discharge between carbon electrodes in a hydrogen atmosphere yields graphene composed of two or three layers. The underlying principle behind synthesis is that; in the presence of hydrogen, graphene sheets do not roll into nanotubes and hence bilayers can be formed. Nitrogen Doped Graphene (NG) sheets are produced by carrying out arc discharge of graphite electrodes in the presence of H_2+pyridine or H_2+Ammonia[16] as shown in Fig.2. For varying concentrations of Nitrogen (N), these sheets exhibit semi-conducting properties (p-type or n-type behaviour).

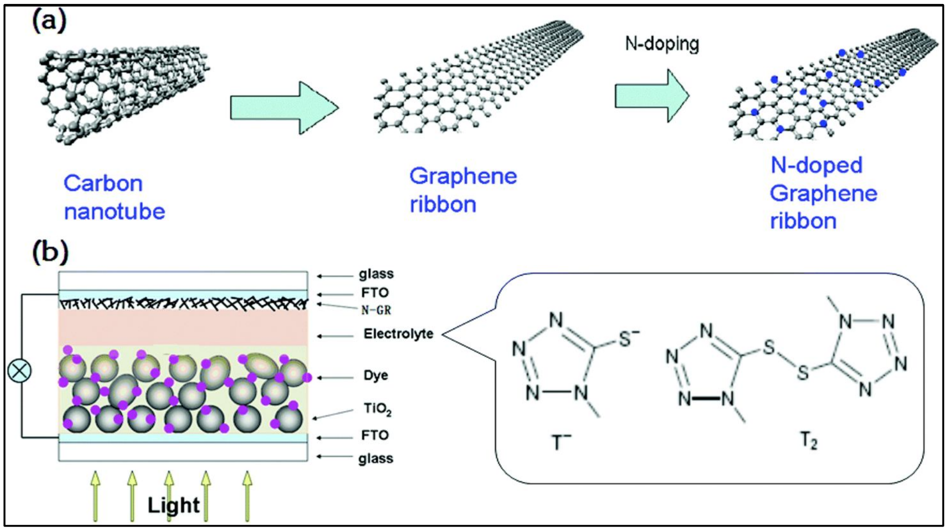

Figure 2: N-doped Graphene ribbons used as electrodes [16].

Nitrogen doped graphene is emerging as a promising Pt free catalyst as it shows one step four electron ORR pathway and has excellent stability as compared to Pt catalyst. This was reported by Ping Chen et al. In addition to arc discharge method, NG can also be produced by chemical vapour deposition and thermal annealing with NH_3[17]. However at higher temperatures, nitrogen precursors (NH_3, pyridine or pyrrole) are toxic, which limits the practical applications[18]. Hence, a variety of transition metal oxide nanocrystals (e.g. CoO, Co_3O_4, Mn_3O_4, ZnSe, Fe_3O_4, Co) on the surface of NG have been designed as catalysts[19]. Synthesis of Nitrogen doped graphene carbon nanotube nanocomposite is carried out by a hydrothermal process using graphene oxide oxidised multi-walled carbon nanotube and ammonia as precursors at a low temperature of 180^{o}C[19]. A similar analysis was conducted by Hui Liu et al. who showed that the unique structure endows the composites with enhanced ORR performance and the optimal composite showed improved durability and methanol tolerance [8].

Sample	N Content (%)
N-Graphene (800)	2.8
N-Graphene (900)	2.8
N-Graphene (1000)	2.0

Table 2: Nitrogen Content in different N-doped Graphene samples[20].

The nitrogen doped graphene with different concentrations of nitrogen tabulated in Table 2 was obtained by heating under high purity Ammonia mixed with Argon (Ar) at 800^{o}C (N-graphene (800)), at 900^{o}C (N-graphene (900)) and 1000^{o}C (N-graphene (1000)).The optimum temperature is 900^{o}C. Also, N-graphene (900) promotes four electrons ORR pathway in alkaline solution. Quaternary type nitrogen species play an important role for ORR activity.

B. *Polymer Electrolyte Membrane Fuel Cell*

1) *General Overview:* As a result of high power density, convenient fuel supply, relatively low operating temperature and long lifetime, polymer electrolyte membrane fuel cell (PEMFC) has potential residential and mobile applications. Polymer electrolyte membrane is the key component of fuel cell, which helps to transport protons from anode to cathode and complete the electric circuit in PEMFC[21].
   However, commercialization of PEMFC is hindered by several issues such as high cost, low reliability and poor long-term durability, among which durability has been recently recognized as one of the central issues to be tackled. This has led to the discovery of new materials that can help overcome some of these drawbacks.

2) *Recent advancements in PEMFC:* The drawback of high cost can be reduced to 60% of the current cost using graphite (with machine flow channels) or any other carbon composite and metal alloys as a bipolar plate. The advantages of these bipolar plates shown in Fig.3 is that they provide high surface and bulk electric conductivity, enhanced mechanical strength, chemical stability and are light weight.

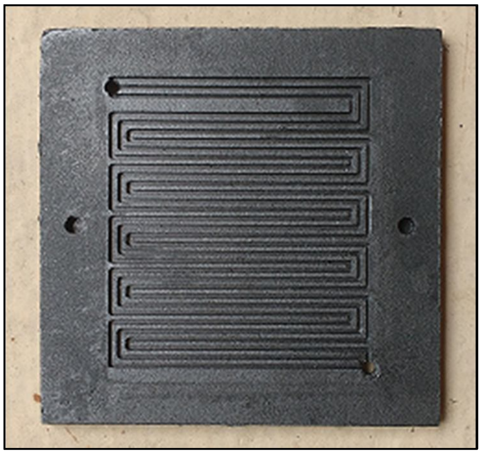

Figure 3: Flow field design on a bipolar plate [22](Serpentine flow field design)

A single cell unit of the PEMFC comprises of the membrane electrode assembly (MEA) sandwiched between two bipolar plates, which in turn is placed between two conducting plates as shown in Fig 4. The polymer electrolyte membrane is sandwiched between two electrodes. These electrodes consist of a catalyst layer and a gas diffusion layer (GDL). The role of the GDL is to support the membrane and to felicitate diffusion of gas [22].

There are two kinds of carbon composite plate; composite A which is manufactured into a plate by hot-pressing the compound powder and then gas channels are machined in its surface to make the plate bipolar; composite B which is fabricated directly into a bipolar plate by molding the compound powder and applying compression pressure at an adequate temperature [23].The juxtaposition of the two composites is shown in Table 3.

Figure 4: Membrane electrode assembly (MEA) synthesized by authors based on Decal process[24] published in literature for this review

Property	Graphite	Composite A	Composite B	Required
Bulk resistivity (ohm cm)	16.85	131.1	151.6	< 100
Density (g/cm^3)	1.95	1.69	1.82	< 5
Gas tightness at 5 bar	No leak	No leak	No leak	No leak
Water absorption (%)	0	0.133	0.287	< 0.3

Table 3: Comparison between electrical and physical properties of graphite, composite A and composite B [23].

In spite of similar bulk and contact resistance of the carbon composites, composite B bipolar plates has better performance than composite A bipolar plates, particularly at high current densities, due to the higher surface energy resulting in better water removal. Various other modifications have been made to membrane materials in PEMFC whose properties and performance have been discussed in Table 4.

Type of Membrane	Structure	Physical Properties	Performance
Perfluorinated membranes	Fluorinated backbone like PTFE. Fluorocarbon side chain. Ionic clusters consisting of sulfonic acid ions attached to the side chains.	Strong and stable in both oxidative and reductive environments.	High proton conductivity and durable.
Partially fluorinated membrane	Fluorocarbon base. Hydrocarbon or aromatic side chain.	Relatively strong in comparison to perfluorinated membranes, but degrade fast.	Less durable than perfluorinated. Low performance but comparable proton conductivities.
Non-fluorinated hydrocarbon membranes	Hydrocarbon base with polar groups.	Possess good mechanical strength. Poor chemical and thermal stability.	Poor conductors of protons Exhibit low durability on account of swelling of polar groups into the polymer matrix.
Non-fluorinated aromatic membranes	Aromatic base with polar/sulfonic acid groups.	Good mechanical strength. Chemically and thermally stable even at elevated temperatures.	Good water absorption Relatively high proton conductivity.
Acid–base blend membranes	Incorporation of acid component into an alkaline polymer base.	Stable in oxidizing, reducing and acidic environments. High thermal stability.	Exhibit proton conductivity comparable to Nafion.

Table 4: Physical properties, structure and performance of various different polymer electrolyte membranes [25].

Recently, Malik et al. prepared a Poly(vinyl alcohol) (PVA) membrane and carboxylic and sulfonic acid group containing quantum dots because of its ability to form a film, good chemical resistance and more functional groups that are reactive. The quantum dots are cross linkers, proton donors and carriers. The newly synthesised membrane showed greater thermal stability due to the formation of three-dimensional network structures in the presence of the Functionalized Quantum Dots (FQDs)[26].

C. Carbon Nanotube based Fuel Cell

The electron and the proton-conducting medium must be accessible for effective utilisation of the Pt catalyst. For a Pt-based conventional fuel cell prepared by the ink-process, the electron conducting medium provides interactions of the Pt particles in the catalyst layer. Nafion and Pt-supporting carbon particles are blended together to form a proton conducting medium. The carbon particles conduct electrons and the Nafion conduct protons[27]. Carbon particles get isolated inthe catalyst layer due to the Nafion added in the conventional ink-process for proton transport causing poor electron transport.

Multi-walled carbon nanotubes as an alternative to platinum support for proton exchange membrane fuel cells (PEMFC) are used as a way to reduce cost of fuel cells. Carbon nanotubes can be selectively produced directly on the carbon paper by chemical vapor deposition (CVD) with electrodeposited cobalt catalyst.

As compared to conventional carbon powders in PEMFCs, Carbon nanotubes have enhanced unique structural, electrical and mechanical properties. Carbon nanotubes are differentiated into two major types: single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). A SWNT is a cylindrical tube consisting of a single sheet of graphene. A MWNT re cylindrical tubes containing several sheets of graphene with the axis of each sheet coaxial to the other and hence, have a relatively high electrical conductivity. The production of the MWNTs is carried out by a resistive joule heating process with carbon paper (dipped in a solution containing silica and group VIII metal salts) as a catalyst as shown in Fig 5. However, Silica gel can hinder the electrical contact between the firmly attached MWNTs on the carbon paper. Currently, the method implemented to grow MWNTs on carbon paper is through electrodeposited Co catalysed chemical vapor deposition[28]. Selective deposition of Co catalyst in the electrolyte solution can enable selective growth of MWNTs. After the array of nanotube is generated, Pt catalyst is selectively deposited across the carbon paper. All Pt catalyst particles that are electrodeposited by the non-ink process are accessible to the external circuit of PEMFC.

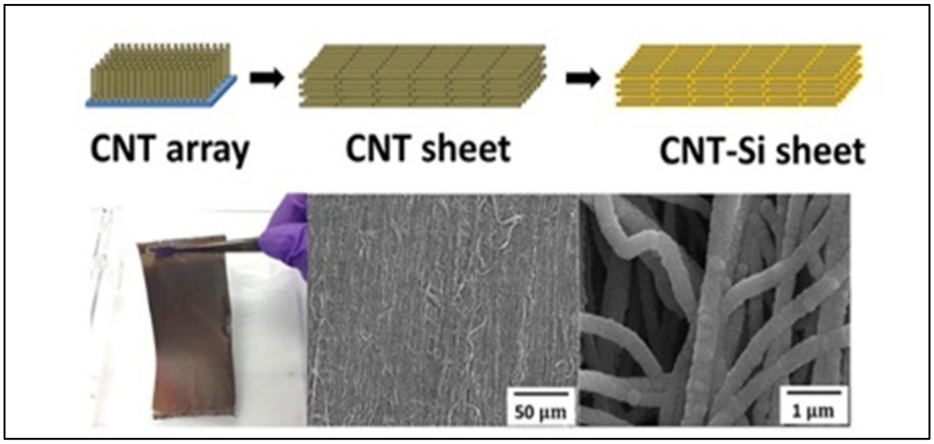

Figure 5: Carbon Nanotube arrays [20]

Higher Co loading and repetition of both Co electrodeposition and subsequent CVD carbon nanotube growth in order to obtain a high yield of MWNTs on carbon however results in a higher loading of Co on the substrate, causing an increase of Co particle size, and the diameter distribution of MWNT becomes broader, such as 20-130 nm[28].

There are various applications of Carbon Nanotube composites in microbial fuel cell. A composite of carbon nanotube (CNT)/polyaniline (PANI) can be used as an anode material for high power microbial fuel cells. For high energy generation, bacteria are used as catalyst to oxidize organic and inorganic matter in a microbial fuel cell. Power output can be improved by suitably modified cathode and optimization of bacteria inoculums. Electron transfer, bacteria attachment and substrate oxidation are influenced by the anode structure and material. The conventional materials used in MFC like carbon cloth and carbon paper have less electrolytic activity for the anode microbial reactions which has led to the development of carbon nanotube composites. CNTs have cellular toxicity which leads to cell death and proliferation inhibition, as CNTs are not suitable for MFCs unless modified to reduce cellular toxicity [29].

Higher Electrical Conductivity, relatively facile processability and environment stability makes Polyaniline (PANI), an important conducting polymer. The electronic properties of PANI can be controlled by both doping and de-doping and protonation processes. The polymer can be used to detect microorganisms such as E.coli. It not only provides protection to bacteria but also generates a high current density due to electro-catalysis. The limitations to the use of PANI are the lower conductivity and poor electron transfer. However, PANI fibers containing CNTs show improved mechanical strength and electrical conductivity. This composite can be constructed by method of layer-by-layer assembly in order to produce a multilayer film. The specific surface area and charge transfer capability is enhanced by the addition of CNTs to PANI[29].

D. Microbial Fuel Cell

With the increased consumption of paper products and natural fibre the recycling of recovered paper has gained importance.

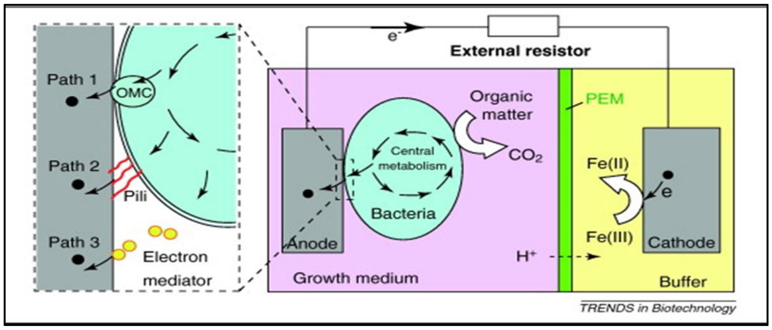

Figure 6: General Representation of Microbial Fuel Cell [30]

The two cathodic and anodic chambers of the microbial fuel cell are separated by a cation selective hexacyanoferrate membrane which acts as an electron acceptor in the cathodic chamber. Microbial fuel cells [31] are biological fuel cells that utilise electrons produced by bacterial metabolism. Electron transport to the anode is either direct or through physical contact. Mediators are used to provide this contact. This is shown in Fig 6. The performance of the microbial fuel cell is determined by the parameters and factors like: (a) use of right consortium of bacteria for higher power densities. (b) Instability at higher voltages. (c) Selection of appropriate electro mediator. Due to its nanometre size, high stability, good electronic conductivity and high accessible surface area, CNTs (both multi-walled nanotubes (MWNT) and single walled nanotubes (SWNT)) are used. Methylene Blue (MB), Neutral Red (NR) and Nano fluids (NF) are used as electron mediators, glucose as substrate and E.coli Bacteria as a biocatalyst in the anaerobic dual chambered MFC [32].

High Quality multi-walled nanotubes can be obtained by catalytic chemical vapour deposition and the chemical reactivity of the surface which is relatively inert can be improved by functionalization of MWNT with carboxyl groups. Also the CNT based electrodes are activated between open-circuit potential (OCP) and high current densities to activate the catalyst materials at the electrodes before use as electrodes in MFC.

Single chambered cells show good outputs using sewage sludge as substrates while the dual-chambered cells show good output using pure cultures of E.coli which was capable of generating 45mW/m^2 at 75 mA/m^2. The maximum OCP that can be generated by MFC is in the range of 0.80-0.89V. The various outputs for corresponding operating conditions were summarised in Table 5. The maximum power and open circuit potential for different types of electrode materials were summarised in Table 6 after a critical literature review.

Operating Condition	Output
Microbial fuel cell containing only substrate and no bacteria	Negligible current which rapidly falls to zero.
MFC containing both substrate and bacteria	OCP suddenly increases to 0.2 V and gradual increase in potential thereafter.
MFC containing Methylene Blue (MB) as electron mediator and graphite CNT as electrodes along with substrate and bacteria.	Delivers maximum of 151.6mW/m^2 and an OCP of 0.462 V.

Table 5: Output Characteristics for different operating conditions of Microbial Fuel Cell [28].

Electrodes	Electron Mediator	OCP (V)	Maximum Power (mW/m^2)
Plain Graphite	MB	0.481	151
	NR	0.604	386
Pt/MWNT	MB	0.912	1342
	NR	0.902	2163

Sn-Pt/MWNT	MB	0.884	1430
	NR	0.840	2470
	NF	0.941	1994

Table 6: Maximum Power and Open Circuit Potential for different electrode and electron mediator combination [28].

E. *Direct Formate Fuel Cell*

Direct formate fuel cell (DFFC) is operated using alkaline potassium formate as fuel and Pd as anode while Ag as cathode electro-catalysts within an intermediate temperature range of 80-120^{o}C.

1) *Direct Formate Fuel Cell:* Potassium formate salt solution (HCOOK) in alkaline medium is not volatile at 100^{o}C and hence show facile electrode reactions like electro-oxidation of formate ions and electro-reduction of oxygen. These properties make DFFC potentially high-performance and environment friendly method. The products of formate salts can be obtained from renewable sources through artificial photosynthesis and are inexpensive. In addition to this, the reaction products are only carbonate and water.

A DFFC operated with 6 mol dm^{-3}and at 120^{o}C gives a peak power density of around 160mWcm^{-2} over a current density range of 250 to 550 mA cm^{-2}[33].

The cell reactions at the electrodes in Direct Formate Cell are as follows [34]:

$$HCOO_{ad}^{-} \rightarrow H_{ad} + COO_{ad}^{-} \tag{1}$$

$$H_{ad} + OH^{-} \rightarrow H_2O + e^{-} \tag{2}$$

$$COO_{ad}^{-} \rightarrow CO_2 + e^{-} \tag{3}$$

For these reactions, there is no CO poisoning on the Pd catalyst at the electrode. Also, oxidation of adsorbed COO^{-} and desorption of hydrogen each contributes towards the charge transfer of one-electron. Due to lack of industrially viable anion-exchange membranes, development of membrane- less strategy has evolved based on the principle that the higher ORR active cathode catalyst (Pt) does not have catalytic activity for Formate Oxidation Reaction (FOR) and hence the fuel crossover can be avoided [34]. The anolyte used in the chamber between the anode and the cathode catalyst layers is aqueous solution comprising HCOOK as fuel and KOH as supporting electrolyte.

2) *Membrane-less Direct Formate Fuel Cell:* The alkaline anion-exchange membrane in traditional alkaline fuel cells provides not only a conductive path for the OH^{-} ion migration but also prevents the crossover of the liquid fuel and the oxidants. In case of a membrane-less alkaline fuel cell, the supporting electrolyte KOH sustains the migration of OH^{-} ions. Therefore for a membrane-less direct formate fuel cell, Oxidation of potassium formate does not take place at the cathode as the cathode catalyst Pt does not catalyze reaction. The feasibility of the cathode oxidant to cross over depends on diffusivity and solubility of oxygen in an aqueous alkaline solution. Since the solubility is fairly low, the anion-exchange membrane used in the alkaline DFFCs appears to be not necessary[34]. Fig 7. Shows a schematic of a membrane-less direct formate fuel cell.

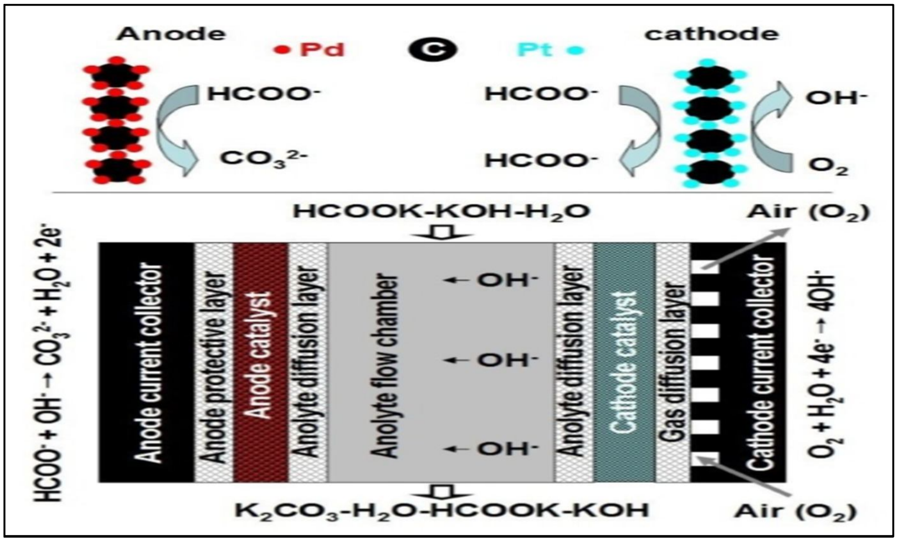

Figure 7: Membrane-less Direct Formate Fuel Cell[34]

In order to prevent the anolyte flow washout to the catalyst, two anolyte diffusion layers made of carbon fiber paper were applied to each side of the cell between the catalyst layers and the anolyte flow. Furthermore, two pieces of carbon fiber paper were additionally placed to each side of the cell between the catalyst layers and the current collectors. The one at the cathode serves as a gas diffusion layer, and the other at the anode is used to protect the anode catalyst[35]. Maximum power density of 267 mW cm^{-2} was obtained. When KOH was removed from the fuel stream, the maximum power density decreased to 157 mW cm^{-2} which is 85% of the maximum power density obtained from Direct Alcohol Fuel Cell (DAFC). But alcohol fuels require KOH to be added to the fuel stream to increase the level of performance. The use of formate as a fuel provides an advantage that KOH may not be used to obtain competitive performance. The performance of DFFC decreases when air is used as oxidant in place of pure oxygen.

Electrolyte	Oxidant	Maximum Power Density (mW cm^{-2})	Current Density at 0.6 V (mA cm^{-2})
2 M KOH	Oxygen	267	408
	Air	167	256
No Electrolyte	Oxygen	157	298
	Air	105	80

Table 7: Summary of fuel cell data for direct formate fuel cell and specified spray painted ion exchange membrane[35].

Table 7 shows the summary of fuel cell data for DFFC containing 1 M HCOOK and specified spray painted anion exchange membrane.

III. FUTURE PROSPECTS - METAL ORGANIC FRAMEWORK FOR FUEL CELLS

Recent advancements in the field of materials have led to the discovery of a 3 dimensional framework commonly referred to as Metal Organic Framework (MOF). MOFs are highly porous materials formed by inorganic ions or clusters coordinated to organic ligands[36]. By selecting appropriate metal centres, ligands, and synthetic conditions, the pore size can be precisely tuned and the spatial cavity arrangement precisely controlled. The pore size is usually around the micro – meso range. MOFs can be modified in many ways like impregnation of a desired element or creating a composite MOF. This leads to a tailor made material suitable for specific applications such as sequestration, adsorption, energy storage, optics, absorption etc. [37].

Their well-defined 3-D structures provide the highest possible volumetric density through regularly arranged cell structures and so can be successfully used as catalysts for ORR pathways[38]. MOFs can also be used for improving proton conduction as good as NAFION membranes[39]. Junjie Mao and team synthesized copper (II)-2, 2′-bipyridinebenzene-1, 3, 5-tricarboxylate (Cu-bipy-BTC, bipy=2,2′-bipyridine) and studied its electrochemical properties[40]. There was an increase in the peak current and a positive shift of the ORR potential compared to the conventional Platinum based electrodes.

Similarly, MOFs can also be successfully implemented as membranes in a Polymer Electrolyte Membrane. Although porosity doesn’t help in fuel cells – due to increase in voltage loss as a result of leakage – and crystallinity is not favored – as transport of ions is preferred in a system without long range order – MOFs are still better options for membranes[41]. This can be explained by the following properties of MOFs: (i) The molecules in the interstitial spaces act as barriers for fuel leakage. (ii) The metal ion/clusters of ions present can conduct protons or other functional groups. Currently, this particular aspect of MOFs is the most sought after research area in the field of materials[42].

IV. CONCLUSION

The recent interest in development of sustainable and renewable energy sources have led to the advent of fuel cells. For commercial applications of the newly developed fuel cell technologies, following factors will play a key role:1. Easy integration of the fuel cell for various purposes 2. High conductivity and higher area of contact for ions 3. Significant cost reduction as compared to the traditional and conventional methods 4. Substantial ecological and economic advantages. The critical parameters for the advanced fuel cells to be market friendly are lifetime, efficiency and the cost. Market segments with more relaxed restrictions on the performance are significant for first applications. The market segments where fuel cells can have major applications: Telecom and transportation (10%), rural (25%), Portables and consumer products (2%) and residential and commercial (51%).Fuel cells open up a myriad of sources for electricity generation subject to constraints of catalyst and electrode prices. Recent developments in new materials, hybrids and composites have been aimed at overcoming the shortcomings of the conventional components of the fuel cells. There exists room for further development of fuel cells as the most lucrative clean technology for the future with the upcoming metal organic framework (MOF) materials. MOFs are a class apart due to their versatility. However, further research for their economic scale up is required. Given the vast number of possible permutations of metal centers and organic linkers, the outlook of the applications of MOFs in fuel cells remains promising.

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