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Recent developments in fuel cell technology–A detailed insight

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Abstract

Increased demand for global energy resulted in the discovery of fuel cells. In past, non-renewable fossil fuels were the major source of energy all over the world. Their excessive use by human beings has resulted in polluted environment upto an alarming level through emission of greenhouse gases. Contrary to non-renewable energy resources, fuel cells produce water as a by-product thus, are environment friendly and reduce the pollution upto 99%. This article highlights different types of fuel cells, their working principles, proton exchange membranes including perflourinated ionomeric membranes and non-perflorinated ionomeric membranes used in novel proton exchange membrane fuel cells with great stress over microbial fuel cells and electrode material that can increase the efficiency of fuel cells. Among several described fuel cells, microbial fuel cells (MFCs) both mediated (requires a mediator) and unmediated (require redox proteins like cytochromes to transport electrons directly to the anode causes an increase in current densities utilizing bacterial interactions occuring in nature) fuel cells are of great interest these days. In short, this article provides a detailed insight into advanced fuel cell technologies along with their efficiencies and probable merits and demerits.

Key words: Fuel cells, perflourinated ionomeric membranes, cytochromes, microbial fuel cells

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1. Introduction

Global energy consumption by human civilization is increasing day by day and has reached at an alarming level due to the development of industries and emerging population. In order to deal with the depleting global energy, alternative sources for generating renewable energy are essentially required [1]. Nuclear energy, fossil fuel and renewable energy are considered as major sources of energy. Increasing demand for more energy is causing a decline in the supply of fossil fuel ultimately posing a threat to our environment and human life [2-3]. Moreover, population growth, rapid urbanization and industrialization are polluting the environment; thus it was needed to solve the issue regarding environmental pollution and energy crisis. Fuel cells were made 160 years ago by Sir William Grove [4].

There exists a difference between fuel cell and batteries. In batteries energy is obtained from the ions and oxides that are already present in electrolyte solution of the battery. In fuel cells, continuous supply of oxygen and fuel is needed to precede a chemical reaction and generate electricity with efficiency between 40-60%. If heat evolved during the reaction can somehow be controlled than the efficiency can be increased upto 85%. Other side products formed depends on the type of fuel used. At present, development of cheap, eco-friendly and high-performance energy storage systems are the most explored research zones all over the globe. Fuel cells have proved to be the most favorable energy conversion and storage electrochemical system. Several types of fuel cells are known however, all contains electrolyte, cathode and anode in common. Whole assembly allows the movement of ions (protons) between the two sides of the fuel cell.

Electrolyte is made up of such substances which allow the movement of ions but not of electrons. A catalyst at anode causes the fuel to get oxidized and generate electrons and ions (protons). Electrons travel the external circuit and reach the cathode and produce electricity whereas ions move through electrolyte from anode to cathode. Another catalyst at cathode causes oxygen, ions and electrons to give water and other products. Fuel cells are categorized based on electrolyte used in the fuel cell and startup time, one second for PEM and ten minutes for SOFC. The overall process occuring is simple and converts chemical energy into electrical energy without passing through intermediate stages and generation of harmful

gases. Fuel cells have drawn excessive attention as a future alternative source of energy [5].

Fig.1 shows the main processes occuring within a typical PEMFC [6]. Hydrogen (H_2) in molecular form is given to the anode where it is oxidized to give electrons and hydrogen ions, as shown. The chemical reaction is shown in following equation (eq.1):

$$\mathbf{H_2 \rightarrow 2H^+ + 2e^-} \ldots\ldots\ldots (\mathbf{eq.1})$$

The electrons given off at anode pass through the external circuit and reach cathode where it combines with the hydrogen ions and externally supplied oxygen to give the reaction showed in the equation (eq.2).

$$\mathbf{\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O} \ldots\ldots\ldots \mathbf{eq.2}$$

The overall reaction in the fuel cell produces heat, water and electrical work as follows (eq.3):

$$\mathbf{H_2 + \frac{1}{2}O_2 \rightarrow H_2O + Heat} \ldots\ldots\ldots \mathbf{eq.3}$$

By-products of the reaction i.e. heat and water should be removed from the system non-stop in order to maintain the temperature conditions needed for the power generation. Thus, heat and water control are key areas in the competent design and operation of fuel cells. The relations between a fuel cell, principles of operation, features, advantages and areas of applications are summarized in Table 1, Table 2 and Table 3.

2. Fuel Cell Technologies

2.1. Working Principle

Currently fuel cells offer applications in several fields including their use in undersea stations, spacecraft, tractors, buses, automobiles, forklifts and spacecraft. The output power produced at full load is 0.7 volts. In order to get desired voltage, fuel cells can be connected in series and parallel set-up. However, fuel cells are diverse field of science in which material science, electrochemistry, engineering economics, thermodynamics and electrical engineering all dimensions join; making this a difficult task.

2.2. Categorization of Fuel Cells

2.2.1. Alkaline Fuel Cell

Alkaline fuel cells were introduced in 1960's and known to use an anion exchange membrane to separate cathode and anode compartments. The assembly consists of electrode in form of membrane sandwiched between anode and cathode, both the anode and cathode consists of catalyst layer and diffusion layer. The comparison of AEMFC and PEMFC working principle has been illustrated in Fig.2. Diffusion layer of both electrodes (cathode and anode) comprises of 2 layers, a supporting layer containing either carbon paper or carbon cloth and a micro-porous layer containing a blend of hydrophobic polymer and carbon powders. The catalyst layers are commonly a mixture of ionomer and electro-catalysts forming a three phase boundaries for the electrical and chemical reactions, *i.e.*, oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR). Main role of diffusion layer is providing support to the catalyst layer also dispensing reactants homogeneously and transporting electrons to the current collector [7].

Several different types of fuels are known however, hydrogen is abundantly used fuel in alkaline anion exchange membrane fuel cell (AAEMFC)'s. Water saturated hydrogen fed to the anode is channeled towards the anode diffusion layer to the anode catalyst layer, where hydrogen combines with hydroxide ions to give electrons and water as product [8].

The anodic reaction is (eq.4):

$$\mathbf{H_2 + 2OH^- \rightarrow 2H_2O + 2e^-} \ldots\ldots\ldots \mathbf{E_a^0 = -0.83V} \ldots\ldots\ldots \mathbf{eq.4}$$

Oxygen is supplied at cathode which is transported to the cathode catalyst layer through the diffusion layer and is reduced to hydroxide ions in the presence of water (eq.5).

$$\mathbf{\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-} \ldots\ldots\ldots \mathbf{E_c^0 = 0.40V} \ldots\ldots\ldots \mathbf{eq.5}$$

Hydroxide ions produced are conducted through the anion electrolyte membrane for HOR. The overall reaction combining the HOR and ORR is expressed as (eq.6):

$$\mathbf{H_2 + \frac{1}{2}O_2 \rightarrow H_2O} \ldots\ldots\ldots \mathbf{E^0 = 1.23V} \ldots\ldots\ldots \mathbf{eq.6}$$

Fuel cell efficiency is affected by several parameters such as temperature, pressure and humidity of gas streams. The performance of electrolyte membrane plays a significant role in commercialization of solid alkaline fuel cells. AEMs play a substantial role in transport of hydroxyl ions from cathode to anode to undergo electrochemical reaction and providing barrier for electrons, fuel and oxidant between the two electrodes. The properties that an ideal AEM must possess involves ion conducting channels, mechanical and chemical stability [8].

2.2.2. Solid Oxide Fuel Cell (SOFC)

SOFC (Fig.3) is a device which converts chemical energy to electrical energy by fuel oxidation. As described previously that fuel cells are classified on the basis of electrolyte used, SOFC uses solid oxide or ceramic electrolyte. The apparatus comprises of electrodes made up of porous conducting material (anode and cathode) and a dense layer of ceramics between these electrodes. Activation of ceramics requires high temperature upto 500 to 1,000°C. Oxygen is reduced to ions at cathode, which than move towards the cathode where they can electrochemically oxidize the fuel. The by-products of this reaction are two electrons and water, these electrons travel across the external circuit where they can perform work. Whole cycle is repeated when electrons again enter the cathode material. Inter-connect could either be made up of ceramic or metallic layer present between each individual cell and combines the electricity produced by cells connected in series. Interconnect must be stable as it is exposed on both the reducing and oxidizing sides at high temperature. Based on this reason, ceramics have been thought to be more successful material used in forming interconnects in comparison to metals. Hydrogen reaction occuring at anode (eq.7) and reaction of oxygen occuring at the cathode (eq.8) are shown below:

$$\mathbf{H_2 + O_2^- \rightarrow H_2O + 2e^-} \ldots\ldots\ldots \mathbf{eq.7}$$

$$\mathbf{12O_2 + 2e^- \rightarrow O_2^-} \ldots\ldots\ldots \mathbf{eq.8}$$

The overall reaction is shown in (eq.9)

$$\mathbf{H_2 + 12O_2 \rightarrow H_2O} \ldots\ldots\ldots \mathbf{eq.9}$$

Solid oxide fuel cell reaction is show in eq.10.

$$\mathbf{CO + O_2^- \rightarrow CO_2 + 2e^-} \ldots\ldots\ldots \mathbf{eq.10}$$

The diffusion coefficient for CO molecules is low as compared to H_2 molecules. Several parameters effect the performance of fuel cells such as pressure, temperature, gas concentration and type of fuel gas [9]. Costa-Nuns et al reported low performance of CO fed Ni-YSZ anode. In order to improve the performance Cu–CeO_2–YSZ anode should be preferred over conventionally used materials. When CO_2, H_2 and CO stream are given then, water gas shift (WGS) reaction (eq.11) is considered to occur simultaneously.

$$\mathbf{CO + H_2O \rightarrow H_2 + CO_2} \ldots\ldots\ldots \mathbf{eq.11}$$

2.2.3. Molten Carbonate Fuel Cell (MCFC)

Molten-carbonate fuel cells (MCFCs) (Fig.4) require high temperature of 600°C or above to operate and use an electrolyte made up of mixture of carbonate salt suspended in chemically inert, porous matrix of beta-alumina solid electrolyte (BASE). MCFCs normally can attain efficiency around 60% which can be increased upto 85% if waste heat is somehow controlled. MCFCs don't need an external source for the conversion of fuel to hydrogen. Due to the high operating temperature, fuel given to the system is converted to hydrogen within the fuel cell itself by a method known as internal reforming which reduces the cost. The produced hydrogen gas reacts with CO present in electrolyte to generate electrons, carbon dioxide, water and small portion of other chemicals. The electrons pass across the external circuit generating electricity and returning back to the cathode where oxygen from air, electrons and carbon dioxide produced at anode forms carbonate ions regenerating the electrolyte and thus completing the circuit. The chemical reactions for an MCFC system can be expressed as follows (eq.12, eq.13 and eq.14):

$$\mathbf{CO_3^{2-} + H_2 \rightarrow CO_2 + 2e^-} \ldots\ldots\ldots \mathbf{(At\ Anode)} \ldots\ldots\ldots \mathbf{eq.12}$$

$$\mathbf{CO_2 + \frac{1}{2}O_2 + 2e^- \rightarrow CO_3^{2-}} \ldots\ldots\ldots \mathbf{(At\ Cathode)} \ldots\ldots\ldots \mathbf{eq.13}$$

$$\mathbf{H_2 + \frac{1}{2}O_2 \rightarrow H_2O} \ldots\ldots\ldots \mathbf{(Overall\ Reaction)} \ldots\ldots\ldots \mathbf{eq.14}$$

The main shortcoming of MCFC set-up is durability. The corrosive electrolyte utilized and high operating temperatures promotes corrosion and breakdown of components thus decreasing cell life. Presently, researchers are discovering materials that are resistant to corrosion to be used in fuel cell set-ups without effecting cell's performance and efficiency [10-11].

2.2.4. Phosphoric Acid Fuel Cell (PAFC)

PAFCs were manufactured in 1960s to be used in space shuttles and uses phosphoric acid as an electrolyte at temperature roughly between 250-300°C with efficiency from 37 to 42%. The reaction process involves the removal of hydrogen from the fuel using platinum catalyst, hydrogen can pass through phosphoric acid whereas electrons are unable to pass. Regardless of the fact that PAFCs are at present famous stationary fuel cells, they still depend on hydrocarbon fuels which leads to the poisoning of catalyst and emission of greenhouse gases. The poisoning of catalyst can be overcome by synthesizing carbon paper electrodes coated with platinum catalyst but it renders the fuel cell production expensive [12].

3. Fuel Cell Applications of Novel Proton Exchange Membranes

3.1. Types of Proton Exchange Membrane

3.1.1. Perflourinated Ionomeric Membranes

The Perflourinated polymers due to fluorine's high electronegativity and small size have firm Ce-F bond and less polarizabilty. The polymers because of their chemical inertness, thermo-stability and increased acidity due to sulfonic acid group in $-CF_2SO_3H$, have been used in chlor-alkali method and acting as proton exchange membranes for applications in fuel cell [13]. The described membranes are produced by monomer polymerization and could be made cationic and anionic for further applications. DuPont in 1966, explained the thermal and chemical stability of fluorocarbon-based ion-exchange membranes (Nafion). Perflourinated membranes possess high equivalent weight (EW) that limits its usage in fuel cells as they consume great power density [14]. Comparable polymers known as Flemion were generated by Asahi Chemical. Of the three main categories, the DuPont product is known to be more efficient due to its mechanical strength, proton conductivity and chemical stability [15].

3.1.2. Non-Fluorinated Hydrocarbon Membranes

An additional form of materials that could be utilized to prepare PEM are non-fluorinated hydrocarbon polymers which can either be aromatic or aliphatic polymers containing hexagonal ring of benzene in the backbone of polymer membrane or attached in the form of pendants to the main polymeric backbone. Currently, one of the most favorable material for production of high-performance proton conducting PEMs is to utilize hydrocarbon polymers for the backbone [16]. Using hydrocarbon membranes give definite benefits like commercially available, cheap and allows the insertion of other reacting groups [17]. Hydrocarbon based polymers have water binding capacity over a wide range of temperature and the adsorption is restricted to the bound polar groups. These polymers can be recycled by conventionally used techniques and their decomposition can be reduced by an appropriate molecular design [17-18]. Poly-aromatics membranes are hard and have the ability to withstand high temperature (TG 200°C) due to the presence of inflexible and bulky aromatic compounds [19]. The attached aromatic rings offer sites for electrophilic and nucleophilic substitution reactions. Polyether ketones (PEK), polyether sulfones (PESF) with fluctuating number of ketone and ether functionalities (such as PEKEKK, PEKK, PEEK etc.), poly (arylene ethers), polyesters and polyimides (PI) are significant examples of main chain poly-aromatics. Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) are most suitable to be applied in PEMFCs due to its high glass transition temperature, hydrophobic nature, hydrolytic stability and mechanical strength. The structure of PPO is relatively simple at the same time allows modification at benzyl and aryl positions through electrophilic, nucleophilic, radial substitution and metalation. On the basis of thermal stability and from oxidant point of view poly-aromatics are favored to be applied in fuel cells [20].

3.2. Proton Conduction Mechanisms in PEM

Modern PEM could be synthesized through co-doping of and UiO-66-SO_3H and UiO-66-NH_2. The combined effect of both UiO-66-SO_3H and UiO-66-NH_2 resulted in large number of proton channels that enhanced the conductivity of proton under humid conditions. It was that appreciably smaller quantity of UiO-66-SO_3H and UiO-66-NH_2 were more useful in the enhancement of proton conductivity and water retention capacity. In addition to this, stability at higher temperature and large volumes of water of these two above mentioned MOFs guaranteed an efficient proton conductivity stability of the co-doped PEM. In the meantime, the trapping effect of MOF for methanol greatly decreased the permeability of co-doped PEM for methanol. This work provided a helpful parameter needed to design several diverse functionalized MOFs to help enhance proton conductivities of PEMs [21].

3.3. Durability, Cost and Compatibility of PEM

PEMs determines the lifetime of fuel cells. Due to their light weight and controlled emission of greenhouse gases PEM fuel cells are primarily applied in transportation. Reportedly, operational stability of 5,500 hours for cars and 20,000 hours for buses was observed by using PEMs. PEM fuel cells uses compressed hydrogen as fuel, preferred to be used in buses than in cars due to the large volume offered to store fuel and have reported efficiency upto 40% for buses. PEM fuel cells require pure hydrogen for operation whereas others can be operated using methane and thus more flexible. It can be used on small scale, until pure hydrogen is available on commercial level. An analysis was performed to discover several different membrane designs which are supposed to increase durability. Technical-economic cost model (TCM) design showed that different parameters like labor distribution, material selection, fabrication methods, energy consumption, production volume and financial parameters varies the cost per unit production. Utilizing the cost analysis platform, it was observed that the effect of additive on overall cost is minor when the process adopted for production is unchanged. By comparing the results obtained with the market standards, it was concluded that current standard assumptions are envisioned for conservative investment [22].

4. Microbial Fuel Cells: New Technology for Energy Generation

4.1. Electrode Materials

Electrode materials are the area that can possibly be explored to optimize the output power obtained from MFCs. For a material to be an effective electrode it must contain certain characteristics like it should be inexpensive, large surface area, high current densities and show favorable electron transfer.

4.1.1. Carbon Based Electrodes

Carbon based electrodes have vast applications in industrial and analytical fields due to high efficiency in heterogeneous electron transfer kinetics. There are five known allotropic forms of carbon [23]. After the discovery of graphene, there has been a fast growth in research areas regarding the use of graphene and other two dimensional materials as electrode materials, especially in field of electrochemistry. Carbon based nanomaterials retain several favorable characteristics such as greater specific surface area, adsorption of molecules and increased electron transfer [24]. Electrodes based on carbon are now-a-days material of choice for MFCs as growth of microbes accelerates on the surface of metal anode [25-26]. A number of electrodes based on carbon have been checked for use in MFC setups; these involve carbon felts [27], graphite rods [28], carbon meshes [29] and carbon cloths [30].

4.1.1.1. Graphite

Graphite exhibits extraordinary electrochemical characteristics and pronounced biological compatibility with *E. coli* bacterium. An investigation taken out by Lovely and Chaudhuri showed that by increasing the surface area of graphite, increased the microbial colonization and hence power outputs. Graphite rods were compared against Graphite felt electrodes and a three times increase in production of current was reported (0.57 mA m^{-2}; 620 mV). Researchers compared graphite rods and porous graphite foam and the results have shown that although both have same surface area, the porous graphite foam generated 2.4 times more current (74 mA m^{-2}; 445 mV) due to higher concentrations of cells that were able to attach to the graphite foam electrodes [31].

4.1.1.2. Graphene

Graphene is an allotropic form of carbon in which each carbon is sp^2 hybridized and atoms are arranged in a single layered 2D hexagonal lattice [32]. These characteristics enabled physical strength [33], electron mobility at room temperature ($2.5\times10^5 cm^2V^{-1}s^{-1}$) [34] and a theoretical great surface area estimated at 2630 m^2g^{-1} [35]. Graphene has the ability to withstand great current densities (reported as one million times higher than copper) [36]. These characteristics are best for effective and efficient transfer of electron thus render graphene an excellent material to be used for making electrodes in MFCs system.

Earlier graphene was used as an excellent anode material in MFC set-up containing pure culture of *E. coli* and has shown greater power density of 2668 mWm^{-2}, which was greater than the modified electrodes of poly-tetra-fluoro-ethylene and stainless steel mesh respectively [37]. Xiao *et al*., illustrated the difference among two varying forms of graphene with different multilayer forms (*ca.* 50–100 μm). The prepared graphene sheets had more defects than pristine graphite as depends on the method utilized for synthesis that involve thermal treatment of GO through 'Hummers' synthesis and crumpled graphene particles (*ca.* 0.2–5.0 μm) formed through an aerosol-assisted capillary compression process [38]. These different forms of graphene were layered on electrodes made from carbon cloth (loading rate:~5 $mgcm^{-2}$) and were tested to evaluate whether there is an effect of roughness and surface area on the output density in MFCs set-up [39]. The result concluded described that crumpled graphene particles not only increased the surface area but also increased the power density (3.6 W m^{-3}) which was double than that of the electrodes modified by activated carbon (1.7 W m^{-3}).

Anode made up of three dimensional macro porous graphene scaffold reported the highest power density of 5.61 W m^{-2}/11,220 W m^{-3}. Ren *et al*., illustrated the capacity of two dimensional nanomaterials like graphene to be used in MFCs set-up as electrode material. Raman spectroscopy is an influential characterization tool to identify the number of layers present in graphene based electrodes [40]. The disadvantage that hinders the use of MFCs on commercial scale is reliability and cost. It is expected that with increase in usage of 2D-nanomaterials such as graphene, its cost of production will significantly decrease [41].

4.1.1.3. Carbon Nanotubes

Carbon nanotubes (CNTs) discovered by Iijima, are rolled up graphene sheets with diameter within range of nanometers. Carbon nanotubes are classified into single walled and multi walled carbon nanotubes based on the number of layers contained within the internal structure [42-43]. CNTs have shown good electrochemical properties due to a number of features like size to surface area ratio, hilarity and micrometer size length. SWCNTs and MWCNTs usually have diameters in range of 0.8–2 nm and 5–20 nm, individually, though MWCNT have diameters that may exceed above 100 nm and have a hollow geometry [44-45].

CNTs have illustrated improved electrochemical properties in contrast to other commonly employed electrodes being utilized in MFC technologies. The

electrical and chemical activity of glassy carbon electrode (GCE) was modified with MWCNTs using *Shewanella oneidensis*, experimental results showed that incorporation of CNTs increased the current density to $9.70 \pm \mu A\ cm^{-2}$, 82 times greater in comparison to GCE control. CNT-modified cathodes have resulted in power density of $329\ mW\ m^{-2}$, that was two folds greater than the density achieved from carbon cloth cathodes ($151\ mW\ m^{-2}$) [46-47].

SWCNTs containing hydroxyl group was compared with MWCNTs containing hydroxyl groups and reports have proved that MWCNTS with hydroxyl groups have shown more power density of $167\ mW\ m^{-2}$ than SWCNTs and 130 times more efficient in comparison to carbon cloth control. Hence, MWCNTs with hydroxyl groups are a potential substitute for anode material in comparison to commonly utilized carbon cloth because of their microbial attachment, electron transfer capacity and substrate oxidation/diffusion rates [48].

4.1.2. Non-Carbon Based Electrodes

Non-carbon based electrodes are also utilized in MFC setup. In 2007, cathode and anode made from stainless steel were prepared by Dumas *et al*., The anode was inserted in marine deposit that was connected to cathode in the superimposed seawater. Power density obtained by this SMFC configuration caused low output ($4\ mW\ m^{-2}$) in comparison to the laboratory control ($23\ mW\ m^{-2}$). It was proposed that this may be due to the damage of biofilm on cathode caused by factors including damage offered by waves to the electrical connection and grazing fish [84]. The results obtained can be compared to electrodes based on carbon used in SMFCs (with similar-sized anodes:~$0.18\ m^2$) with a stainless steel cathode and graphite plate anode, smooth graphite electrodes ($28\ mW\ m^{-2}$) and a carbon brush cathode with single graphite rod anode [49-50].

Commercially available uncoated titanium and titanium coated with platinum were trailed as non-porous bio-anodes and related with smooth and coarse graphite. Impedance spectroscopy and polarization curves displayed that the performance of bio-anodes increased in the following order: uncoated titanium<flat graphite<platinum coated titanium<roughened graphite. Un-coated titanium anode have shown considerably high anode potential (>−150 mV *vs.* Ag/AgCl at R=1000 Ω) and lowest current than other electrodes. Results supported the fact that uncoated titanium is not a good material to be used for anode in MFC setup [51].

In 2015, Baudler *et al*., studied the effect of titanium, copper, cobalt, nickel, silver and gold electrodes against graphite electrode. Among these metals copper has shown the highest current density of $1515\ \mu A\ cm^{-2}$, than gold with current density of $1175\ \mu A\ cm^{-2}$ and silver displaying $1119\ \mu A\ cm^{-2}$ respectively, that were somewhat greater than graphite control ($984\ \mu A\ cm^{-2}$) [52]. The results obtained for copper and silver were amazing, as the metals were well known for their antimicrobial metals and extensively used for surface coating of medical equipment [53]. It was illustrated that electrode respiring bacteria belonging from secondary biofilm (which are highly *Geobacter* dominated) have shown the capacity to colonize, adhere and form biofilms on surface of both silver and copper electrodes. The thickness of these produced biofilms range from $249 \pm 21\ \mu m$ to $154 \pm 10\ \mu m$, respectively. According to this fact both silver and copper electrodes play an important role in MFCs optimization. Among non-noble metals (stainless steel, nickel, titanium and cobalt) stainless steel resulted in highest current density ($674\ \mu A\ cm^{-2}$) and then nickel ($384\ \mu A\ cm^{-2}$). Current densities obtained from titanium and cobalt was insignificant compared to other materials used for electrode synthesis. Decline in current density shown by non-noble metals is due to metal oxide formation that offer a barrier to the transfer of charge among metals and biofilms[52-54].

Ritcher *et al*., demonstrated the capability of gold electrodes in combination with *G. sulfurreducens* (ATCC 51573), with 40 mM of fumarate as an electron acceptor and 10 mM acetate as electron donating specie to be used in MFCs set-up. Results have shown that after *ca*. 6–10 days the current became stable at 0.4–0.7 mA and this current was comparable to anode made up of carbon fibre under identical circumstances. The electrons were probably transported to the gold anode through contact between *G. sulfurreducens*. However, several experimental works has shown that use of gold electrodes with *Shewanella putrefaciens* were not appropriate to be used in MFCs. The difference in electrochemical response is attributed to the change in mechanism of electron transfer among different bacterial species. As *S. putrefaciens* is linked with the help of proteins exposed on the bacterial cell surface and *G. sulfurreducens* is linked by direct transfer of electron. Conflicting results were due to the different electrochemical ways through which bacteria interacts with the surface [55-56].

4.2. Electron Transport Mechanism

Exo-electrogenic bacteria have the capacity transport electron either through direct or indirect electron transfer mechanism (Fig.5) [57]. Direct transfer mechanism needs physical interaction between electrode surface and bacterial cell through redox active proteins and nanowires. In indirect transfer mechanism, no physical connection is required instead involves molecules that shuttle electrons [58]. There are three ways through which electrons can be transferred including electron mediators, cytochrome and

nanowires that bacteria can utilize in order to donate electrons to anode in MFC set-up [59].

4.3. Mixed Community Microbial Fuel Cells

Several type of techniques through which bacteria can transfer electrons were considered though, some monoculture strains exhibited the ability to give power densities as high as strains that were injected in mixed microbial communities. For instance, anodic biofilm have the ability to give power densities about 6.9 W per m^2 (projected anodic area). Few bacteria present in biofilms of MFC have illustrated that some cells do not directly interact with anode, but by indirectly interacting with other bacteria can contribute to electricity generation. *Brevibacillus* spp., (strain PTH1) found in abundance in MFC community has shown such behavior, it alone gives low power output but when interacts with *Pseudomonas* spp., an increase in electricity production was observed.

Some members of *Pseudomonads* that are florescent in nature have the ability to produce and secrete pyocyanin (Secondary metabolite). Varying results were reported when pyocyanin was added to non-pycocyanin producing MFC biofilms. Rabaey *et al*., illustrated that when pyocyanin was added to *Enterococcus faecium* (strain KRA3), it caused an increase in peak power from $294 \pm 49\ \mu W\ m^{-2}$ to $3977 \pm 612\ \mu W\ m^{-2}$, almost thirteen times increase. Whereas addition of pycocyanin to *E. coli* (ATCC 4157), showed a decrease in power output by 50% ($117 \pm 16\ \mu W\ m^{-2}$ to $50 \pm 53\ \mu W\ m^{-2}$ [60]. A probable reason could be selective antimicrobial action of pycocyanin which showed highest antimicrobial activity against aerobic strains of bacteria. This approach can be applied in MFC setup to remove organic compounds like toluene from waste and converting it to electricity [61].

Interaction occuring among biofilm of mixed microbial community is complex but yet can be understood with great ease. Pure culture of MFC (*G. sulfurreducens*) gave power output of $461 \pm 8\ mW\ m^{-2}$, in comparison to mixed community MFC biofilm that has shown power of $576 \pm 25\ mW\ m^{-2}$ carried out under same experimental conditions. One approach utilized fungus *Trametes versicolor* which gave power density of $0.78\ W\ m^{-3}$. Fernández de Dios *et al*., proposed that bacteria were able to attach and transport electron from the *T. versicolor* filamentous networks. Moreover, *T. versicolor* has shown the ability to generate oxidative enzymes that gave oxidation reduction mechanism that includes transport of electrons from donor to acceptor. Mixed community biofilm have the capacity to produce electricity through several other ways and will play a significant role in future for the improvement of MFCs [62-63].

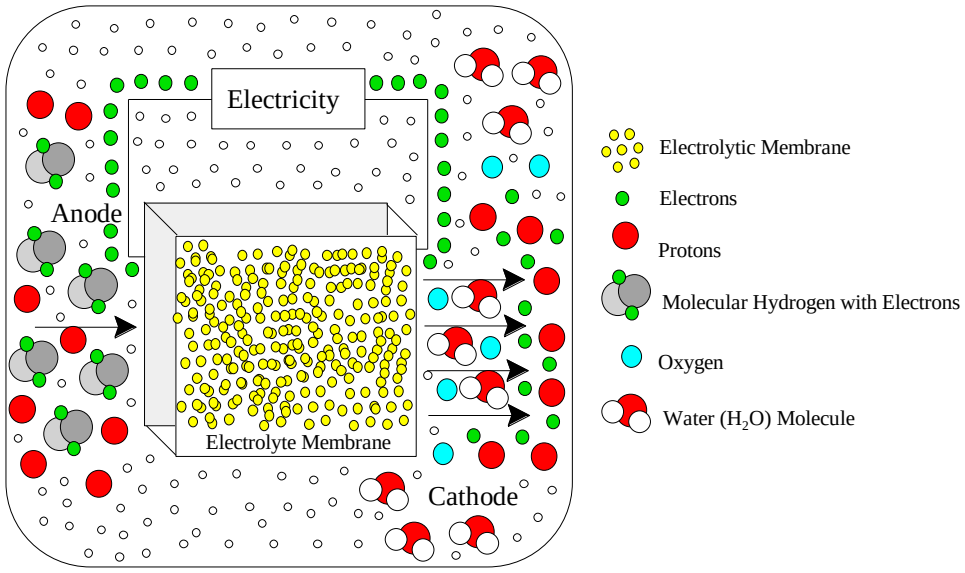

Fig.1 Schematic illustration of PEMFC operation

Table 1 Properties of fuel cells

Principle of Operation	Properties
Electrochemical energy conversion	➢ Great and constant efficiency ➢ Less noise production ➢ Low toxic emissions ➢ High energy density
Low energy transformation	➢ Low toxic emissions ➢ High and constant efficiency

	➢ Prompt load-following
Operates as long as fuel is provided	➢ High energy density ➢ Long run operation cycles
Expansion by adding cells to a stack and/or stack to a system	➢ High integrability with renewable sources modularity
Operates best when pure Hydrogen supplied	➢ High integrability with renewable sources ➢ Less toxic emissions
Static operation with no dynamic parts	➢ Low noise production ➢ Modularity
Fuel restoration fueling options	➢ Less toxic emissions ➢ Long run operating cycles ➢ Fuel plasticity
Direct alcohol fueling option	➢ Long run operating cycles ➢ Prompt load-following ➢ Fuel plasticity

Table 2 Applications of fuel cells based on their characteristic features

Features	Applications
Great constant efficiency	➢ Impetus systems ➢ Low power consuming vehicles ➢ Supporting power units ➢ Distribution generation
Less toxic emissions	➢ Impetus systems ➢ Low power consuming vehicles ➢ Supporting power units ➢ Distribution generation
Long run operating cycles	➢ Transportable applications ➢ Impetus systems ➢ Low power consuming vehicles ➢ Emergency back-up
High energy density	➢ Transportable applications ➢ Impetus systems ➢ Low power consuming vehicles ➢ Emergency back-up
Prompt load-following	➢ Impetus systems ➢ Low power consuming vehicles ➢ Supporting power units ➢ Distribution generation
Modularity	➢ Supporting power units ➢ Distribution generation ➢ Transportable applications
Fuel flexibility	➢ Distribution generation ➢ Transportable applications ➢ Emergency back-up

Table 3 Advantages, disadvantages and limitations of fuel cells

Types of fuel cell	Applications	Advantages	Limitations	Status
Proton exchange membrane	Buses, cars, medium to large-scale stationary power generation and portable power supplies	Low temperature operation, compact design; long operating life; quick start-up, adapted by major automakers and operates at 50% efficiency	Heavy auxiliary equipment, needs pure Hydrogen, high manufacturing costs and complex heat, water management	Most widely developed; experimental production
Alkaline	Terrestrial transport (German submarines) Space (NASA)	Low operational and manufacturing cost, fast cathode kinetics, does not need heavy	Use of corrosive liquid electrolyte, large size, needs pure hydrogen and oxygen	First generation technology, gain interest due to low operating cost

		compressor		
Molten carbonate	Large scale power generation	Great efficiency; utilize heat for co-generation	Restricted service life, Electrolyte uncertainty	Well developed; semi-commercial
Phosphoric acid	Medium to large-scale power generation	Heat for co-generation, commercially available, lenient to fuel	Costly catalyst, low efficiency, limited service life	Developed but faces competition in operation from PEM
Solid oxide	Medium to large-scale power generation	Takes natural gas directly, highly efficient, lenient to fuels, operates at 60%, no reformer needed, efficiency, co-generation	High temperature required; exotic metals, expensive, low specific power oxidation issues	Least developed, Advances in stack design and cell material sets off new research
Direct methanol	Most suited for portable, stationary and mobile applications	No humidification or compressor needed, compact design, feeds directly off methanol	Operates at 20% efficiency, complex stack structure, slow load response	Laboratory prototypes

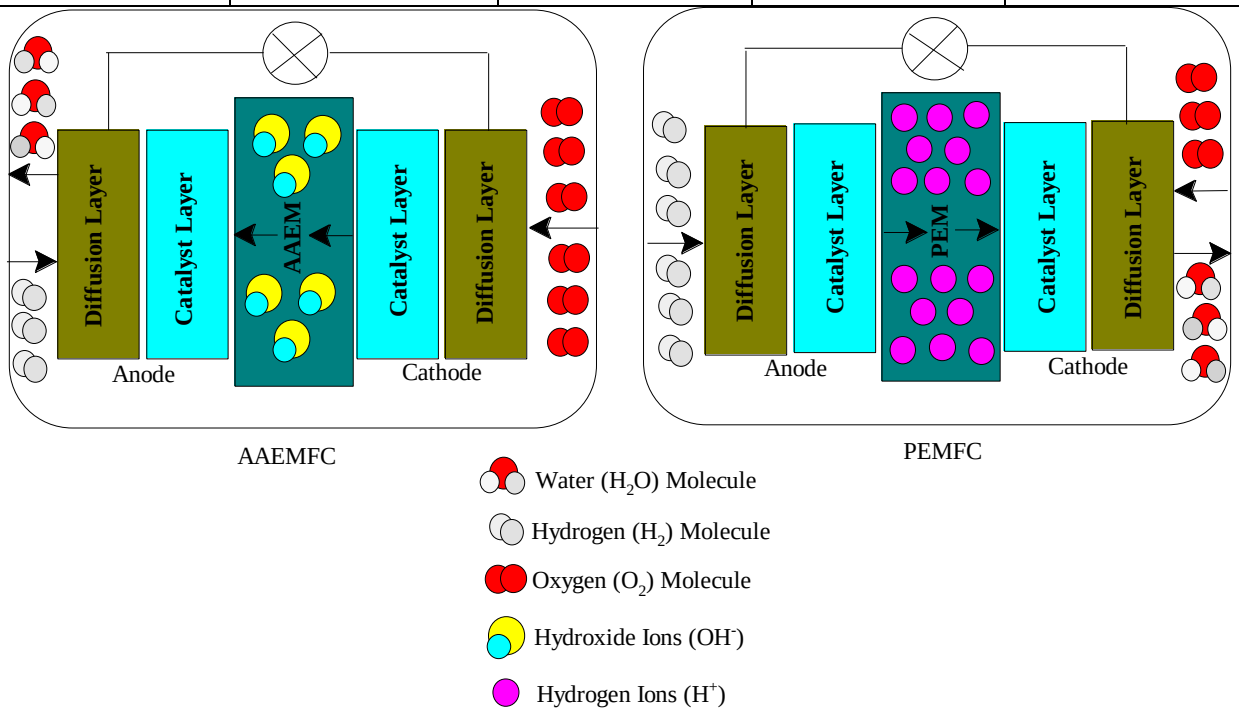

Fig.2 Working principle of AAEMFC and PEMFC [8]

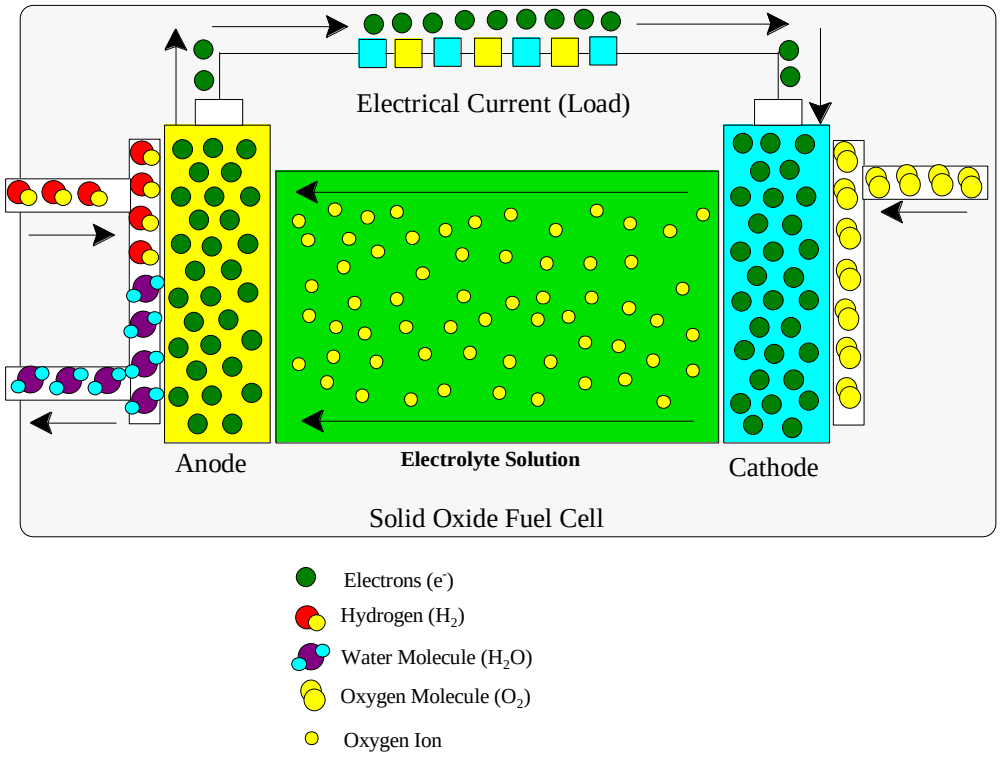

Fig.3 Schematic diagram showing SOFC set-up

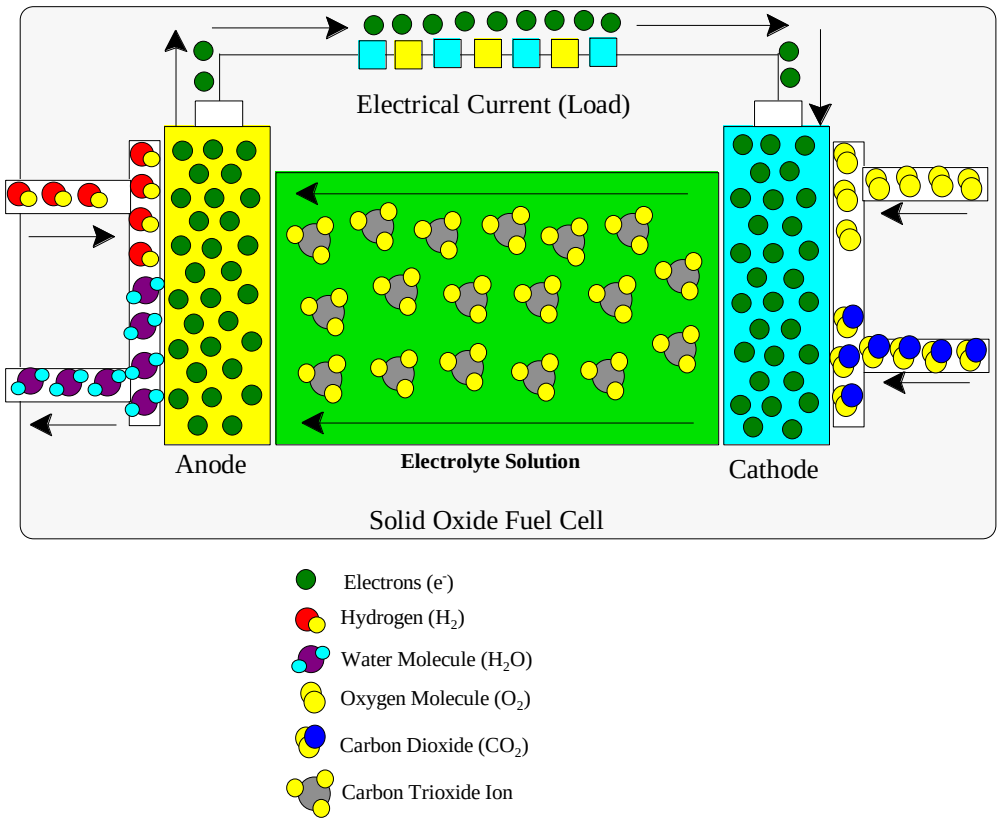

Fig.4 Molten carbonate fuel cell (MCFC) assembly

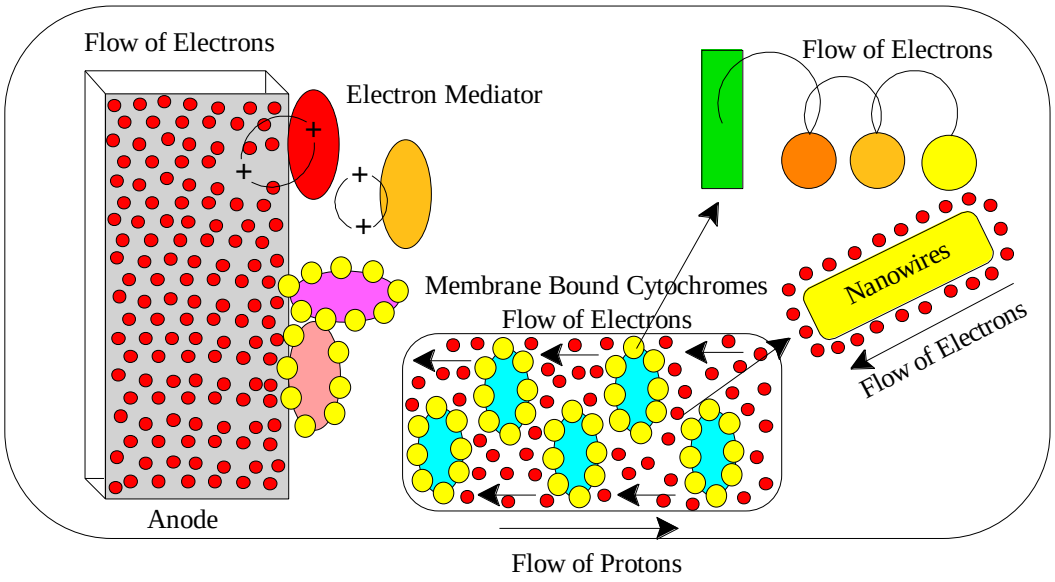

Fig.5 Three different ways of electron transport shown by bacteria

Summary

Fuel cells are portable devices that generate electricity as far as constant oxygen and fuel are fed to the system. They are divided into several types depending upon the cell pressure, temperature, electrolyte and type of fuel used. MEA is regarded as main component of PEMFC and contains PEM between carbon papers coated with catalyst. Several factors restricts commercialization of this tool that include durability, costly and hydrogen storage issues. One condition of constant temperature supply must be maintained to prevent the cell destruction due to excess heat. The PEMFC are light, portable and use polymer membrane which make fabrication of cell easy. Fuel cells are mostly used for transportation and durability is the main factor which decides the excellence of any type of fuel cell as the membranes and flow plates begin to degrade with time decreasing the efficiency. One possible solution is the development of such electrodes that could increase the production of electricity, great durability, improves stability, efficiency and performance of MFCs. Apart from this, cathode catalysts for oxidation-reduction reactions also increased the capital cost for MFC. The future advanced integrated MFC systems will be more reliable sources of energy creation.

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