A succinct review on fuel cells

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Abstract. The role of renewable energy is becoming significant in the current scenario due to increasing power demand, instability of fuel prices and economic-environmental glitches. Fuel cell stood as one of the emerging and leading contributors in the realm of renewable energy because of its higher efficacy, cleanliness and economic supply of demanded energy to the consumers. This article gives a brief knowledge on the different types of fuel cell technologies along with their working principles, pros, cons and application of fuel cells in various sectors. It also discusses the techno-economic issues of this current technology. Also briefed about the future recommendations to wide spread this technology for better economic and environmental solutions.

Keywords: Fuel cell, Renewable energy, Socio-economic solutions, I-V Characteristics.

1. Introduction
The consumption of energy is increasing day by day in all forms but at the same time sources of energy are depleting at the same rate. The context of renewable energy is evolved in this situation due to increased awareness in public for safeguarding environment and current status of fossil fuels. Among all the energy generating systems, the world is shifting more towards fuel cells as equal as solar energy because of fuel cells are capable of generating heat and electricity at an operation. Fuel cells directly transform chemical energy into electricity and generates water as its byproduct [1,2]. Even though, the conventional devices generate electricity from chemical energy but ended up with less conversion efficiency when compared to fuel cells. The fuel cells are literally seen as the device with collective features of heat engine and batteries; similar to an engine, fuel cells can function for longer duration as fuel is accessible without any transitional mechanical energy transformation and the features of fuel cell are almost similar to batteries [3]. It is intended that current article may be beneficial for forthcoming investigators to know the concept of fuel cell in a broader manner.

2. Fuel cell approach
Christian Friedrich Schönbein, a Swiss scientist, discovered the fundamental principle of fuel cell in 1838. First fuel cell accidentally developed by Sir William Grove by reversing the electrolysis of water in 1839. A 5kW alkaline fuel cell was first illustrated by Francis Bacon in 1950 at Cambridge University. After the fruitful evolution of alkaline fuel cells, NASA required a compact system to produce electricity. In 1970s, an alkaline fuel cell of 12kW capacity was developed for space shuttle orbiter of NASA to offer consistent power without any backup usage. Later in the mid-1960s the studies on the fuel cells was more elaborately concentrated on the further advancement of different fuel cells for stationary power and transportation applications. Further the international government agencies have predominantly increased the opportunities for further research and development in fuel cells [3]. But in all the countries it took almost after 50 years for development due to its high installation cost. Later, the development of power conversion devices leads to the reduce in the decreased the installation cost.

2.1. Principle of Fuel cells
Fuel cells are direct energy conversion devices that transform the chemical energy into electricity and generates water and heat as its byproduct as shown in Fig.1[4] and the fuel cell comprises of electrodes immersed into electrolyte. The oxygen from air is continuously fed to cathode and the hydrogen is continuously fed to anode of fuel cell. At anode, hydrogen split into positive ions and electrons are released. The electrolyte allows only the positively charged hydrogen ions and they flow from anode to cathode. These free electrons moved to cathode from anode through the external load connected.The oxidant reacts with cathode to form water. The chemical reactions involved are given as:

At Anode: 
\[ H_2 \rightarrow 2H^+ + 2e^- \] (1)

At Cathode: 
\[ \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \] (2)

Overall Reaction: 
\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \] (3)

2.2. Fuel cells categorization
The fuel cells are categorized on the basis of electrolyte and fuel choice. Currently there are six types of fuel cells are serving in the realm of renewable energy.

i. Proton exchange membrane fuel cell (PEMFC)
ii. Alkaline fuel cell (AFC)
iii. Phosphoric acid fuel cell (PAFC)
iv. Molten carbonate fuel cell (MCFC)
v. Solid oxide fuel cell (SOFC)
vi. Direct methanol fuel cell (DMFC)

They are again categorized on the basis of operating temperature.

i. Low Temperature (50-250 °C) for PEMFC, AFC and PAFC.
ii. High Temperature (650-1000 °C) for MCFC and SOFC
2.2.1. Proton Exchange Membrane Fuel Cell (PEMFC)

The proton exchange membrane fuel cell comprises of a solid polymer electrolyte for swapping the ions between the electrodes, which is an insulator for electrons and conductor for protons. The fuel cell operates at a temperature of as low as 100 °C. The chemical reactions involved in the fuel cell are given in Eqns (1) – (3) [5]. The key benefits of PEMFCs are its quick startup power and higher densities for automobiles. Also, its low operating temperature makes it more viable in applications like transportation, mobile phones, bicycles and laptop computers etc. The main disadvantages of fuel cell are its low operating efficacy about 40%-45% and the other lagging factor is that use of platinum which is not cost effective. The PEMFC based sources of power are also being advanced for the household, hot water and building electricity applications [6]. The PEMFC is subcategorized into Direct Ethanol Fuel Cell (DEFC) and Direct formic acid fuel cell (DFAFC).

2.2.1.1. Direct Formic Acid Fuel Cell (DFAFC): The inlet fuel of DFAFC is formic acid (HCOOH) comprises of minute organic molecules fed directly to anode. It has a key benefit that the formic acid doesn’t cross over the polymer which results the high concentration efficiencies and low power density compared to Methanol. This particular fuel cell at 60 °C operating temperature generates an open circuit voltage of 0.55V which is comparatively low than the theoretical value given by Gibbs free energy. So as to improve the efficiency, the Richard Masel’s group at the University of Illinois utilizes catalyst as palladium [7–9].

2.2.1.2. Direct Ethanol Fuel Cell (DEFC): The main difference between the PEMFC and DEFC is input fuel. In PEMFC, Hydrogen is used as an input fuel whereas in DEFC, Ethanol is used as input fuel. In the DEFC a Nafion catalyst is used. The input fuel Ethanol is easily accessible from biomass through fermentation process. In this cell, at anode, the liquid ethanol is oxidized with the mixture of water and hydrogen ions, electrons and CO\(_2\) are generated. The chemical reaction entangled is similar to PEMFC and the generated voltage is of 0.5V to 0.9V. The first DEFC powered vehicle is presented by University of Applied Sciences in France [10–13]

2.2.2. Alkaline Fuel Cells (AFC)

It is one of the earlier approaches of fuel cells employed in space missions of NASA. Previously, after its British inventor, it is coined as Bacon fuel cell. It has a capability to obtain the efficacy of 60% to 70% at an operating temperature of 100°C range as similar to PEMFC. Here aqueous solution of Potassium Hydroxide (KOH) is used as electrolyte. Quick starting is the main advantage of this fuel cell but the disadvantage is that is very sensitive to carbon dioxide. It requires a distinguished system to remove the carbon dioxide from air. The utilization of electrolyte of corrosive nature is also a drawback that its life span is also shorter. Henceforth, this is not employed for commercial applications and only used in space shuttles and transportation. The AFC is subcategorized into Protonic Ceramic Fuel Cell (PCFC) and Direct Ethanol Fuel Cell (DEFC) [6,14–16].

2.2.2.1. Protonic Ceramic Fuel Cell (PCFC): It is basically a novel type of fuel cell with ceramic electrolyte material. The PCFC is capable of operating at higher temperatures of 750°C and the hydrocarbon fuel gaseous molecules supplied to anode are directly oxidized without any reformer. As the electrolyte is solid, the membrane cannot dry out like in the PEMFCs or there is no leakage of liquids as in the case of PAFCs. The open circuit voltage generated is almost equal to the given theoretical value. The only disadvantage is low current density and it can be improved by decreasing the thickness of electrolyte, optimized electrodes and improved conductivity. The studies are mainly focused to increase the efficiency to a range of 55%-65% [17–19].

2.2.2.2. Direct Borohydride Fuel Cell (DBFC): In this cell, Sodium Borohydride (NaBH\(_4\)) is utilized as input fuel mixed with H\(_2\)O and generates Borax (NaBO\(_2\)) and hydrogen (4H\(_2\)). This cell operates at a low temperature of 70°C. The key benefits of this particular DBFC are it is not operated with high cost
platinum catalyst, high open circuit voltage and high-power density. But it has a very low efficacy of 35% and henceforth the studies are more focused on the development of efficient DBFC by utilizing the various catalysts namely Ni, Pd or Au instead of platinum to minimize the borohydride hydrolysis. This DBFC approach is still in the advancement stage and researchers are more focusing on the NaBO$_2$ recycling [20,21].

2.2.3. Phosphoric Acid Fuel cells (PAFC)
The operating temperature of this fuel cell is about 150-200°C which is almost twice of the PEMFC operating temperature. In this scenario liquid phosphoric acid is utilized as an electrolyte and it is very resistive towards the scums in hydrocarbon fuels. The chemical reactions are as same as PEMFC but only difference is input fuel [10]. The high operating temperatures lead to cogeneration of hot water and electricity. But the main disadvantage is that PAFC also uses the platinum catalyst which is not cost effective. It has been developed commercially and the 100kW, 200kW and 500kW plants are already available. A system of 1.3MW capacity is already tested in Milan and more PAFCs are installed at Japan, USA and Europe [22,23].

2.2.4. Molten Carbonate Fuel Cell (MCFC)
The operating temperature of this MCFC is about 600°C-700°C and it comprises of two good conductive porous electrodes are in contact with molten carbonate cell. The key benefit of this fuel cell is that it has higher efficiency of 50-60% and it doesn’t require any reformer and metal catalyst because of its high operating temperature [6,24]. This cell has slow startup and not resistive to Sulphur record as its disadvantages. It is mostly employed for large and medium power applications.

2.2.5. Solid Oxide Fuel Cells (SOFC)
These fuel cells are normally operated at high temperatures about 1000°C and utilize a solid ceramic material that is dense yttria stabilized zirconia as electrolyte. It has a high efficiency of 50-60% and also due to its internal reforming capability it doesn’t need any separate reformer to extract hydrogen[6,25]. The high cost, slow startup and not tolerant to Sulphur content are recorded as its main drawbacks. It is mostly employed for large and medium power applications. In 1997, a Ceramic Fuel cell industry illustrated a prototype fuel cell system of 5kW capacity. Yakabe et al. [26] advanced a SOFC of 3kW and analyzed he main parameters to enhance the efficiency of SOFC in micro-grid system. Currently, the studies are focusing to develop the commercial model of 250kW capacity.

2.2.6. Direct Methanol Fuel Cell (DMFC)
This cell is totally new and innovative approach when correlated to others. Like PEMFC, it uses a polymer electrolyte but the fuel used is liquid methanol or alcohol is used in place of hydrogen. During chemical reactions, the anode attracts hydrogen by dissolving liquid methanol (CH$_3$OH) in water so as to eradicate the external reformer requirement. Basically, a single DFMC can supply 0.3 to 0.5V under loaded conditions and mainly employed as the substitute for batteries in cameras, notebook computers and some portable electronic devices. The key benefit of this fuel cell is that anode attracts the hydrogen from the methanol and lessens the total price because of reformer absence. Its characteristic features are identical to PEMFC, but their performance is restricted to methanol crossover to cathode from anode which drops the performance and the slow kinetics of methanol electrochemical oxidation at anode [27–29].

3. Comparison of Fuel cells
A broad and concise comparison of the above said six fuel cell approaches based on the different categories is depicted in the Table 1. It is clear that PEMFC is more appropriate for household and business applications because of its low temperature operation and quick start up but when it is for medium/large power applications, the suitable option is SOFC and MCFC. SOFCs have all the intriguing benefits but its high capital cost is its main drawback. Henceforth, the researchers are mainly
focused on decreasing the operating temperature as well as its high capital cost. These key and intriguing benefits made SOFCs as a trending approach for stationary power production from range of 2kW to some MW capacity. The AFCs are employed for few special space programs, and the PAFCs is employed for commercial applications and for transportation. [5,6,22,25–27,30–33] Currently, almost 2500 fuel cells are employed throughout the world for stationery applications and also for portable applications like mobile phones and laptops etc., [34–37]

| Parameter | PEMFC | AFC | PAFC | MCFC | SOFC | DMFC |
|-----------|-------|-----|------|------|------|------|
| Electrolyte | Solid polymer membrane (Nafion) | Liquid solution of KOH | Phosphoric acid (H₃PO₄) | Lithium and potassium carbonate (LiAlO₂) | Stabilized solid oxide electrolyte (Y₂O₃, ZrO₂) | Solid polymer membrane |
| Fuel | Pure H₂ | Pure H₂ | Pure H₂ | H₂, CO, CH₄ and other hydrocarbons. | CH₃OH |
| Operating Temperatu re (°C) | 50-100 | 50-200 | Approx. 200 | Approx. 650 | 800-1000 | 60-200 |
| Efficiency | 40-50% | 50% | 40% | >50% | >50% | 40% |
| Reformer | Yes | Yes | Yes | No | No | No |
| Applications | Household; UPS; transportatio n; emergency services such as industry; hospitals and banking; commercial | Space Shuttles; Portable Power and transportatio n. | Cogeneratio n; portable power; transportatio n. | Industries, Powerplants and transportatio n. | Household; cogeneratio n; utility power plants; portable power. | It is employed as replaceme nt for batteries in laptop and mobiles. |
| Benefits | Quick startup, High power density and non-corrosive electrolyte. | Quick startup and high-power density. | Generate high grade waste heat. | Highly efficient and no metal catalyst required. | High grade waste heat and highly efficient. | Cost effective |
4. I-V Characteristics
The voltage of fuel cell is very low around 1.2V. As the fuel cell having low voltage, it is required to stack as many as possible fuel cells connected in parallel and series to obtain the required power capacity. The characteristic curve of voltage and current of fuel cell is as shown in fig 2 [32]. It is depicted that a linear region exists because the rise in current density tends to drop in voltage due to its ohmic nature. This particular region is known as ohmic polarization. At low current, the ohmic loss become less significant; the enhancement in output voltage is primarily because of the chemical reactions and this region is known as active polarization. At high current, the voltage drops significantly due to the fall of efficiency of gas exchange and it is mainly because of water overflooding in catalyst. This region is known as concentration polarization. The fuel cell performance is enhanced by the electrical and thermodynamic efficiency of the system.

5. Recent advances in Fuel cells
The choice of optimal size of fuel cell is more significant to meet the required load demands for various applications [31]. The research is mainly concentrating on the PEM, MCFC and SOFCs to reduce the fuel cell stack cost and to enhance the life span. Currently, the development of 7kW PEMFC is being carried out for household applications by plug power and a cell with capacity of 250kW is under testing by Ballard power generation system. The extensive research on MCFCs for stationary power application is being carried out by the Department of Energy (DOE) and Fuel Cell Energy, Inc. have researched. Many MCFCs with different capacities from 250kW to 400kW are being developed for cogeneration in various parts of the world such as Holland, Italy, Germany and Spain[3–6,38] Moreover, the future is research is mainly targeting the development of PEMFC and PAFCs for cogeneration of heat and power.[39,40] The research is also concentrating on the development of 100kW to 1MW DMFC and other fuel cell types for commercial applications [7,17,20–22,26,41–43].
6. Conclusions
This review paper gives a succinct information on the principle, working, chemical reactions involved and broad categorization of different fuel cell approaches. It also concisely discussed about the type of electrolyte, type of fuel, operating temperatures, key benefits and drawbacks of particular fuel cell technologies and their appropriate applications along with I-V characterization curve. The recent advances in fuel cells have been elucidated and compared the different types of fuel cell approaches. It is depicted that from this discussion, the PEMFC is suitable for almost all applications because of its high-power density, long life span, quick start up and lower cost. But MCFCs and SOFCs are best suited for large and medium power applications due to their promising efficacy, internal reforming and cogeneration of power and heat. A more focused research on the development of long life and cost-efficient fuel cell approaches is required for the benefit of the society.

References:
[1] Wang C and Nehrir M H 2006 Distributed generation applications of fuel cells Power Syst. Conf. 2006 Adv. Metering, Prot. Control. Commun. Distrib. Resour. PSC 244–8
[2] Bougdehne Stambouli A and Traversa E 2002 Fuel cells, an alternative to standard sources of energy Renew. Sustain. Energy Rev. 6 295–304
[3] Cook B and Anonymous 2002 Introduction to fuel cells and hydrogen technology Eng. Sci. Educ. J. 11 205–16
[4] Xinhong Huang 2006 Fuel Cell Technology Distributed Generation: An Overview ISIE 2006, July 9-12, 2006, Montr. Quebec, Canada Fuel
[5] Ellis M W, Von Spakovsky M R and Nelson D J 2001 Fuel Cell Systems: Efficient, Flexible Energy Conversion for the 21st Century Proc. IEEE 89 1808–17
[6] Farooque M and Maru H C 2001 Fuel Cells - The Clean and Efficient Power Generators Proc. IEEE 89 1819–29
[7] Mozsgai G, Yeom J, Flachtsbart B and Shannon M 2003 A SILICON MICROFABRICATED DIRECT FORMIC ACID FUEL CELL 1738–41
[8] Rice C, Ha S, Masel R I, Waszczuk P, Wieckowski A and Barnard T 2002 Direct formic acid fuel cells J. Power Sources 111 83–9
[9] Aslam N M, Masdar M S, Kamarudin S K and Daud W R W 2012 Overview on Direct Formic Acid Cells (DFACs) as an Energy Sources APCBEE Procedia 3 33–9
[10] https://en.wikipedia.org/wiki/Direct-ethanol_fuel_cell
[11] Kamarudin M Z F, Kamarudin S K, Masdar M S and Daud W R W 2013 Review: Direct ethanol fuel cells Int. J. Hydrogen Energy 38 9438–53
[12] Akhairi M A F and Kamarudin S K 2016 Catalysts in direct ethanol fuel cell (DEFC): An overview Int. J. Hydrogen Energy 41 4214–28
[13] Ma K B, Kwak D H, Han S B, Park H S, Kim D H, Won J E, Kwon S H, Kim M C, Moon S H and Park K W 2018 Direct Ethanol Fuel Cells with Superior Ethanol-Tolerant Nonprecious Metal Cathode Catalysts for Oxygen Reduction Reaction ACS Sustain. Chem. Eng. 6 7609–18
[14] Gülzow E 2004 Alkaline fuel cells Fuel Cells 4 251–5
[15] Tomantschger K, McClusky F, Oporto L, Reid A and Kordesch K 1986 Development of low cost alkaline fuel cells J. Power Sources 18 317–35
[16] Burchardt T, Gouérec P, Sanchez-Cortezon E, Karichev Z and Miners J H 2002 Alkaline fuel cells: Contemporary advancement and limitations Fuel 81 2151–5
[17] Coors W G 2003 Protonic ceramic fuel cells for high-efficiency operation with methane J. Power Sources 118 150–6
[18] https://en.wikipedia.org/wiki/Protonic_ceramic_fuel_cell
[19] Duan C, Tong J, Shang M, Nikodemski S, Sanders M, Ricote S, Almansoori A and O’Hayre R 2015 Readily processed protonic ceramic fuel cells with high performance at low temperatures Science (80-. ). 349 1321–6
[20] Jamard R, Salomon J, Martineau-Beaumont A and Coutanceau C 2009 Life time test in direct
borohydride fuel cell system. *J. Power Sources* **193** 779–87

[21] Colominas S, McLafferty J and Macdonald D D 2009 Electrochemical studies of sodium borohydride in alkaline aqueous solutions using a gold electrode *Electrochim. Acta* **54** 3575–9

[22] O’Sullivan J B 1999 Fuel Cells in Distributed Generation 568–72

[23] Kanuri S V and Motupally S 2013 Phosphoric Acid Fuel Cells for Stationary Applications *Encyclopedia of Sustainability Science and Technology*

[24] Watanabe T 2012 *Molten Carbonate Fuel Cells* vol 45

[25] Swider-Lyons K E, Carlin R T, Rosenfeld R L and Nowak R J 2003 Technical issues and opportunities for fuel cell development for autonomous underwater vehicles 61–4

[26] Yakabe H, Sakurai T, Sobue T, Yamashita S and Corporation K 2006 Solid Oxide Fuel Cells as Promising Candidates for Distributed Generators H. Yakabe and T. Sakurai, 00 369–74

[27] Garcia B L, Sethuraman V A, Weidner J W, White R E and Dougal R 2004 Mathematical Model of a Direct Methanol Fuel Cell *J. Fuel Cell Sci. Technol.* **1** 43

[28] http://www.fuelcelltoday.com/technologies/dmfc

[29] Hogarth M P and Hards G A 1996 Direct methanol fuel cells: Technological advances and further requirements *Platin. Met. Rev.* **40** 150–9

[30] Canha L N, Popov V A and Farret F A 2005 Optimal characteristics of fuel cell generating systems for utility distribution networks 2002 37th Intersoc. Energy Convers. Eng. Conf. IECEC 597–602

[31] Cheng K W E, Sutanto D, Ho Y L and Law K K 2001 Exploring the power conditioning system for fuel cell *PESC Rec. - IEEE Annu. Power Electron. Spec. Conf.* **4** 2197–202

[32] Soltani M and Bathaea S M T 2008 A new dynamic model considering effects of temperature, pressure and internal resistance for PEM fuel cell power modules 3rd Int. Conf. Deregul. Restruct. Power Technol. DRPT 2008 2757–62

[33] Choi W, Howze J W and Enjeti P 2006 Development of an equivalent circuit model of a fuel cell to evaluate the effects of inverter ripple current *J. Power Sources* **158** 1324–32

[34] Pasricha S, Keppeler M, Shaw S R and Nehrir M H 2007 Comparison and identification of static electrical terminal fuel cell models *IEEE Trans. Energy Convers.* **22** 746–54

[35] del Real A J, Arce A and Bordons C 2007 Development and experimental validation of a PEM fuel cell dynamic model *J. Power Sources* **173** 310–24

[36] Corrêa J M, Farret F A, Popov V A and Simões M G 2005 Sensitivity analysis of the modeling parameters used in simulation of proton exchange membrane fuel cells *IEEE Trans. Energy Convers.* **20** 211–8

[37] Jacobs T and Beukes J 2006 Suitability of fuel cell technology for electricity utility standby power applications *INTELEC. Int. Telecommun. Energy Conf.*

[38] Meng J 2004 A distributed power generation communication system 483–6

[39] Lakshminarayanan V and Karthikeyan P 2016 Optimization of flow channel design and operating parameters on proton exchange membrane fuel cell using MATLAB *Period. Polytech. Chem. Eng.* **60** 173–80

[40] Arun Saco S, Thundil Karuppa Raj R and Karthikeyan P 2016 A study on scaled up proton exchange membrane fuel cell with various flow channels for optimizing power output by effective water management using numerical technique *Energy* **113** 558–73

[41] Garcia-Rodriguez L 2002 Seawater desalination driven by renewable energies: A review *Desalination* **143** 103–13

[42] Thiagarajan V, Karthikeyan P, Thanarajan K, Neelakrishnan S, Manoharan R, Chen R, Fly A, Anand R, Karuppa Raj T R and Sendhil Kumar N 2019 Experimental investigation on DMFCs using reduced noble metal loading with NiTiO 3 as supportive material to enhance cell performances *Int. J. Hydrogen Energy*

[43] Thiagarajan V, Manoharan R, Karthikeyan P, Nikhila E, Hernández-Ramírez A and Rodriguez-Varela F J 2017 Pt nanoparticles supported on NiTiO 3 /C as electrocatalyst towards high performance Methanol Oxidation Reaction *Int. J. Hydrogen Energy* **42** 9795–805