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## POPULAR FUEL CELL TYPES – A BRIEF REVIEW

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***Abstract:** Fuel cells (FCs) are well-known and very efficient devices that utilize the chemical energy of a fuel—most commonly of hydrogen, in order to generate electricity. Namely due to the high efficiency, as well as the compactness, stable operation under different conditions, high flexibility, and the low environmental impact, fuel cells are applicable in many sectors and are regarded as a potential replacement of internal combustion engines. Depending on the type and size, fuel cells can be successfully utilized in electronic devices; personal equipment; commercial back-up or surveillance systems; in all types of vehicles, in ships; and for power and/or heat generation. There exist various types of fuel cells suitable for different applications which can be divided based on fuel and electrolyte type, operating pressure and temperature, electrical efficiency and other criteria. This research aims at briefly reviewing the basics of the fuel cell technology in order to highlight its benefits and reliability, as well as to mention and compare the most popular and widely used types and their applications.*

***Keywords:** Fuel cell, Hydrogen, Energy efficiency, Electrolyte, Anode, Cathode.*

## **INTRODUCTION**

Lower emission energy conversion technologies such as fuel cells (FCs), in combination with alternative fuels and energy carriers such as hydrogen, are applied globally ever more often in order to tackle the problems of climate change, environmental pollution and depletion of fossil resources (Singh et al., 2021). Fuel cells operate at high electrical efficiencies of up to 65%, they possess a simple construction, and have a broad range of applications across power, industry and transport sectors. The FC technology has been extensively researched in the last 30 years and a number of different constructions have been successfully developed. Among the many FC types a few have proven to be the best in terms of reliability, efficiency, cost and manufacturability, and are already commercially available: Proton Exchange Membrane FC (PEMFC), Alkaline FC (AFC), Phosphoric Acid FC (PAFC), Molten Carbonate FC (MCFC) and Solid Oxide FC (SOFC). The PEMFC has gained the most popularity, being universal for applications from small electronic devices to propulsion for buses, trucks and small ships.

The European Commission has recently initiated a number of policies which aim at popularizing hydrogen as a reliable and clean energy carrier. These policies encompass plans for establishment of production, storage and delivery facilities for green hydrogen, as well as retrofitting some of the existing production facilities with carbon capture technologies in order to decarbonise them (European Commission, 2020). Fuel cells, as one of the main consumers of hydrogen as a fuel, are also to be encouraged with focus on development of new materials, new electrolytes, and hybrid power systems that contain FCs (Buonomano et al., 2015; European Commission, 2020). Improvement of production methods for some types of FCs is also vital so as to lower their cost.

Thus, this paper aims at briefly reviewing the most popular types of FCs, comparing their characteristics, and drawing a conclusion about their most suitable application, based on the available literature, as a contribution to the European efforts for promotion of the technology.

## EXPOSITION

### Fuel cell fundamentals

Fuel cells have a simple working principle that is illustrated in Figure 1. They consist of two electrodes - an anode and a cathode, and an electrolyte that is sandwiched in between them. The electrodes are coated with a catalyst layer. Fuel is supplied at the anode where its molecules dissociate under the activation of the catalyst into hydrogen protons and electrons. The electrons travel to the cathode through an external circuit, thus creating electrical current. The hydrogen protons react with the oxidant either at the anode or the cathode (depending on the type of electrolyte and its conductive mechanism) to form water and heat. Thus, fuel cells systems convert the chemical energy of the fuel to electrical energy via a one-step electrochemical reaction. Appropriate management of the heat and water by-products should be performed in order for the system to work at optimal levels.

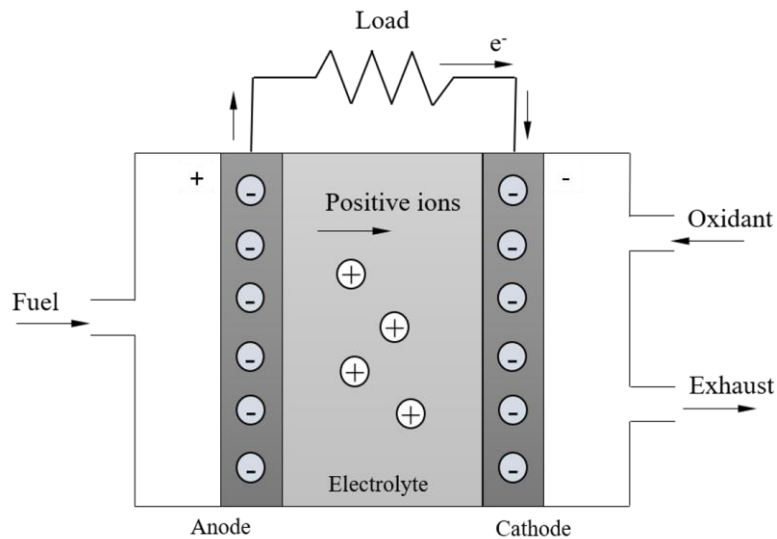


Fig. 1. Basic operating principle of a fuel cell (Ehsani et al., 2018).

It is noteworthy, that SOFCs and MCFCs have higher operating temperatures than the rest of the FC type which enables the processing not only of pure gaseous hydrogen, but also of hydrocarbons (HCs) that are reformed internally in order to extract their hydrogen molecule. The residual gases from the reforming process should also be taken appropriate care of. The specific reactions of each of the most popular fuel cell types and their working principles are discussed later in the article.

Both fuel cells and heat engines use hydrocarbons as fuel and air as oxidant, yet due to the nature of the reactions occurring in them, they vary significantly in efficiency. Heat engines use combustion which is limited in terms of efficiency by the Carnot cycle, and additionally run through a few steps to generate electrical energy. In contrast, fuel cells directly convert chemical to electrical energy and their practical electrical efficiency reaches 65%. Fuel cells also generate less environmental pollutants, and in cases when pure hydrogen gas is utilized as a fuel, the emissions are in fact only of water – see Table 1. Another advantage of fuel cells is the lack of moving parts, therefore almost no vibrations and noise are present during their operation. Nonetheless, FCs lack the maturity and low cost of heat engines, as an FC is usually a few times more expensive than a conventional internal combustion engine (ICE) of the same power range, due to their complicated production processes and the embedment of expensive catalysts (Sharaf and Orhan, 2014).

Fuel cells and batteries have similar working principles, yet FCs continue to produce electricity as long as reactants are supplied to them, unlike batteries where electrical energy is generated until the expenditure of one of the chemical reactants (Wilberforce et al., 2017). FCs have been tested many times and their lifespan can reach up to 8000 hours for transportation purposes and up to 80000 hours for stationary power generation (Andersson and Froitzheim, 2019). Nonetheless, they degrade depending on the operating time. The degradation of FCs is associated with the loss of power that the fuel cell stack can supply at a given operating point. The state of health of the stack is referred to as the current loss of power at nominal conditions compared to the reference power at nominal conditions when the FC is brand new (Vichard et al., 2021).

Loss of performance occurs at all components of the cell. For example, a PEMFC which is composed of electrodes, an electrolytic membrane (see Table 1), gas diffusion layers and bipolar plates, requires good water management in order to stay well humidified. Bad water management leads to membrane dry out which increases resistive surfaces and potentially creates cracks. Bad oxidant filtering and operation at extreme temperatures can also lower the performance of FCs, but such damage is not always irreversible (Vichard et al., 2021).

Typically, a FC supplies voltage in the range 0,4 – 1 V depending on the type and operating conditions. The voltage drop is due to three main factors: ohmic voltage drop due to ohmic resistance from the components of the fuel cell; activation voltage drop due to the extra energy required for overcoming the activation barriers of the reactants; and concentration voltage drop due to the lack of ions at the positive electrode to carry the reactions (this voltage drop is higher at high loads of the cell and is based on the slow diffusions of ions through the electrolyte). Fuel cells are combined in fuel cell stacks in series to deliver higher voltage, or in parallel for higher current density (Ehsani et al., 2018).

Fuel cells, similar to heat engines, cannot operate independently – they need additional aggregates. A simple fuel cell system is shown in Figure 2. The hydrogen gas is supplied from a hydrogen cylinder through a pressure regulator and a supply valve to the FC. The fuel is stored in the vessel under pressure, typically 20, 35 or 70 MPa and via the pressure regulator is reduced to the operating pressure of the stack. Air for oxidation is fed to the cells with the help of a compressor and a humidifier, while the excess water is discarded through a purge valve. Thermal management is applied by means of a fan. Certainly, the excess heat can be utilized for additional electricity generation, for steam production, or for heating. The amount of excess heat depends on fuel cell type and the topology of the system. The supply and purge valves, fan and fuel cell operating regime are all managed by the system controller. Normally, fuel cell systems are hybridized with batteries or supercapacitors (SCs) to achieve better system dynamics - the batteries/SCs meet the electrical demand in transient modes when the fuel cell is slow to react. Practically, fuel cell systems include more aggregates that ensure its efficient operation.

Fuel cells can be divided based on different criteria:

- Electrolyte – solid or liquid, acidic or alkaline;
- Operating temperature – low or high temperature FCs;
- Structure – planar, monolithic, tubular; not all FC types can adopt each structure;
- Application – portable, stationary or transportation.

In Table 1 are highlighted and compared some of the most important features of the five most popular types of fuel cells – Proton Exchange Membrane FC (PEMFC), Alkaline FC (AFC), Phosphoric Acid FC (PAFC), Molten Carbonate FC (MCFC) and Solid Oxide FC (SOFC). In Table 2 are listed their advantages and disadvantages. In the next subsections the most popular fuel cell types are discussed in more detail.

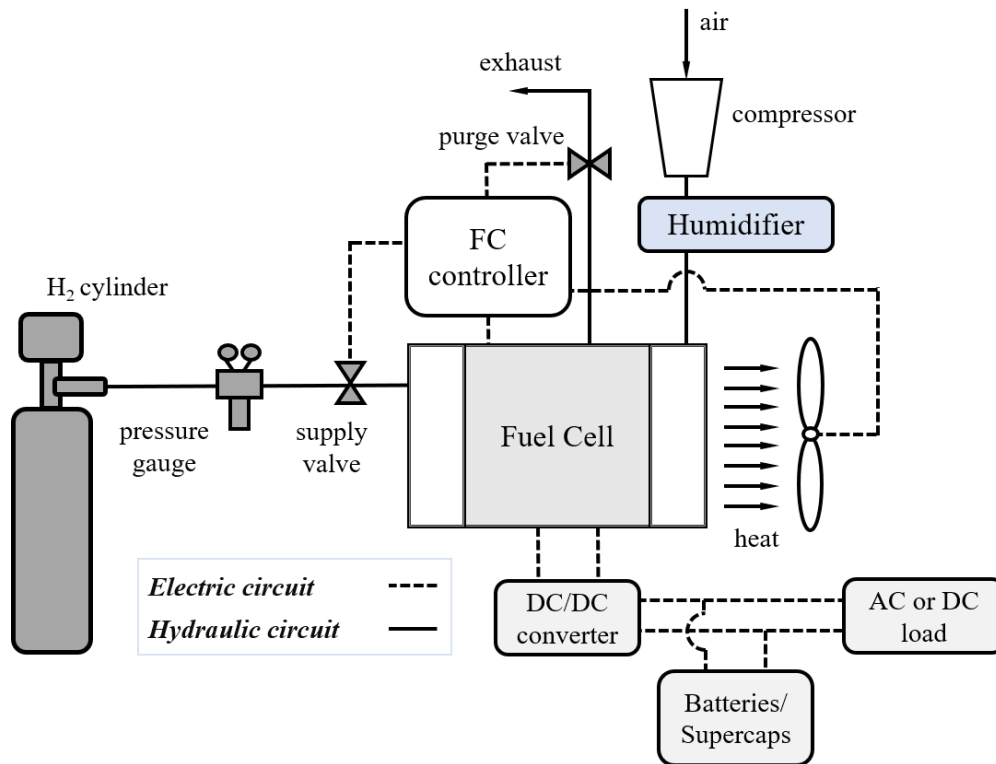


Fig. 2. A basic fuel cell system.

Table 1. Comparative summary of the most popular types of fuel cells (Andersson and Froitzheim, 2019; Biert et al., 2016; Ehsani et al., 2018; Inal and Deniz, 2020; Olabi et al., 2021; Spiegel et al., 2007; Wilberforce et al., 2016)

Type	Fuel	Electrolyte	Operating temperature	Electrical efficiency	Emissions
PEMFC	Hydrogen (99.99% purity)	Solid polymer membrane, acidic	60 to 200 °C	40 to 60%	Water
AFC	Hydrogen (99.99% purity)	Aqueous Potassium hydroxide – KOH	50 to 230 °C	50 to 65 %	Water
PAFC	Hydrogen	Liquid phosphoric acid – H <sub>3</sub> PO <sub>4</sub>	150 to 220 °C	35 to 45% (85% in cogeneration)	Water
MCFC	Hydrogen Methane Natural gas	Liquid alkali carbonates – Li <sub>2</sub> CO <sub>3</sub> /Na <sub>2</sub> CO <sub>3</sub> /K <sub>2</sub> CO <sub>3</sub>	600 to 800 °C	50 to 65% (85% in cogeneration)	Water (CO <sub>2</sub> and HC if fuel internally reformed)
SOFC	Hydrogen Methane Natural gas Other Fuels	Solid yttria-stabilized zirconia YSZ	600 to 1200 °C	55 to 65% (85% in cogeneration)	Water (CO <sub>2</sub> and HC if fuel internally reformed)

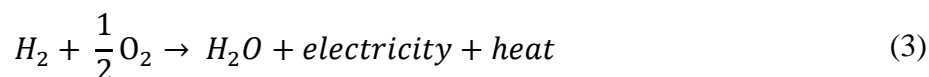
Table 2. Advantages and disadvantages of most popular types of fuel cells (Andersson and Froitzheim, 2019; Biert et al., 2016; Ehsani et al., 2018; Inal and Deniz, 2020; Olabi et al., 2021; Sharaf and Orhan, 2014; Spiegel et al., 2007; Wilberforce et al., 2016)

Type	Advantages	Disadvantages
PEMFC	<ul style="list-style-type: none"> <li>- Low operating pressure, temperature and start-up time</li> <li>- Simple and compact design</li> <li>- High current, voltage and power density</li> <li>- Solid Electrolyte</li> </ul>	<ul style="list-style-type: none"> <li>- Fragile PEM</li> <li>- Requires constant stack humidification and thus water management</li> <li>- Requires platinum catalyst and high fuel purity</li> <li>- Intolerance to CO and sulfur</li> </ul>
AFC	<ul style="list-style-type: none"> <li>- High efficiency and low start-up time, low operating temperature</li> <li>- Easy to operate and easy thermal management</li> <li>- Low weight and volume</li> <li>- Solid Electrolyte when using AEM</li> </ul>	<ul style="list-style-type: none"> <li>- Very high intolerance to CO and CO<sub>2</sub></li> <li>- Requires high oxidant and fuel purity</li> <li>- Prone to leakage liquid electrolyte, introducing handling problems + sealing issues when not using AEM</li> <li>- Requires platinum catalyst and high fuel purity</li> </ul>
PAFC	<ul style="list-style-type: none"> <li>- Cheap electrolyte</li> <li>- Low operating temperature and reasonable start-up times</li> <li>- Mature technology</li> <li>- Increased tolerance to impure hydrogen as fuel</li> </ul>	<ul style="list-style-type: none"> <li>- Requires platinum catalyst</li> <li>- Intolerance to CO and sulfur</li> <li>- Stack must be kept above 42°C – the freezing point of electrolyte, requires extra hardware which makes it heavier and larger</li> <li>- Low efficiency</li> <li>- Liquid corrosive acidic electrolyte which requires careful handling</li> </ul>
MCFC	<ul style="list-style-type: none"> <li>- Internal HC fuel reforming</li> <li>- Inexpensive catalyst</li> <li>- High efficiency</li> <li>- Generation of a lot of waste heat</li> </ul>	<ul style="list-style-type: none"> <li>- Need of heat management due to high operating temperature</li> <li>- Intolerance to sulfur</li> <li>- Liquid electrolyte requires careful handling due to high temperature corrosion and evaporate losses</li> <li>- Corrosion of metallic parts</li> </ul>
SOFC	<ul style="list-style-type: none"> <li>- Internal HC fuel reforming</li> <li>- Inexpensive catalyst</li> <li>- High efficiency</li> <li>- Generation of a lot of waste heat</li> <li>- Wide variety of modular configurations</li> <li>- Solid electrolyte</li> </ul>	<ul style="list-style-type: none"> <li>- Need of heat management due to high operating temperature</li> <li>- Intolerance to sulfur</li> <li>- Brittle electrolyte, strict material requirements</li> <li>- Longer start-up times and immaturity and high cost of the technology</li> </ul>

### Proton Exchange Membrane Fuel Cell (PEMFC)

PEMFCs are the dominating and most researched fuel cell technology. They operate at ambient temperatures in the range -40 to 120 °C, have high peak power density and use hydrogen gas with high purity as fuel. They are developed primarily for portable, transportation and small stationary power generation purposes. The used electrolyte is a solid proton exchange polymer membrane (notably Nafion ®) that has good thermal and mechanical stability but requires

expensive electrocatalysts (mostly platinum) to support the reactions at low temperatures (Wang et al., 2021). The operating principle of PEMFC is shown in Figure 1, the anode reaction is described in (1), cathode in (2), and overall reaction in (3). The most notable assets and downsides of PEMFC are presented in Table 2.



The pure hydrogen (99.99%) used as fuel in PEMFC has high and rapid reactivity and does not contaminate the catalysts and electrolyte. A PEMFC consists of a membrane-electrode-assembly with catalyst layers and the electrolyte, gas diffusion layers, gas flow channels and bipolar plates. The membrane is the conductive area of the ions between the two carbon-supported electrodes and also separates the reactant gases and the electrons between the electrodes. Reactions occur at the catalyst layers, while the gas diffusion layers (built from carbon fiber-based materials) provide mechanical support for the electrolyte and act as a pathway for the inlet and outlet chemicals and for the electron conduction. Gas flow channels distribute the reactants and remove the products from the FC, whereas the bipolar plates provide mechanical support for the gas flow channels. Hence, the materials used to construct bipolar plates are thermally and electrically conductive, highly resistive to corrosion and robust. Most notably metals and carbon composites are used for this purpose (Wang et al., 2021).

Research is ongoing to lower the cost of PEMFCs, by adopting alternative materials, especially for the catalysts and membrane. The most notable current and future use of the technology is in the transport sector. It is commercially applied in fuel cell hybrid electric passenger vehicles such as the Toyota Mirai and Hyundai Nexo, as well as in forklifts and bicycles, and its possible implementation in buses, heavy-duty vehicles and yachts has been seriously investigated (Fan et al., 2021; Wee, 2007).

### Alkaline Fuel Cell (AFC)

AFC has a similar working principle to PEMFC, but uses an alkaline solution of KOH as an electrolyte and thus the ions conduction mechanism is different – hydroxyl ions (OH<sup>-</sup>) travel from the cathode (where air and water are supplied and the oxygen is reduced) to the anode (where pure hydrogen as fuel is fed) to form water. The anodic and cathodic half-reactions are given in (4) and (5).



PEMFCs are superior to AFCs due to higher power density, therefore, PEMFCs are utilized instead of AFCs where application is needed. More recently special solid polymer anionic exchange membranes (AEMs) have been developed to replace the liquid electrolyte in AFCs, hence making them more competitive to PEMFCs. The idea is that such an electrolyte requires less management than the liquid one in AFCs and also guarantees higher power density, close to the one of PEMFCs. AEM is less corrosive than the PEM, which additionally allows for a wider range of materials intended for the bipolar plates, membranes and catalysts, making them less expensive but also simultaneously maintaining a relatively high power density (Firouzjaie and Mustain, 2020).

However, AEMFCs are facing roadblocks of their own – more complex water dynamics than PEMFCs and very high intolerance to CO and CO<sub>2</sub>. Additionally, contemporary AEMFCs have shorter lifetime than traditional AFCs and there have been no catalysts free from platinum or other precious metals to demonstrate high and stable performance in this type of FC. Nonetheless, a lot

of research is being conducted in this field to create efficient and cheap AEMFCs for applications in portables, transportation and small-scale stationary systems (Ferriday and Middleton, 2021).

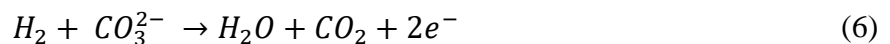
### Phosphoric Acid Fuel Cell (PAFC)

PAFC is the most mature fuel cell technology and the first marketed one. It has the same working principle as a PEMFC, with half-reactions shown in (1) and (2), overall reaction – (3), but the adopted electrolyte is phosphoric acid  $H_3PO_4$ . PAFCs have lower efficiency than the PEMFCs and AFCs, but they fall under the mid-temperature category with operating temperatures in the range 150-220 °C, which allows for combined heat and power generation (where the overall efficiency of the system is up to 85%) and also for increased tolerance to fuel impurities. Moreover, they possess increased tolerance to CO and sulfur, a cheap electrolyte, yet utilize precious metals as catalysts (Sammes et al., 2004).

PAFCs, however, are less power dense than PEMFCs and have a liquid corrosive electrolyte which requires additional hardware for good management, therefore they are intended for small-scale stationary power production plants for example for powering small office buildings, houses, family hotels, small hospitals, fueling stations etc.

### Molten Carbonate Fuel Cell (MCFC)

MCFC is a technology that operates at high temperatures in the range 600-800 °C and utilizes a molten carbonate salt as an electrolyte. most commonly  $Li_2CO_3$ ,  $Na_2CO_3$ , or  $K_2CO_3$ . The reactions at the anode and cathode are given in (6) and (7) respectively.



The electrolyte conducts carbonate ions  $CO_3^{2-}$ , thus it is necessary to provide carbon dioxide additionally to the oxidant at the cathode to form the carbonate group. This does not mandatorily mean that  $CO_2$  should be supplied externally, as it could be recycled from the anode (Ehsani et al., 2018). The high operating temperatures of such fuel cells also allow for internal (at the anode compartment of the FC) processing of light hydrocarbon fuels such as natural gas which can take advantage of the already existing production facilities and delivery infrastructure for the fuel. The residual combustible anode-off gasses from the internal reforming process can be burned in a burner chamber of a gas turbine, or in an internal combustion engine, hence making MCFCs suitable for inclusion into hybrid cycles.

MCFCs also employ cheap non-precious metal catalysts such as nickel for the activation of the reactants, and are less prone to CO poisoning due to the same reason being the high operating temperatures. Furthermore, MCFCs achieve better electrical efficiency than PAFCs (up to around 60%), and can also be used for combined heat and power generation where the overall efficiency may reach 85%.

However, the technology has lower energy density than PEMFC, requires good system thermal management and the electrolyte is very corrosive, lowering the lifetime of the stack. The issues of long start-up times and what source of heat to use to initiate the start-up process are also evident. Nowadays new tubular cells are designed with better stability and robustness, higher energy density and longer lifetime, thus making MCFCs more sustainable (Kawase, 2017).

MCFCs are applied in large stationary power generation where the desired rated power output is between 200 kW and a few MWs, similarly to PAFCs and are also researched for implementation in ships in a hybrid cycle with a gas turbine or an internal combustion engine.

### Solid Oxide Fuel Cell (SOFC)

SOFCs, similarly to MCFCs, operate at high temperatures (600-1200 °C) and utilize non-noble metals for catalysts, preferably nickel. They can process via internal reforming a variety of

fuels including conventional diesel and gasoline fuels, ammonia, synthetic and biofuels (Sasaki et al., 2004). The electrolyte is a solid yttrium-stabilized zirconia (YSZ) which conducts oxygen ions  $O^{2-}$ , the anodic and cathodic reactions are shown in (8) and (9).



SOFCS have higher electrical efficiency than MCFCs, their electrolyte is solid and does not require  $CO_2$  to function properly. The high operating temperature and fuel flexibility enable for application of SOFCs in advance hybrid cycles for cogeneration with dynamic performance and good handling of transient modes in a similar fashion to ICEs. In addition, these hybrid cycles are more efficient than ICEs and emit significantly less harmful chemicals.

The disadvantages of solid oxide fuel cell stacks are similar to the ones of the other high-temperature fuel cell technology, namely: materials' corrosion, long start-up times, lower power density than PEMFC and the need for good heat management. Nonetheless, the development of the technology has led to good results accounting to 80 000 hours lifetime of a stack for stationary power generation (Andersson and Froitzheim, 2019). SOFCs are used exactly for stationary power generation, and are tested as main power units (MPU) or as auxiliary power units (APU) in heavy-duty vehicles and ships.

## CONCLUSION

Fuel cells are a promising technology with high efficiency, stable operation and low environmental impact suitable for a number of different applications. Based on the review of five most popular FC types, the following conclusions regarding their use, challenges and future development can be made:

- PEMFCs and AFCs are good for small portable use such as electronic devices, military and other equipment and battery chargers. They are also suitable for propulsion of forklifts and other small vehicles, bicycles, passenger cars, and generation of power for small facilities. The most serious challenges before the widespread use of these types are the lack of production, storage and delivery facilities for pure hydrogen, as well as the high cost of used catalysts. Work is ongoing on the building of such facilities, the embedment of cheaper catalyst materials and lowering the catalyst load while maintaining functionality of the cells.
- PAFCs are suitable for small stationary power plants and for powering small buildings where cogeneration is applicable high purity of hydrogen is not attainable. The development of this FC type seeks to lower the catalyst costs, increase the electrical efficiency, and optimise the electrolyte handling hardware.
- MCFCs and SOFCs are applied in mid to big-scale power generation plants, possibly in hybrid cycles and for cogeneration. SOFCs in particular are particularly convenient as MPU or APU in big transport means due to the fuel flexibility and the solid electrolyte. Researchers are working on cheap production technologies, protective coatings against the high-temperature corrosion and optimal management of the systems for such FCs.

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