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CHAPTER 3

Fuel cells systems for sustainable ships

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3.1. Introduction

The purpose of this chapter is to provide an overview of the state-of-the-art and future perspectives of fuel cell systems for sustainable ships. Specifically, section 3.2 introduces fuel cell working principles, types and systems. In section 3.3, the characteristics of the most important fuel cell types are discussed. Section 3.4 provides an overview of relevant fuel processing and treatment technologies, after which operational characteristics are detailed in Section 3.5. Aspects relevant to maritime fuel cell application are discussed in Section 3.6, followed by an overview of current applications and future outlook in Section 3.7.

3.2. Fuel cell principles

Invented already in 1838, fuel cells can hardly be referred to as a novel technology. However, the interest in fuel cells has gained renewed interest in the past decades for their role in renewable energy systems [1]. The electrochemical cells can be used to convert electricity to hydrogen, referred to as *electrolysis*, and convert it back to electricity. Sharing large similarities with batteries fuel cells were referred to as *gas batteries* in the early days. Electrochemical conversion of electricity to fuels and back is regarded as a key technology for storage, transport and use of renewable electricity [2].

Fuel cells are well-known from their application in hydrogen-powered cars, where they are used to convert hydrogen to electricity with high efficiency and no emissions other than water vapor. However, fuel cells can in principle electrochemically oxidize any fuel, including hydrocarbons, alcohols and ammonia [3]. In contrast to conventional power generation systems fuel cells do not rely on a thermodynamic heat cycle. Therefore, the fuel is not combusted first to produced heat. Although both can achieve the same efficiency in theory, fuel cells have lower heat and conversion losses, while the formation of pollutants is avoided [4].

Interest with regard to the implementation of fuel cells in shipping dates back from a global energy crisis in the 1970s due to the prospects of efficient, clean on-board power generation. The technology was eventually applied for air independent propulsion in submarines [5]. Yet in spite of a number of demonstration projects, the technology

is not commercially applied in ships till date. Recently, the development of fuel cell technology is accelerated, driven by strong international emission reduction ambitions. However, various fuel cell types and solutions are investigated, while experience with maritime application is limited.

Fuel cells rely on electrochemical production within the cell to produce electricity. In this regard, their working principle is inherently different from internal combustion engines, where fuel is combusted to produce heat. The thermomechanical energy is subsequently converted into mechanical work and, if desired, electricity. Fuel cells are in that respect similar to batteries, but in contrast the energy is extracted from fuel and oxidant which are continuously supplied to the cell. No hazardous air pollutants are produced in this electrochemical reaction, neither does it generate any noise or vibrations. Therefore, fuel cells provide an interesting alternative for internal combustion engines, which are conventionally employed for electricity generation in the maritime industry today.

3.2.1 Working principle

Fuel cells consist of at least three functional layers: an ion conducting membrane and electronically conducting electrodes for fuel and air. This is commonly referred to as the membrane electrode assembly (MEA) or positive electrode-membrane-negative electrode (PEN) structure. The membrane is a dense, gas-tight and electronically isolating layer which conducts mobile ions. The electrodes are usually porous structures which allow reactants, products and electrons to diffuse to and from the reaction sites, which are in close vicinity to the membrane. These reaction sites are typically located at the interface of the gas, an electronic conductor and an ionic conductor, more commonly referred to as the triple phase boundary. In addition, a catalyst is usually incorporated in the electrodes to facilitate the electrochemical reaction and, therefore, achieve a sufficiently high reaction rates.

Fig. 3.1 shows a simplified schematic of a fuel cell with a proton conducting electrolyte when fueled with hydrogen. The fuel and oxidant compartment are separated by a membrane with electrodes on either side. Hydrogen is supplied at the fuel electrode, the *anode*, while air is supplied at the oxygen electrode, the *cathode*. The membrane is a gas-tight and an electric isolating material, but mobile ions, protons in this case, can migrate from the anode through it to react with oxygen at the cathode, producing water. The flux of protons is driven by the chemical potential over the membrane, which results in an electric potential known as the electromotive force. The electrons released during hydrogen oxidation at the anode travel through an external circuit to be recombined in the oxidation reaction at the cathode. This yields an electric current and enables the fuel cell to provide useful work.

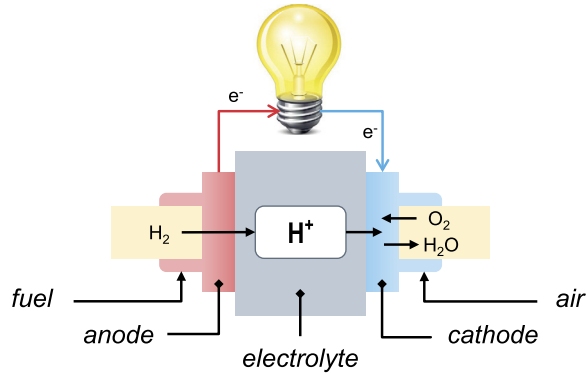


Figure 3.1 Simplified schematic of the working principle of a fuel cell with a proton conducting electrolyte.

3.2.2 Fuel cell types

Different fuel cell types are distinguished by the functional membrane materials used. The well-known low temperature proton exchange membrane fuel cells (LT-PEMFCs) use a polymer membrane and are, therefore, sometimes referred to as polymer electrolyte membrane fuel cells. Other fuel cell types include the alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). In addition, variants on these types are developed, such as the direct methanol fuel cell (DMFC), which is based on the LT-PEMFC but uses methanol, and the high temperature (HT-)PEMFC, where phosphoric acid is stabilized in a polymer membrane. The protonic ceramic fuel cell (PCFC) shares many similarities with the SOFC, but uses a proton conducting electrolyte material.

Different membrane materials dictate specific operating conditions. The LT-PEMFC operates at temperatures between 65 °C and 85 °C, which is favorable for water management. The HT-PEMFC is operated between 140 °C and 180 °C, where the protonic conductivity is sufficiently high and the polymer membrane is still chemically stable. The ceramic membranes employed in SOFCs require temperatures ranging from 500 °C to 1000 °C to have sufficiently high ionic conductivity, depending on the electrolyte material and thickness. These operating temperatures in turn determine the material the cells and systems. An overview is shown in Fig. 3.2.

3.2.3 Fuel cell systems

The electric potential of a fuel cell, determined by the electromotive force, is typically well below 1 V. Both the clamping voltage and electric power generated can be increased by connecting cells in series, as shown in Fig. 3.3. Interconnects or bipolar plates separate the air and fuel flow between subsequent cell layers and gaskets are used to seal the layers. Bipolar plates are often designed to uniformly distribute air and fuel to

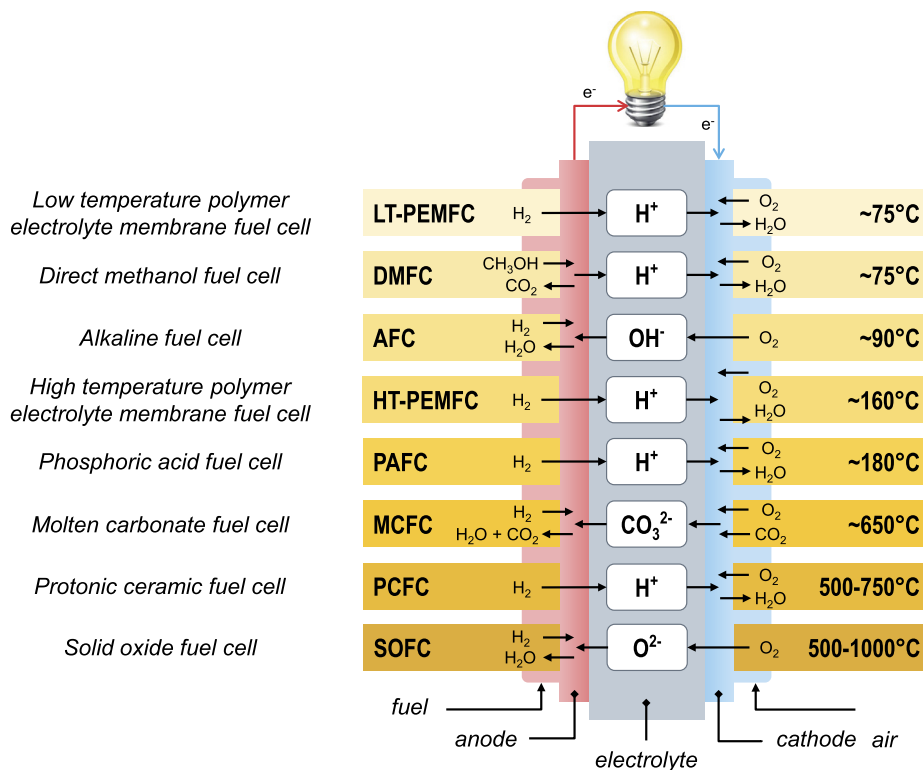


Figure 3.2 An overview of commonly applied fuel cell types, including an indication of their typical operating temperature and the mobile ion in the electrolyte.

over the active cell area. For low temperature fuel cells they often contain channels for the coolant as well. Fuel and air can be supplied via either internal or external manifolds.

The electric power is generated in the fuel cell stack, which is therefore the core component in the system. However, in order for it to function fuel, air and coolant have to be supplied to it at the right conditions. This is taken care of by the balance of plant (BoP), which may include pumps, blowers, valves, heat exchangers, humidifiers, filters, chemical reactors, ejectors, burners, gas cleaning, electric actuators, electric power converters and everything else that is needed for the fuel cell system to function. The fundamental characteristics of different fuel cell types are determined not only by their operating principles, but also by the BoP required to support their operation. A distinction is sometimes made between the *cold* and *hot* BoP in high temperature fuel cell systems, where the latter refers to high temperature components such as heat exchangers and chemical reactors.

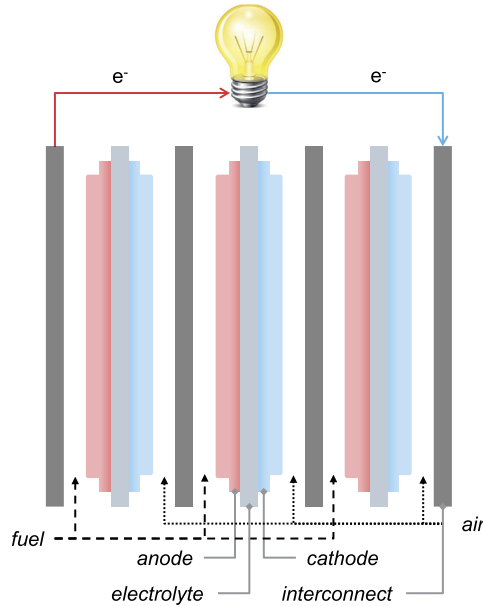


Figure 3.3 Fuel cells connected in series to form a stack. It can be seen that while the cells are electronically connected in series, they are usually in parallel with respect to fuel and air flow.

3.3. Fuel cell characteristics

The various types of fuel cells introduced in Section 3.2.2 have distinctively different physical characteristics. Among the vast amount of different types, the LT-PEMFC, HT-PEMFC and SOFC are generally regarded as most promising for maritime applications [6]. Therefore, the physical characteristics are described in more detail in this section.

3.3.1 LT-PEMFC

The LT-PEMFC is well-known for its application in many motive types including cars, buses, trucks, trains, airplanes and ships. It relies on a solid polymer-acid membrane, typically perfluorsulfonic acid (PFSA) which conducts protons when wetted. The need for a hydrated membrane implies that this type of fuel cell has to be operated below the boiling point of water. LT-PEMFCs typically operate above 65 °C to prevent flooding by condensed product water, but below 85 °C to prevent dehydration and subsequent degradation of the polymer membrane [7]. With few exceptions, platinum is almost exclusively used to catalyze the electrochemical reactions and achieve reasonable power densities at these low operating temperatures.

Water management is a critical aspect of LT-PEMFC operation. Dehydration of the membrane leads to a reduction in ionic conductivity, while flooding of the electrode

inhibits access of the reactants to the reaction sites. The wetting of the membrane can be sustained by the water generated in the electrochemical reaction, while excess water has to be removed. Specifically developed gas diffusion layers can facilitate transport of gaseous reactants to the reaction sites while effectively removing liquid water from the electrode pores [8]. The platinum catalyst is commonly dispersed on carbon supports at both electrodes.

The bipolar plates are another important part of the LT-PEMFC stack. They play a role in fuel and air distribution, water and heat management, separate air and fuel and conduct electric current. Bipolar plates for PEMFCs can be made from graphite, (coated) metals or composites [9]. The material choice largely determines weight, size, cost, functionality and lifetime. Metal interconnects are, for example, used in automotive applications to achieve high power densities and low cost, but have a shorter lifespan than the graphite type.

LT-PEMFC systems usually employ an air filter and air compressor to supply cathode air. The air is subsequently humidified, either internally in the stack or externally. The fuel, most commonly hydrogen, needs to be supplied at the right pressure and temperature as well. A fuel recirculation blower or ejector is often used to create a homogeneous distribution of (humid) hydrogen in the stack [10]. A small part of the fuel (<1%) will be purged to prevent contaminant build-up in the anode compartment. PEMFCs are typically liquid cooled, typically with a mixture of water and anti-freeze additives (e.g. ethylene glycol, diethylene glycol or propylene glycol) [11]. The system will, therefore, also contain a coolant pump and heat sink, such as a radiator. Raisin filters are installed to filter ions from the coolant which cause leakage currents in the stack. A typical LT-PEMFC layout is shown in Fig. 3.4.

LT-PEMFCs are relatively intolerant for fuel impurities. This is mainly due to their relatively low operating temperature which leads to strong adsorption of contaminants to the platina catalyst at the fuel electrodes [13]. Sulfur and carbon monoxide, both found in hydrogen produced from natural gas, are known to affect the lifetime and performance of LT-PEMFCs considerably. Carbon dioxide is reported to cause adverse effects as well, mostly via carbon monoxide formed in side reactions. Ammonia contamination leads to rapid degradation as well, as it poisons the membrane material [14].

In principle, LT-PEMFCs may operate on reformed hydrocarbon fuels and cracked ammonia, provided that the concentrations of sulfur, ammonia and carbon monoxide are all well below <1 ppm [15,16]. LT-PEMFCs equipped with fuel processing plants have been constructed and demonstrated. In practice, however, most LT-PEMFC systems are designed to use hydrogen with a high purity grade (>99.98%) to achieve a satisfactory lifetime with minimal catalyst (platina) loading.

LT-PEMFC systems have matured primarily in mobile applications, including passenger cars, material handling equipment and, more recently, busses and trains. Reduction of the size and weight of the repeating units yields high specific powers and

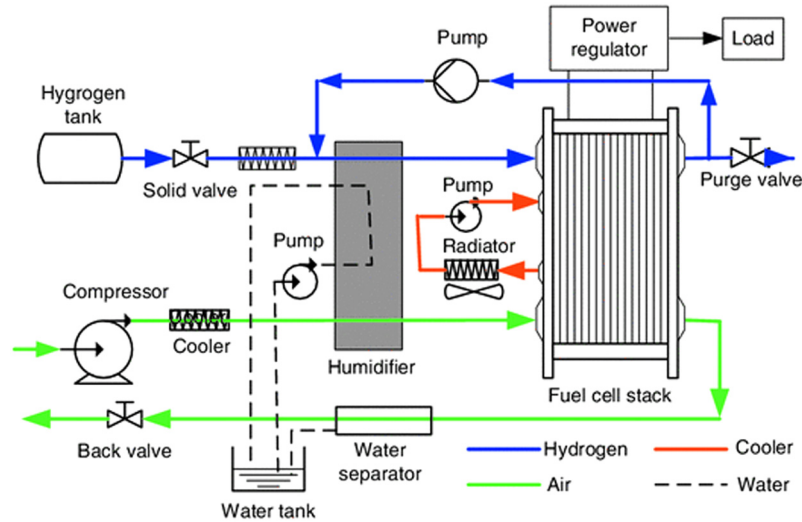


Figure 3.4 Example of an LT-PEMFC system layout. The fuel cell stack is conditioned by the BoP which includes, among others, a fuel recirculation pump, air compressor and valves. Both fuel and air are humidified with water separated from the exhaust. Figure reproduced from [12].

power densities. In addition, the number of BoP components is low compared to other fuel cell types. Specific powers vary from 125 to 750 W/kg and power density from 50 to 400 W/L at system level. LT-PEMFC systems attain efficiencies in the range of 40–60%LHV depending on system design, operating point and state of health.

3.3.2 HT-PEMFCs

The HT-PEMFC is the result of efforts to combine a stable solid polymer membrane and operation at temperatures above the dew point of water. This avoids water management issues encountered in the low temperature counterpart. A polybenzimidazole (PBI) polymer matrix doped with phosphoric acid (H_3PO_4) is most frequently used as the electrolyte material [17]. As such, the HT-PEMFC is essentially a variant on the PAFC, but avoids the issues with the acidic liquid electrolyte in this fuel cell type. This type of fuel cell has good ionic conductivities at temperatures between 120 °C and 180 °C [18].

There are many advantages to the higher operating temperature of this type of fuel cell. The kinetics of the electrochemical hydrogen oxidation reaction are faster, while the absence of liquid water in the electrodes reduces the concentration losses. Both increase the power density of the cell. Another advantage of the elevated operating temperature is the reduces vulnerability to fuel impurities. Especially the tolerance to carbon monoxide increases due to the lower adsorption on the catalyst at higher temper-

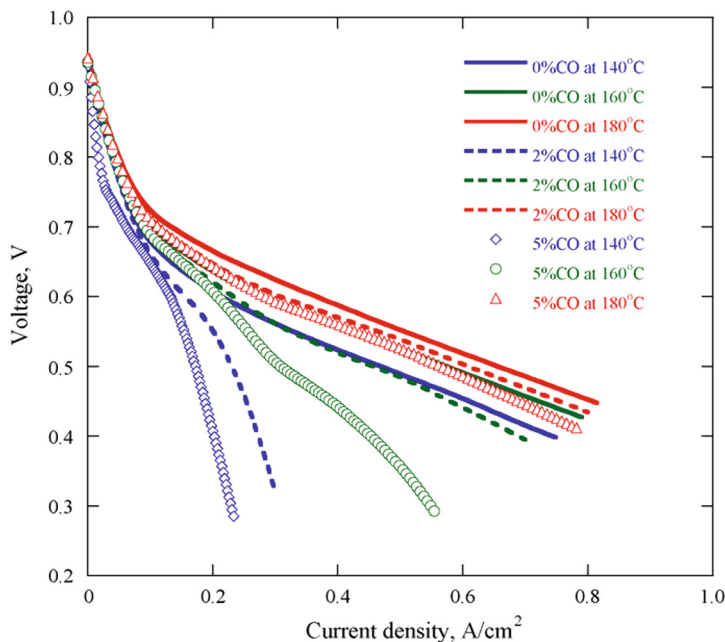


Figure 3.5 Current–voltage characteristics of a HT-PEMFC at different temperatures and CO percentage fuel stream, obtained by Das et al. [19].

atures, as can be seen in Fig. 3.5. This is particularly interesting for the use of non-pure hydrogen feeds like hydrocarbon reformates.

Platinum is still required to achieve satisfactory electrochemical performance metrics. In practice, platinum loading is often higher than for LT-PEMFCs to increase lifetimes. Achieving satisfactory lifetime is the biggest challenge for HT-PEMFCs, which is largely due to leaching of phosphoric acid from the membrane. This not only reduces the proton conductivity, but also corrodes electrodes, stack and system components [20]. Although lifetimes up to 20000 hours have been achieved in laboratory conditions, the lifetime of stack may be as low as 5000 hours in practical systems [18].

Similar to the LT-PEMFC, the MEAs are combined with gas diffusion layers, gaskets and bipolar plates. The latter separate cathode and anode compartment, provide homogeneous fuel and air distribution, remove excess heat effectively and conduct electricity. The challenge is to do so in a relatively corrosive high temperature environment, which can be achieved with surface-treated graphite [21]. A water mixture may be used to cool HT-PEMFC stacks, but this may lead to evaporation. Alternatively, thermal oils can be used to control the temperature of this type of fuel cell [22].

HT-PEMFC are usually more complicated than the low temperature version at system level, despite avoiding water management components. This is partly due to the

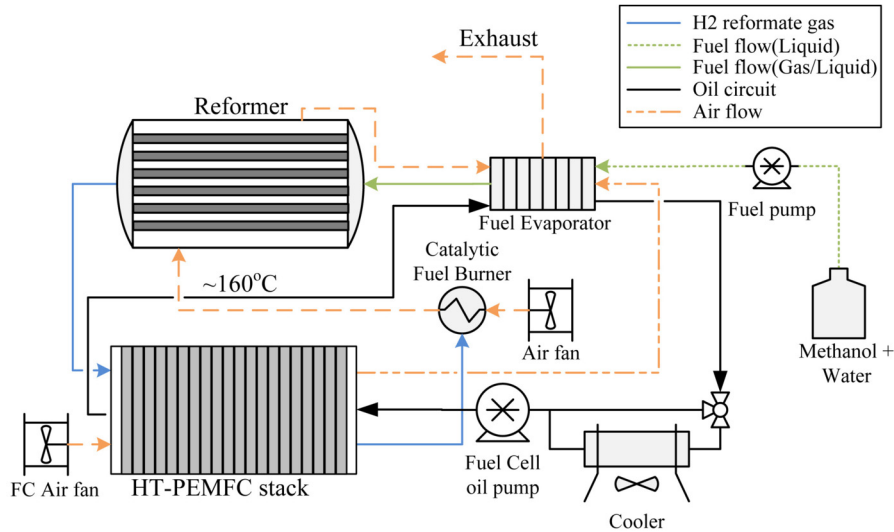


Figure 3.6 Example of a HT-PEMFC system layout with an integrated methanol reformer and fuel evaporator, obtained from Araya et al. [23].

higher operating temperature, which complicates heat management. More importantly, HT-PEMFC systems are often configured to operate on reformed fuels, for which a reformer is often incorporated in the system. A layout of such a system analyzed by Araya et al. [23] is shown in Fig. 3.6. Methanol is reformed before it is fed to the stack. Unconverted hydrogen is in turn used to fuel the burner for the reformer, enhancing heat integration in the system. Evaporators may be used as well to evaporate liquid fuels and water and heat exchangers can be employed to further increase thermal integration.

The additional fuel treatment components and insulation material lower the specific power and power density of HT-PEMFC systems. Specific powers ranging from 100 to 250 W/kg and power densities varying from 50–100 W/L may be expected. Fuel utilization is limited for reformat fuels due to the need to remove the reaction products, primarily steam and CO_2 , from the anode compartment. Combined with burning of additional fuel to generate heat required for evaporation and reforming, HT-PEMFC efficiencies are typically somewhat lower than LT-PEMFCs. A common range is 30–50%LHV depending on system design, load factor and state of health.

3.3.3 SOFC

SOFCs employ ceramic membranes which are operated at elevated temperatures. Examples of functional electrolyte materials are yttrium stabilized zirconium (YSZ), scandium stabilized zirconium (ScSZ) and gadolinium doped cerium (GDC) oxide [24]. Doping the cationic sub lattice with lower valance cations (for example replacing Z^{4+} with Y^{3+})

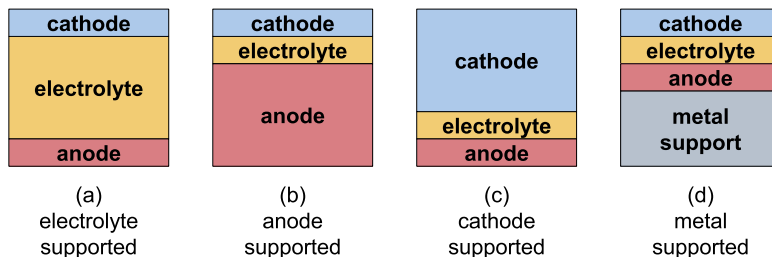


Figure 3.7 Schematic examples of (a) electrolyte, (b) anode, (c) cathode, and (d) metal supported SOFC designs.

creates oxygen vacancies due to charge neutrality. These oxygen vacancies facilitate oxide ion (O^{2-}) conductivity at high temperatures, varying from 500 °C to 1000 °C.

Good ionic conduction and fast electrochemical reaction kinetics are important advantages of the high operating temperature. Due to their high operating temperature, SOFCs can rely on non-noble hydrogen oxidation catalysts at the anode, such as nickel. Lanthanum strontium manganese is often used as the oxygen reduction catalyst at the cathode due to its low reactivity with the commonly used YSZ electrolyte. Perovskites, such as lanthanum strontium cobalt ferrite, are used at the low temperature range as their mixed ionic and electronic conductivity increase the electrochemically active area [25].

SOFC electrodes are usually porous structure made of both ceramic electrolyte material and metal catalyst. These so-called *cermet* electrodes increase the interface between the oxygen conducting ceramic, current conducting metal and gas channel, referred to as triple phase boundary. A large triple phase boundary length facilitates high current densities. Cermet electrodes also improve the thermal expansion coefficient match of different active layers, lowering thermal stresses at the electrode–electrolyte interfaces [24].

Many cell designs have been developed over the years. An important distinction can be made between tubular and planar designs. The tubular design is robust and there are fewer edges that need to be sealed. The planar design, exclusively used in other fuel cell types, offers higher power density, less thermal stress and is more easily manufactured [26]. Planar designs can have co, counter and cross flow configurations for the internal fuel and air flows. Counter flow results in a higher stack temperatures, thus improving stack performance, but co flow leads to lower internal temperature gradients [27]. Cross flow essentially combines both aspects and enables easier manifold design for air and fuel [28].

Another distinction is made in the mechanically supporting layer. Originally, thin fuel and air electrodes were supported by a thick electrolyte. A relatively high operating temperature is usually necessary in this design to achieve high ionic conductivity and, therefore, high power densities. Alternatives have been developed to reduce the thick-

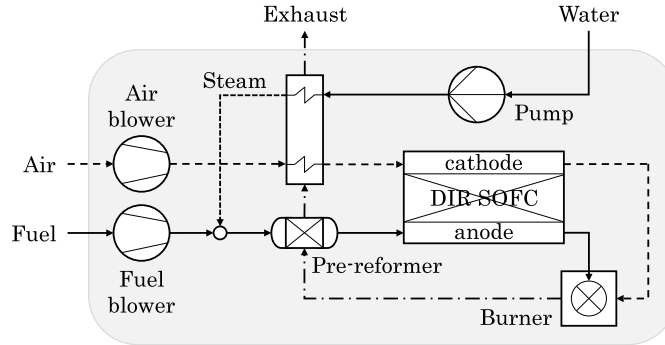


Figure 3.8 A simplified layout of a typical SOFC system fueled with hydrocarbons. The fuel is pre-reformed before it enters the stack. Hot gases from the off-gas burner are used to heat the pre-reformer, air pre-heater and evaporate steam for the reformer. Water may be condensed out of the cooled exhaust gas [37].

ness of the electrolyte material, while ensuring structural integrity. The anode supported design employs a thick, porous anode a thin electrolyte and cathode on top [29]. In addition, metal supported cells have been developed where thin active layers are deposited on a porous metal substrate [30]. Together with new bi-layered electrolytes, where the properties of two electrolyte materials are combined in a double layer structure, these developments have reduced the operating temperature of SOFCs from around 1000 °C to as low as 500 °C. Fig. 3.7 provides an overview of different SOFC support structures.

SOFC interconnect (or bipolar plate) selection is especially challenging due to the highly corrosive, high temperature environment in the stack. The highest operating temperatures require ceramic materials such as lanthanum chromite, but reduction of the operation temperatures has enabled the introduction of alloys such as chromia-forming ferritic stainless steels [31]. Although chromia protects the interconnects from oxidation, coatings are necessary to prevent Cr from vaporizing and degrading the electrodes [32]. Similar to PEMFCs, the interconnects fulfill a variety of function in the stack, including fuel and air distribution.

The high operating temperature of SOFCs results in a relatively large BoP. Thermal integration and insulation is a key aspect of SOFC system designs, which will usually incorporate heat exchangers to pre-heat fuel and air using the hot exhaust gas. This reduces the temperature gradient in the stack and helps to maintain the operating temperature. A tail gas burner or combustor is usually used to convert any remaining fuel. Similarly, a burner or heater is required to enable cold starting. In contrast to low temperature fuel cells, which are cooled with a liquid cooling medium, SOFCs are usually cooled with an excess supply of cathode air. Fig. 3.8 shows a simplified layout of a typical SOFC system fueled with a hydrocarbon fuel, such as natural gas.

Table 3.1 Overview of the main characteristics of LT-PEMFCs, HT-PEMFCs and SOFCs based on [38].

	LT-PEMFC	HT-PEMFC	SOFC
Operating temperature [°C]	65–85	140–180	500–1000
Electrical efficiency [%LHV]	40–60	40–50	50–65
Hydrogen purity	>99.98% H ₂	<3% CO	<20 ppm S
Cooling medium	Water mixture	Thermal oil	Air
Specific power [W/kg]	125–750	25–150	20–80
Power density [W/L]	50–400	10–100	10–40
Stack life time [kh]	5–35	5–20	20–90
Start-up time(cold)	≤10 seconds	10–60 minutes	>30 minutes
Load transients [idle-rated]	<10 seconds	<5 minutes	<60 minutes
Capital cost 2021 [\$/kW]	1000–2500	3000–5000	3500–8000
Capital cost 2030 [\$/kW]	60–600	150–1500	500–2000

A key advantage of the elevated operating temperature of SOFCs is their higher tolerance to fuel impurities. Carbon monoxide can be directly oxidized or converted to hydrogen via the water gas shift reaction [33]. Ammonia and light hydrocarbons, such as methane, can be internally decomposed to hydrogen rich mixtures on the anode [34, 35]. Nonetheless, an external pre-reformer is typically used to avoid cold spots induced by the endothermic reforming reaction and avoid the formation of carbon deposits on the fuel electrode [36]. Fig. 3.8 shows a layout of a SOFC system.

The specific power of state-of-the art SOFC systems is low compared to other fuel cell types. Large stationary systems using natural gas or biogas nowadays attain about 20 W/kg and 10 W/L. However, these figures may change drastically if the system is designed for transport applications instead. Promising improvements in stack and system design reveal the potential to achieve a specific power of at least 80 W/kg and power density of 40 W/L. Although these figures are still low compared to most conventional power systems, SOFCs make up with record high fuel efficiencies in the range of 50–65%LHV. Higher efficiencies would in turn reduce fuel consumption and required tank size, and subsequently their associated costs.

3.3.4 Overview

Table 3.1 presents an overview of the most important physical characteristics of the three fuel cell types discussed in this section: LT-PEMFCs, HT-PEMFCs and SOFCs. The LT-PEMFC has clear advantages over their counterparts operating at higher temperatures in terms of specific power, power density, start-up and transients. However, they are usually restricted to the use of pure hydrogen.

SOFCs achieve the highest efficiencies and are most flexible in terms of fuel choice. However, SOFC systems are currently still large and heavy and load transients take a substantial amount of time. HT-PEMFCs combine some of the advantages of the LT-

PEMFC in terms of power density and fuel flexibility. However, efficiencies are typically not as high as SOFCs and meeting the lifetime required for maritime application at system level remains a challenge.

3.4. Fuel processing & treatment

Fuel quality is an essential aspect for performance, reliability and lifetime, since fuel cells are delicate electrochemical devices. Some fuels, especially hydrogen, can be used in most fuel cell systems without extensive pre-treatment steps. Other fuels, for instance hydrocarbons, may require extensive processing before they can be electrochemically oxidized. The extent of the fuel treatment plant depends primarily on:

- Fuel type
- Fuel cell type
- Origin or feedstock
- System requirements

The fuel requirements of different fuel cell types were discussed in Section 3.3. Low temperature PEMFCs are typically fueled with high purity hydrogen, while high temperature SOFCs may reform light hydrocarbons internally. Nonetheless, pre-reformers are commonly used in SOFCs to prevent excessive thermal stresses in the stack, as high endothermic reforming rates may lead to low local temperatures in the inlet section [39]. Even if pure hydrogen is used as a fuel, it may need to be pre-heated and/or humidified. In addition, hydrogen produced from fossil or biomass feedstock may contain contaminants that need to be removed. Commonly applied processing equipment can be subdivided in the following steps:

- Conversion: processing fuel to a hydrogen rich mixture;
- CO removal: lowering the CO content and maximize hydrogen yield;
- Purification: necessary if hydrogen with a high purity is required;
- Other: includes equipment such as humidifiers, evaporators, burners and desulphurization (DeS).

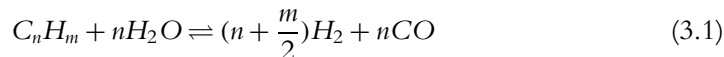
This section gives an overview of these fuel processing steps.

3.4.1 Conversion

Many fuels, such as hydrocarbons, alcohols, ethers and ammonia contain hydrogen and can thus essentially be regarded as a hydrogen carrier. These can be converted to a hydrogen-rich mixture through a chemical reaction, such as reforming and cracking. The reforming reaction converts a hydrocarbon fuel to a hydrogen rich mixture using a reforming agent. Different reforming reactions, including steam or wet reforming, carbon dioxide or dry reforming and catalytic partial oxidation as well as the ammonia decomposition are discussed in this section.

3.4.1.1 Reforming

Steam reforming is a widely used in industry to produce hydrogen from hydrocarbon feedstock. The hydrocarbons react with steam in an endothermic equilibrium reaction, producing hydrogen and CO:

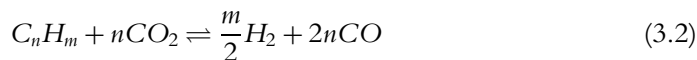


The advantage of steam reforming over most alternatives is that additional hydrogen is released from the steam molecule, while the carbon reacts with oxygen to form carbon monoxide and carbon dioxide. Therefore, the steam reforming reaction has a high hydrogen yield, while the formation of solid carbon is avoided. Steam reforming takes place at elevated temperatures, ranging from as low as 200 °C for methanol up to 1000 °C for methane as well as a catalyst, often nickel-based [40–42].

Heat and steam need to be supplied from an external source in allothermal steam reformers. Both may be recovered from an off-gas burner or high temperature fuel cell, but in other cases this will generally consume auxiliary fuel or power, decreasing the overall efficiency. Adiabatic reformers use the heat available in the fuel stream to reform the fuel. However, this implies that the fuel stream needs to be heated, while the fuel conversion rates are typically low compared to allothermal reformers. High temperature fuel cells enable higher overall system efficiencies through better heat integration with fuel reformers. The waste heat produced by HT-PEMFCs is sufficiently high to evaporate water, especially if some of the unused anode exhaust gas is combusted in a burner.

SOFCs enable a high level of heat integration, as the operating temperature is sufficiently high to sustain reforming reactions [35]. Firstly, the high temperature anode exhaust gas of SOFCs contains large amounts of steam and small amounts of unused fuel. Therefore, anode off-gas recirculation (AOGR) may be employed to improve heat integration in the system [43,44]. Secondly, high temperature flue gas from the afterburner may be used to heat allothermal reformers. Lastly, the reforming reaction may proceed directly at the fuel electrode using the heat and steam produced by the electrochemical reactions. The endothermic reforming provides cooling to an internal reforming stack, thus reducing the need to cool with cathode air and further enhancing system efficiency [45]. Fig. 3.9 shows the synergistic coupling of an SOFC with a pre-reformer.

In dry reforming carbon dioxide is used as a reforming agent instead of steam:



This type of reforming is strongly endothermic and particularly attractive for fuel types that contain relatively large amounts of carbon dioxide, which is sometimes the

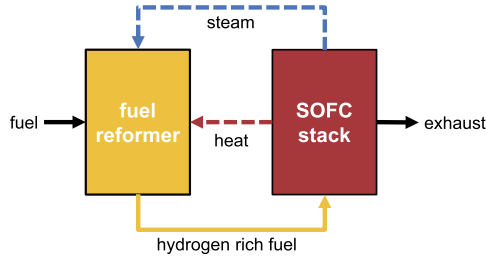


Figure 3.9 Visualization of the synergistic coupling of heat and steam produced in SOFCs with an external steam reformer.

case in biomass gasification and fermentation. Although water management issues are omitted, the high carbon content may lead to the formation of solid carbon on the reforming catalyst. This may occur in an external reformer, but is a notoriously harmful side reaction that might take place on SOFC anodes as well [36].

3.4.1.2 Partial oxidation

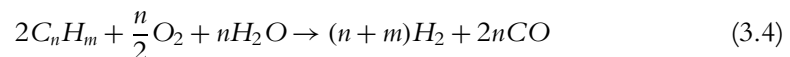
In catalytic partial oxidation (CPOX) oxygen is effectively used as a reforming agent. A part of the fuel is oxidized and the steam and carbon dioxide formed subsequently reform the remaining fuel:



Different from steam reforming, partial oxidation is exothermic and does not require an external heat source nor does it need a supply of steam or carbon dioxide [46]. This is an advantage if no high temperature source of waste heat is available, as it largely simplifies the system. It is also reported that catalytic partial oxidation is inherently easier to control, which can be achieved by modulating the streams of fuel and air [47]. CPOX is occasionally used as start-up mode for steam reformers as well.

3.4.1.3 Autothermal reforming

The efficiency of fuel cell systems with CPOX reformers is typically low compared to those with steam reformers, as a part of the fuel is oxidized in the process. Autothermal reformers address this issue by effectively combining CPOX with steam reforming, such that the exothermic reaction heat from the oxidation matches the endothermic reaction heat of the steam reformer. Therefore, autothermal reformers enable rapid start-up, load modulation and ease of control while mitigating the low efficiency of the CPOX option [48,49].



3.4.1.4 Ammonia decomposition

Ammonia can be synthesized from hydrogen and nitrogen in the Haber-Bosch process which is applied on industrial scale in the fertilizer industry [50]. Recently, ammonia is increasingly attracting interest as a promising hydrogen carrier, being much easier to store and distribute than hydrogen itself due to its liquid form at near-environmental conditions. Hydrogen can be released in a decomposition reactor, also referred to as an ammonia cracker.

Ammonia decomposition or cracking is an endothermic reaction that usually takes place at temperatures above 350 °C in the presence of a catalyst:



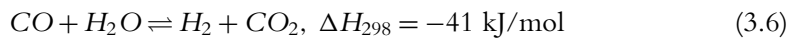
Temperatures in excess of 600 °C are required for full ammonia conversion [51]. Common catalyst materials are ruthenium- and nickel-based. The reaction may, therefore, proceed directly on SOFC anodes as well. On the other hand, this may lead to increased degradation and thermal management challenges [34].

3.4.2 CO removal

High temperature fuel cells can tolerate a substantial amount of CO in the fuel stream, or even use it as fuel. However, even trace amounts can increase degradation significantly in low temperature PEMFCs. The CO content thus needs to be largely reduced or eliminated prior to the fuel cell if reformed hydrocarbon fuels are to be used in low temperature fuel cell systems. This is commonly done via water gas shift (WGS) reactors, followed by either preferential oxidation (PrOx) or selective methanation (SMET).

3.4.2.1 Water gas shift

In a WGS reactor CO reacts with H₂O, which yields CO₂ and additional hydrogen:

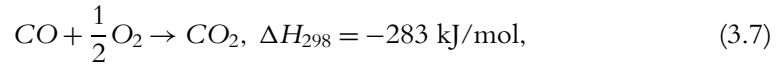


WGS usually occurs parallel in the reformer as well, since the reaction is relatively fast at elevated temperatures. However, low temperatures and steam to carbon ratios up to 3 are required to shift the reaction equilibrium towards low CO and high hydrogen yields. To avoid the necessity of large reactors due to the slower kinetics at low temperatures, a common strategy is to combine a high temperature WGS reactor operating at temperatures in excess of 350 °C followed by a low temperature reactor below 250 °C [52,53].

3.4.2.2 Preferential oxidation

The CO concentrations after low temperature WGS are sufficiently low for HT-PEMFCs, but further reduction of CO concentrations is necessary for LT-PEMFCs.

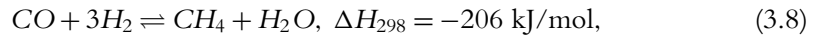
The PrOx reaction



can reduce the CO content in the fuel stream further. The reaction takes place slightly above LT-PEMFC operating temperatures, ranging from 80 °C to 200 °C, in the presence of a catalyst [54,55]. Unfortunately, hydrogen oxidation is an unavoidable side reaction, thus lowering the system efficiency. In addition, a noble catalyst is usually required at low operating temperatures.

3.4.2.3 Selective methanation

SMET is a somewhat unconventional method that can be used to remove trace amounts of CO from the fuel stream. The SMET reaction



yields methane, which is effectively inert in low temperature fuel cells. The exothermic reaction can take place at relatively moderate temperatures between 250 °C and 350 °C, where the equilibrium of the methane steam reforming reaction reverses [56,57]. An appropriate catalyst needs to be selected to avoid the undesired methanation of CO₂, which compromises the hydrogen yield from the reactor. Although this process effectively converts some of the hydrogen produced into methane, it avoids oxidizing a part of the fuel.

SMET may be especially advantageous if the tail gases are further utilized in the system, for example when burning them to generate heat for a reformer [58]. In addition, it avoids the need of external process air thus simplifying system design, thermal management and control [59].

3.4.3 Purification

Even if the contaminant concentrations in the fuel stream are sufficiently low to avoid poisoning of the fuel cell membrane, hydrogen purification may be desired or even necessary to obtain fuel quality within the manufacturer specification. For instance, most LT-PEMFC system developers tailor their products to pure hydrogen, as it allows high fuel conversion in the system and avoids complicated fuel handling. Moreover, even CO₂ can accelerate degradation in low temperature fuel cell systems through local production of CO. Trace amounts of contaminants are subsequently disposed by purging a small percentage of the recirculated fuel gas. Common hydrogen purification methods include adsorption and membrane separation technologies.

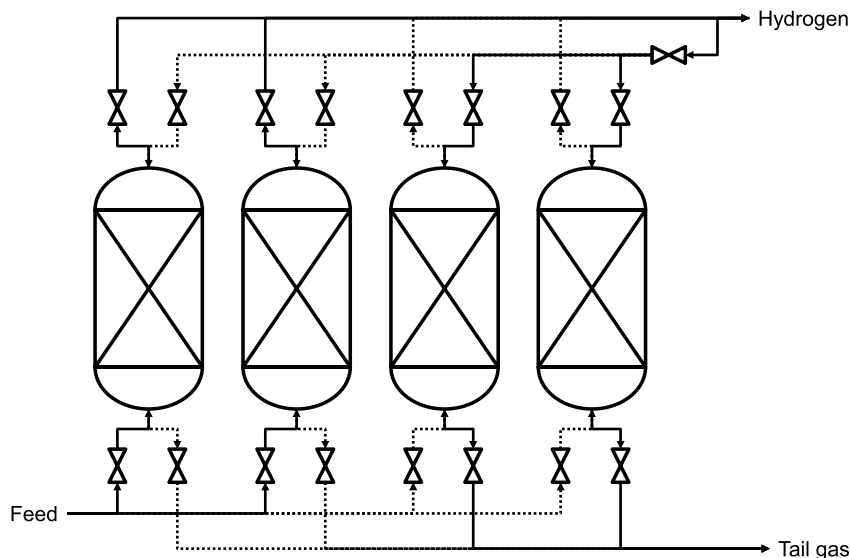


Figure 3.10 A simplified layout of a PSA process, with the two vessels on the left actively adsorbing impurities, generating pure hydrogen, and the two vessels on the right regenerating, producing tail gas.

3.4.3.1 Pressure swing adsorption

Pressure swing adsorption (PSA) is currently the industrial standard to purify a hydrogen stream, commonly produced from reforming or gasification [60]. The process relies on the stronger adsorption behavior of heavier molecules compared to hydrogen and the pressure dependency of the adsorption equilibrium. The process gas is passed over a sorbent material at an elevated pressure, yielding a relatively pure hydrogen flow at the outlet [61].

The process can be subsequently reversed by depressurizing the sorbent to regenerate it, leaving a tail gas that typically contains 15–30% of the hydrogen. Two PSA vessels are usually placed in parallel to enable simultaneous absorption and regeneration, as shown in Fig. 3.10. PSA vessels can be added in series to increase the purity of the product. Adding stages will increase the hydrogen content in the tail gas, thus a trade-off exists between product quality and overall hydrogen yield.

3.4.3.2 Temperature swing adsorption

Although less commonly applied in industrial processes, temperature swing adsorption (TSA) relies on the same principle of PSA. However, a temperature difference rather than a pressure difference is exploited to generate and regenerate the sorbent material, making use of the temperature dependency of the adsorption process [62].

TSA involves heating and cooling of the sorbent material rather than pressurization, which may reduce the parasitic power consumption of the purification system provided that a heat source is available. However, changing between modes is time consuming as the entire sorbent bed needs to be heated or cooled. Similar to PSA, the specific hydrogen production capacity of this hydrogen purification method is relatively low.

3.4.3.3 Membrane separation

While the adsorption-based hydrogen purification methods use the thermodynamic properties of the fuel to separate hydrogen from the product stream, membrane separation makes use of the different permeability of various materials for different molecules. The separation mechanism may rely on Kundsens diffusion, surface diffusion, capillary condensation, molecular sieving or solution diffusion. Therefore, a large variety of membrane materials exist, including metallic, silica, zeolite, carbon-based and polymers [63].

Despite continuous advancements in the development of new membrane materials, Pd-based membranes are till date still most commonly applied [64]. These membranes offer a high selectivity towards hydrogen diffusion and, hence, a high purity product stream. Unfortunately, the product-specific weight and cost of these membranes remain high. In addition, hydrogen embrittlement is an inherent challenge for metallic hydrogen separation membranes. Therefore, researchers are exploring new amorphous and nanocrystalline alloys.

Silica-based membranes hold great potential due to their low cost, ease of production and scalability [65]. Moreover, they are chemically, mechanically and thermally stable. Zeolite membranes can offer an interesting alternative for high temperature separation. Both inorganic and carbon-based membranes are being investigated, but are currently associated with high production cost. Polymer membranes show promising results, but their selectivity and chemical stability are points of concerns [66].

3.4.3.4 Electrochemical membrane separation

Protonic fuel cells can function as hydrogen separation devices themselves, as their primary functional characteristic is to conduct protons exclusively, blocking the transport of other constituents in the fuel. Therefore, the membranes employed in fuel cells may be applied as hydrogen separation membranes themselves [67].

Mild driving potentials are sufficient to yield a relatively pure product gas. The applied potential may be a voltage or a pressure difference [68]. Hydrogen can be simultaneously separated and compressed by applying a higher driving potential. This method provides an interesting hydrogen separation option if a hydrogen buffer tank is present, but it consumes electric power which adds to the auxiliary losses in the system. However, it should be noted that the purification methods described above rely on pressurizing gas flows or sorbent beds, both of which consume parasitic power as well.

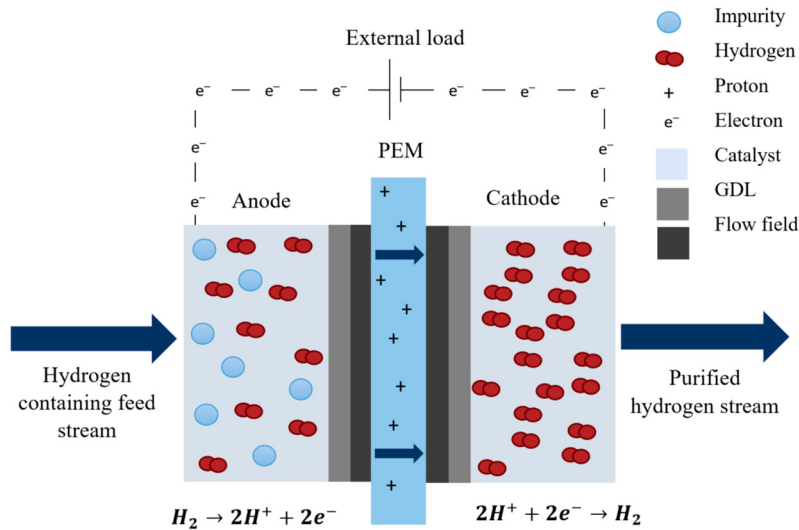


Figure 3.11 Working principle of electrochemical hydrogen separation and compression. Obtained from Vermaak et al. [69].

The polymer electrolyte electrochemical membrane is most commonly considered as a hydrogen separation membrane [69]. An example of this separation process is shown in Fig. 3.11. High proton densities can be attained at moderate conditions and the membranes are mechanically stable. Chemical stability remains a challenge, for example if the process gas stream contains CO as it interacts with the electrodes. Moreover, noble catalysts are still necessary to achieve high specific production rates, leading to high capital cost [70].

More recently, researchers started exploring the ceramic materials that conduct protons at high temperatures, such as BaZrO₃-based [71]. This class of materials is chemically stable and less prone to poisoning. Their ability to operate at high temperature enables direct integration in the reforming process, which also helps to increase hydrogen yield from the reformer, as the equilibrium is shifted. The use of non-noble catalyst materials reduces the specific cost, but the brittle ceramic materials introduce their own specific challenges related to thermal shocks and cycling.

3.4.4 Overview

The fuel processing steps described in the preceding section are finally integrated with the fuel cell system of choice. Fig. 3.12 provides an overview of the various fuel processing steps at their respective typical operating temperature. Therefore, heat integration opportunities can be easily identified from the graph.

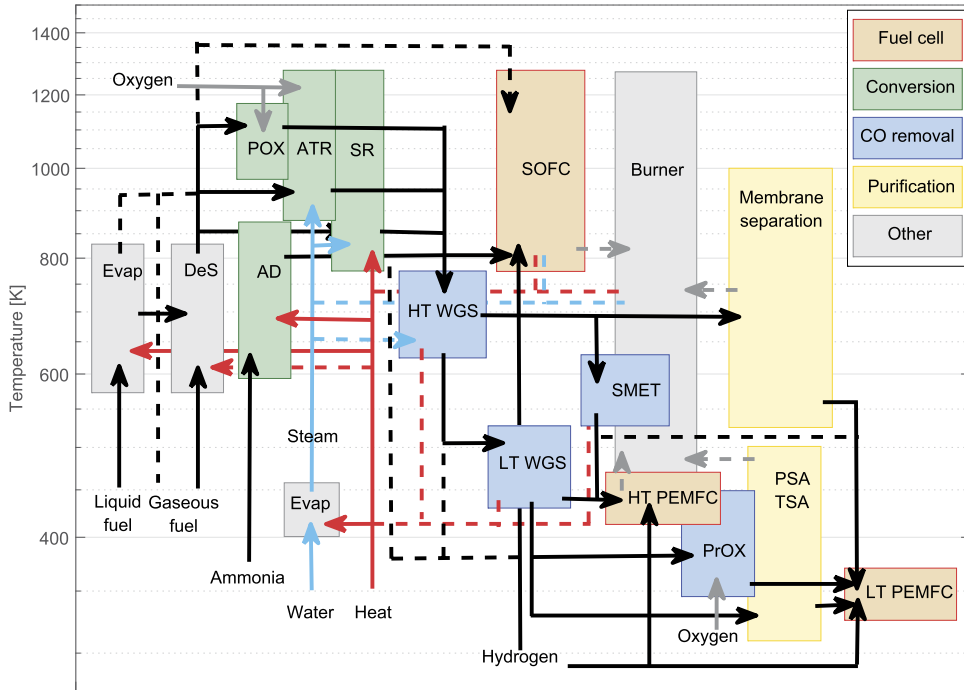


Figure 3.12 Overview of on-board fuel processing steps in fuel cell systems, with indication of their operational temperature. The solid black lines indicate the common process flow direction, while the dashed lines are optional. Other solid lines represent flows of heat, steam and oxygen. Off-gas streams are shown as dotted lines. This figure is an expansion on its original published in [72].

Solid black lines mark a typical fuel processing sequence, for example starting from evaporating a liquid fuel, via desulfurization (DeS), steam reforming, high and low temperature WGS to a HT-PEMFC. The dotted black lines indicated additional (bypass) options that might be considered. The blue lines (light gray in print version) indicate (optional) water/steam supply, and the red lines (dark gray in print version) opportunities for heat integration. Furthermore, different fuel processing stages are indicated by a variety of colors. Auxiliary components like evaporators and burners are indicated in gray.

Fig. 3.12 shows that a substantial amount of fuel processing steps is required to convert conventional ship fuels to a mixture suitable for low temperature fuel cells. It also shows that efficiency may be enhanced through fuel processing equipment selection and integration. An example is the use of retentate from the fuel purification processes to generate heat and steam. The overview reveals that, unless pure hydrogen is available, fuel processing is significantly less complicated for SOFCs. Moreover, high temperature heat and steam produced by the SOFC may be used to evaporate and (pre-)reform hydrocarbons or decompose ammonia.

3.5. Fuel cell operation

The load characteristics of fuel cells differ from internal combustion engines, mostly due to the electrochemical nature of energy conversion. This affects efficiencies, part-load performance, load transients, system start-up and heat recovery possibilities, which are subsequently discussed in this section.

3.5.1 Electrical efficiency

Fuel cells can ultimately attain the same ideal efficiencies as an ideal heat cycle [4]. However, efficiencies may be higher in practice due to the different working principles. The efficiency of a fuel cell is primarily affected by three parameters: operating voltage, fuel utilization and BoP losses [73]. The theoretical efficiency that can be attained by an electrochemical process is determined by the Gibbs energy, which defines the non-expansion work that can be obtained:

$$\eta_{rev} = \frac{\Delta \bar{g}_f}{\Delta \bar{h}_f} \quad (3.9)$$

The efficiency will be lower in practice due to a number of losses. First of all, the operating voltage will generally be lower than the reversible voltage due to internal losses and irreversibilities. In addition, the fuel conversion or fuel utilization is usually less than 100% to prevent fuel starvation and purge inert component and contaminants from the anode compartment. Finally, the power consumption of auxiliary components such as blowers and pumps can be substantial and power conditioning equipment introduces losses, for example inverters.

Fig. 3.13 shows a simplified load curve of a fuel cell system. The no-load voltage without load is usually referred to as the open circuit voltage (OCV). The actual operating voltage will decline as the current density increases due to several internal losses. These losses are generally referred to:

- activation losses
- ohmic losses
- concentration losses.

Activation losses originate from the polarization potential needed to drive the electrochemical reaction. Ohmic losses are a result of the resistance of electrodes and electrolyte, and concentration losses are attributed to mass transfer limitations at high current densities. Once these losses are accounted for, a voltage efficiency may be defined as

$$\eta_{voltage} = \frac{V_{cell}}{E^0}, \quad (3.10)$$

with E^0 being the theoretical reversible fuel cell potential, calculated from:

$$E^0 = \frac{\Delta \bar{g}_f}{nF} \quad (3.11)$$

Here n is the number of electrons involved in the electrochemical reaction (i.e. 2 for hydrogen) and F is the Faraday constant.

The temperature and concentrations of reactants and products vary from inlet to outlet. Therefore, the actual electrochemical process is a heterogeneous reaction in which a variety of intermediate steps contribute to voltage losses simultaneously, at various reaction sites. Moreover, different processes may dominate at different locations in the cell. Ohmic losses, for example, depend on the electrode and electrolyte thicknesses, while activation losses are affected by the catalyst surface and temperature. The concentration losses typically dominate in areas with high local reaction rates. As a result, the current density will vary locally and detailed spatial models are required to capture the individual contributions of different voltage losses accurately. However, the behavior may in many cases be treated linear in specific parts of the operating window. If that is the case, the characteristics mimic ohmic behavior and can be approximated using a so-called area specific resistance (ASR) [74]:

$$V_{cell} = V_{OCV} - I \cdot ASR \quad (3.12)$$

The ASR accounts for all the internal losses in the cells and stacks, which should be quantified in experiments for various conditions of interests. The ASR will change if the operational conditions are changed, and may thus need to be mapped for the entire operating window to accurately predict the electrochemical performance.

Although all fuel may be consumed in theory, fuel utilization is typically less than unity in practical operation. One of the reasons is that contaminants, reaction products and inert gases built up in the anode compartment unless part of the fuel is purged. The fraction of fuel that is effectively oxidized in a fuel cell is referred to as fuel utilization, denoted as u_f . The stack efficiency can be subsequently calculated from:

$$\eta_{stack} = \eta_{rev} \cdot \eta_{voltage} \cdot u_f \quad (3.13)$$

Maximizing fuel utilization is thus important in order to achieve high electrical efficiencies. However, there is a limitation especially in case the reaction product is formed at the fuel electrode, which is the case in fuel types that rely on anion exchanging electrolytes, such as SOFCs [75]. Excessive steam concentrations reduce the reversible voltage and can cause electrode oxidation. In addition, anode off-gas purging is indispensable in case impure hydrogen is used, for example fuel reformates. In this case, products from the reforming reaction will accumulate in the anode compartment and

need to be removed. Even if pure hydrogen is used as a fuel, more homogeneous conditions are achieved across cells and stacks when fuel and air are supplied in excess, particularly in the outlet section.

The system efficiency is obtained by accounting for the parasitic consumption of the BoP components, P_{aux} . For example, electric losses are induced by air compressors, coolant pumps, ventilation blowers, sensors, electrically operated actuators and control systems. Additional fuel is consumed in some systems by burners to generate heat for preheating and fuel conversion. The overall system efficiency thus follows from:

$$\eta_{system} = \frac{P_{stack} - P_{aux}}{P_{stack}} \cdot \eta_{stack} \quad (3.14)$$

The extent of the auxiliary losses varies depending on the fuel cell type and BoP components. For example, a fuel reformer may contribute significantly to the fuel consumption of a low temperature fuel cell system, while the air compressor is often a large consumer in SOFC systems.

3.5.2 Part load performance

Fuel cells systems typically have relatively good efficiencies in part load. In fact, the electrochemical losses generally decrease when the operating current is reduced, thus improving stack efficiency (see Eq. (3.12) and (3.13)). Consequently, the system efficiency usually increases with stack efficiency when the load is reduced. However, the relative contribution of the BoP losses will increase as the load is reduced, eventually leading to lower efficiencies. As a result, fuel cell system efficiencies drop when operated at small load fractions.

Fig. 3.13 shows a typical fuel cell system load curve. While the stack efficiency increases as the load is decreased, the relatively high power consumption of the BoP nullifies this efficiency increase just below 50% load in this specific example. The efficiency starts to drop quickly if the load is further reduced. In addition, fuel cell stacks are usually more difficult to condition properly at low loads. For example, minimal fuel and air flows are required to prevent local starvation and cannot be chosen at optimal values. This further reduces system efficiency, but may also reduce the lifetime or even damage the stack. Therefore, fuel cell manufacturers specify minimum load fractions to ensure reliable operation and guaranteed lifetime. Minimum loads ranging from 10% to 30% of rated power are not uncommon. This limit should be accounted for when designing the system.

3.5.3 Load transients and start-up

Although more critical in high-demanding applications such as dredgers and naval vessels compared to merchant ships, the ability to handle transient loads is an important

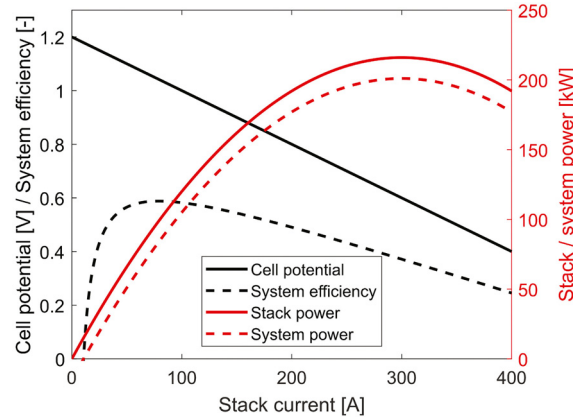


Figure 3.13 Simplified operational characteristics of an arbitrary 200 kW fuel cell system. The cell potential reduces for higher loads, while stack and system power increase until a maximum is reached. The system efficiency peaks just below 50% of the rated power.

requirement for ships. The same holds for start/stop cycling, which occur frequently for specific types of vessels and thus need to be acceptably fast. In contrast, a part of the power plant is operating more or less uninterrupted in other vessel classes.

The time scales associated with the electrochemical reactions are small, thus enabling close to instant load response. However, load response is limited in practice by the inertia of heat, mass and momentum both in the stack and BoP components. Changing the power usually implies that the supply of fuel, air and coolant to the stack have to be adjusted, which is taken care of by pumps and blowers. Their response times and inertia lead to time delays for a new stable flow values to be reached. Changing these flows affects heat and mass transfer in heat exchangers, reformers and humidifiers, in turn adding to the delayed response time of the BoP [76].

The thermal, mass and momentum inertia can introduce significant time delays. Therefore, it takes time to reach a new stable operating point, especially if the set points of auxiliary equipment are adjusted through simple feedback control. There is a substantial risk that the stack operating conditions exceed acceptable limits during load transients, for example inducing fuel starvation, overheating or thermal stresses. Load transient limitations are thus usually specified by the system manufacturer to prevent detrimental operating conditions.

Low temperature PEMFCs are mostly constrained by the time it takes to supply reactants to the stack [77]. Load transients can therefore be performed in a couple of seconds. However, it may take substantially longer to reach a new stable operating point in their high temperature counterpart as the thermal inertia in the BoP increases. Fuel conversion equipment typically adds to the response time, such that large load steps of HT-PEMFCs equipped with reformers may take minutes [78].

Being mostly applied in grid-connected stationary power generation, even small load transients can typically take up to several minutes for SOFC systems [79]. Rapid adjustment of thermal management is compromised by the large thermal inertia due to the high operating temperature. SOFC systems typically use air as the cooling medium, which has a low heat capacity and is often heated as much as 100 °C. In contrast, the liquid cooling medium in low temperature fuel cells is usually not heated by more than 10 °C. As a result, even small load changes can result in thermal stresses and overloading of SOFCs. This dictates slow load transients to allow for the feedback controllers to react, although sophisticated control strategies may improve transient capabilities [80].

Similar to load transients, system start-up of low temperature fuel cells is fast compared to their high temperature counterparts. In principle, LT-PEMFCs may deliver useful work already at ambient conditions, while a large thermal mass needs to be heated to relatively high temperatures before any current can be drawn from an SOFC. Consequently, LT-PEMFCs start-up takes a couple of seconds, while it can take up to several hours to heat a large stationary SOFC plant to its operating temperature [81].

Shut-down procedures can be complicated at a system level, as proper conditions need to be maintained in the sensitive fuel cell components while the balance of plant components is switched off. However, load removal is usually not restricted at stack level and can be achieved in seconds if needed.

3.5.4 Heat recovery & combined cycles

High temperature fuel cells can attain very high efficiencies in combined heat and power (CHP) applications. A part of the heat generated in the electrochemical oxidation reaction is recovered from these systems and used to supply heat. This is similar to the waste heat recovery system applied with diesel engines already. Heat may be recovered from any fuel cell system operated at elevated temperatures, such as the HT-PEMFC, which becomes increasingly interesting as the operating temperature increases. For example, combined efficiencies up to 90% have been achieved on CHP products based on high temperature SOFC technology [82].

Integration may be further optimized through the use of so-called trigeneration systems providing power, heating and cooling. Such systems harness additional cooling cycles such as vapor compression or adsorption refrigeration. Especially adsorption refrigeration offers the potential to reach high overall efficiencies as it utilizes high temperature heat to generate a cooling effect [83].

CHP is particularly interesting for ships with large heating, ventilation and air conditioning requirements, such as cruise ships and vessels transporting cooled or heated cargo [84]. However, the majority of ships may prefer high power generation efficiency over heat integration. Waste heat recovery cycles and combined cycles offer interesting opportunities for these ships, enabling even higher electrical efficiencies [85]. This may

potentially enable higher specific power and lower specific investment as well, at the cost of added complexity.

SOFC integration with gas turbines has been a research topic for decades as it offers a synergetic coupling of the cathode air flow as the gas turbine working medium. This enables effective use of the high temperature heat from the fuel cell exhaust to drive the cathode compressor and generate additional useful work. In a direct coupling configuration the SOFC will be pressurized as well, increasing the power density at stack level [86]. However, the stack usually needs to be contained in a pressure vessel due to limited allowable pressure differences. Proof of concepts SOFC–gas turbine systems have been developed by various manufactures, most recently Mitsubishi. Their 210 kW_e demonstration units MEGAMIE are reported to achieve an electrical efficiency of 53%LHV, with the gas turbine contributing to about 10% of total system output [87].

Alternatively more conventional waste heat recovery power generation systems can be used, such as (organic) Rankine cycles, supercritical Rankine cycles, Kalina cycles, Stirling cycles, closed Brayton cycles and thermo-electric generators. Such systems have been demonstrated on marine diesel engines as well, but cope with low specific power and high specific cost [88]. However, high (renewable) fuel prices may enable a decent return on investment. The reader is referred to Chapter 9 of this book for more elaborate reading on this topic.

More recently, researchers have proposed to use any unconverted fuel from the fuel cells in a reciprocating combustion engine [89]. An immediate advantage is that conventional marine engine technology can be adopted in this configuration. The off-gas from the fuel cell may also be used to enrich fresh fuel to improve combustion properties, thus offering a large degree of freedom in selecting the respective fuel cell and engine powers. Similar concepts have been proposed where SOFCs are used to reform fuel which is subsequently used other fuel cells. For example, Baldi et al. [90] investigate a concept where SOFCs are combined with HT-PEMFCs for cruise ships.

3.6. Maritime application

The success of maritime fuel cell application will ultimately depend on many factors. In this section, the most important aspects of maritime application are discussed. These include the effect on ship design and operation, compliance with emission regulation, reliability, availability, maintenance, safety and economics.

3.6.1 Design and operation

Replacing reciprocating engines with fuel cells had large implications for the on-board power plant weight, size and potentially its location, which ultimately affects the design of ships powered with fuel cells. Some LT-PEMFC systems, especially those derived from automotive products, achieve higher specific powers and power densities than

most diesel engine-generators (see Table 3.1). However, these are all configured to use hydrogen with a high purity. When stored in compressed gas cylinders or cryogenic tanks, hydrogen needs substantially larger storage volumes than traditional fuel oils. This doesn't necessarily impose impossible design challenges if the ship can be refueled frequently, allowing to reduce the size of the fuel storage.

Fuels with a higher energy density may be preferred for ships that require longer autonomy [72]. Although it is in principle possible to process other fuels to high purity hydrogen prior to LT-PEMFCs, as is discussed in Section 3.4, this increases complexity and cost associated with the fuel processing plant. In addition, a significant part of the energy is usually lost in the process.

HT-PEMFCs achieve lower power densities, but omit the need for some fuel purification. This simplifies the system, reduces the size and cost of the BoP and improves the system efficiency. Such systems have, for example, been developed for the use of methanol and demonstrated on a cruise ship [91]. However, the operating temperature is not sufficiently high to reform most fuels without an external heat source.

The high operating temperature of SOFCs enables heat integration for fuel conversion with practically any fuel, including ammonia and even low sulfur diesel [92]. Moreover, SOFCs have a high tolerance for fuel impurities and may even convert ammonia and light hydrocarbons internally at the fuel electrodes. Although this largely simplifies fuel processing requirements and increases the overall efficiency, the specific power and power density of state-of-the-art SOFC systems is relatively still low.

The implications of fuel cell application in ships has far more extensive consequences beyond the size and weight of the power plant itself and the associated fuel storage. Some of the other aspects may include:

- propulsion system
- engine room design & location
- auxiliary systems

Fuel cells may be used to power auxiliaries only, but may provide power for propulsion as well. With the exception of fully electric ships, this affects the propulsion and power distribution systems. Electric propulsion will typically increase conversion losses in the propulsion train. However, these losses may be nullified entirely by the higher efficiency of fuel cells, especially in part load conditions. Fig. 3.14 shows an example of a conventional twin-shaft propulsion power plant layout next to one powered with high temperature fuel cells through a DC electric grid.

While mechanical propulsion dictates the location of the engine room close to the propellers, fully electric concepts increase the flexibility of the power generation location. Since fuel cells produce little noise and vibrations, they may further increase the flexibility in ship design [93]. However, it should be noted that supply of fuel, air and coolant will still be required. In addition, installation in the lower parts of the vessel may still be preferred for stability.

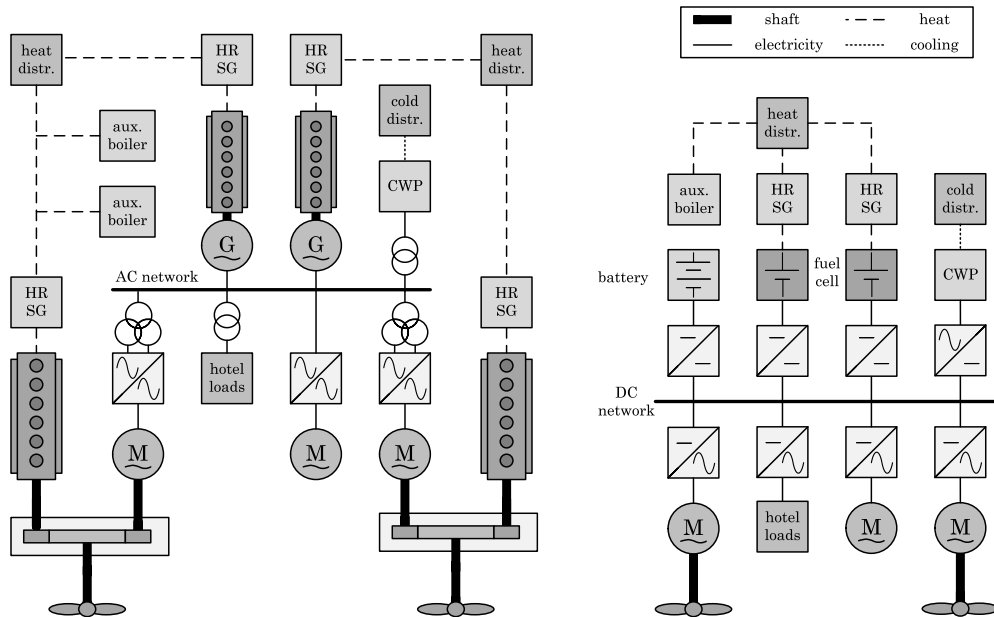


Figure 3.14 Examples of power distribution systems based on conventional technology (left) and based on high temperature fuel cell systems, incorporating a battery and a DC distribution network (right). In both cases, heat recovery steam generators (HRSGs) and a chilled water plant (CWP) are used to supply heat or steam and cold respectively [37].

Conventional diesel engines are equipped with auxiliary systems for fuel treatment, cooling and lubrication. Parts of these systems may remain, be replaced or become superfluous. For example, fuel cell systems do not need extensive lubrication systems due to the limited number of moving components. While an external (liquid) cooling medium is still used in PEMFC systems, SOFCs are generally cooled by cathode air. Fuel treatment depends largely on the fuel cell type and bunker fuel of choice.

3.6.2 Compliance with emission regulations

Fuel cells are commonly advertised as an important building block of zero emission transport. Nonetheless, the type of fuel and system ultimately determine to what extent emissions are effectively avoided. For example, fuels from fossil origin may still result in net carbon dioxide emissions. In addition, nitrous oxides may still be produced in burners.

Ship emissions are often distinguished in well-to-tank (WTT) and tank-to-propeller (TTP) emissions, the first covering the fuel production and distribution stages and the latter including the emissions from the tail pipe. WTT emissions may include emissions of hazardous air pollutants and greenhouse gases at fuel production and processing stages,

but for example also methane emissions from gas production fields or nitrous oxides emitted by LNG carriers. TTP emissions are directly related to the power plant on board.

Fuel cells fueled with any carbon-based fuel will still produce greenhouse gases, unless on-board carbon capture is applied. Of course, net zero greenhouse gas emission may still be achieved if CO₂ is captured during fuel production. Similarly, carbon-free fuel may still result in net GHG emissions if hydrogen from fossil feedstock is used.

Notably, fuel cells and fuel processing equipment are susceptible to sulfur which thus needs to be removed. Consequently, fuel cell systems will not emit sulfurous oxides. A similar rationale holds for particulate matter, which is typically detrimental for the porous fuel cell electrodes and filtered from fuel and air streams. Similarly, unconverted hydrocarbons and carbon monoxide are typically converted in a (catalytic) off-gas burner, a standard component in any fuel cell system with fuel processing equipment.

Nitrous oxides are usually formed at high temperatures and pressures in the presence of nitrogen and oxygen. These emissions are subsequently not formed in low temperature fuel cells. Even the relatively high operating temperature of SOFCs is not sufficient for the Zeldovich mechanism to produce any significant NO_x. However, trace amounts are reported to be formed in the burners employed in SOFCs and externally heated fuel reformers.

Assessing the overall emissions of any maritime power and propulsion system is essential and requires a comprehensive life cycle assessment (LCA). In such an LCA, the emissions during ship production, operation and end of life are properly accounted for. Consequently, a LCA also accounts for emissions associated with fuel cell production, raw material harvesting, fuel consumption and decommissioning [94]. Various studies have indicated that the operation life of a vessel dominates the overall life cycle emissions, mostly related to the consumption of fuels from fossil origin. It may therefore be expected that any fuel saving technology will reduce the life cycle emissions of ships.

Finally, it is noteworthy that fuel cells offer important advantages in terms of emitted noise and vibrations. Environmental protection agencies and policy makers are becoming increasingly aware of the negative consequences of underwater noise produced by ships on sea life. Although the majority of noise is produced by the propeller, some noise is inherently transmitted from other mechanical equipment to the water. Replacing diesel engines by fuel cells removes a major noise emitter, which may also allow the removal of sound isolation.

3.6.3 Reliability, availability, maintenance and safety

The so-called *RAMS parameters*, reliability, availability, maintainability and safety, are commonly used to assess power systems. They qualify the ability of the system to perform its function, remain functional, be repaired if required and not harm its environment [95]. Since ships are generally operated continuously in demanding environmental

conditions far at sea, loss of power is an unacceptable event. Relevant rules and technical standards are developed by classification societies to guarantee the safety of ships as well as their crews and cargo.

Fuel cell systems tend to degrade rather than fail due to the limited number of moving parts and relatively low operating temperatures and pressures [96]. Their modular nature offers additional advantages, as it reduces the risk of single-point failures. Efficiency differences between small and large fuel cell systems are typically due to the BoP only, while installing several smaller diesel engines may increase the fuel consumption considerably [93].

Maintenance in fuel cell systems involves regular inspection and calibration of gas metering and detection systems, replacement of filters and sorbents as well as maintenance to the rotating parts in pumps and blowers. Most notably, fuel cell stacks may need replacement after a certain degree of degradation is reached [97]. The crew should be able to carry out small maintenance tasks during regular operational activities, provided that smaller modules can be switched off individually. Stack replacement may be compared to an overhaul procedure of a reciprocating engine in time, expertise as well as cost [98].

The use of low flashpoint fuels and presence of flammable gases is the most important safety hazard introduced by fuel cell systems. Most renewable fuels considered for ships are classified as low flash point fuels and some of them are toxic. Hydrogen is extremely flammable, can create an explosive atmosphere, is easily ignited. Hydrogen will be present at some point in any fuel cell system, even if hydrocarbon fuels are reformed internally [99]. In addition, on-board reforming of hydrocarbon fuels produces toxic carbon monoxide.

The risks imposed by low flash point fuels can be mitigated by installing forced ventilation, double walled pilings, safety valves and gas detection systems [100]. In addition, the fuel storage and fuel cell installation should be separated from each other as well as safe areas and engine rooms. These and other regulatory aspects are discussed in detail by Vogler et al. [101]. Moreover, the International Maritime Organization recently published interim guidelines in draft for ships using fuel cell power installations in 2021 [102].

3.6.4 Economics

A lack of economic drivers is perhaps still the most important reason for the slow adoption of renewable fuels and their associated power systems. The associated investments and operating costs of renewable maritime solutions are typically a multitude of traditional solutions. The uptake of fuel cells by the maritime sector is partly due to technical challenges, but high capital expenditure (CapEx) and the cost of suitable fuels remain an important contributing factor [103]. A relatively low production volume and the use of non-automated manufacturing processes render fuel cell relatively expensive today.

However, cost reductions expected as a result of improved cell designs, reduction in the use of scarce materials, automated manufacturing processes, incremental learning and economics of scale. In addition, increasingly stringent emission regulations may close the gap to some extent.

Fuel cells enable high efficiencies which may offer a return on investment on the high CapEx due to a lower fuel consumption. For example, green hydrogen may be several times more expensive than conventional fuel oils [104]. Therefore, reducing fuel consumption may easily offset the higher initial investment. Moreover, it reduces the size of fuel tanks which are similarly much more expensive compared to fuel oil tanks. Considering the relatively high specific power, high power density and good transient response of LT-PEMFC systems, they make an appealing case and their uptake is mainly hindered by the costs associated with hydrogen fuel.

Most SOFCs available on the market for stationary applications are configured to use natural gas. Therefore, they provide an interesting alternative for ships already sailing on LNG, offering high efficiencies and low emissions. Unfortunately, fuel savings are not sufficient to justify the high capital cost today. The cost of SOFC systems is currently at least one order of magnitude higher than heavy duty diesel generator sets. HT-PEMFCs fueled with methanol face similar challenges, facing both higher CapEx and fuel cost.

Next to the fuel and capital cost, the total cost of ownership of power systems is affected by the system lifetime and maintenance costs. The yearly operating hours of ships vary from 4000 hours for passenger vessels up to over 6500 hours for international cargo ships [105]. Engines can achieve total life times of 25 years, but require regular maintenance varying from daily checks and weekly filter cleaning to yearly decarbonization and, eventually, a complete overhaul once in about five years [106,101].

Fuel cell systems have few rotating parts, but the lifespan of the system is limited by degradation of the stack and can thus be extended by regular stack replacement. Heavy duty LT-PEMFC systems may be designed to operate for 80,000 hours, with stack replacement every 20,000 to 30,000 hours [107]. This would result in a system lifetime of 12 to 20 years, with stack replacement required every 3 to 7 years. Stack replacement is expected to be the most substantial maintenance requirement, but inspection, filter cleaning and sensor calibration may be necessary as well [108].

Since SOFCs are primarily developed for stationary applications, manufacturers target stack lifetimes of 40,000 to 80,000 hours [109]. While early SOFC systems required stack replacement after 1.5 to 3 years of continuous service, stack lifetimes over 5 years are reported nowadays [110]. Improved stack designs demonstrate substantially lower degradation rates, but time will tell how long they can be operated before stack replacement is economically more attractive.

Today, the introduction of any fuel cell system in shipping imposes many additional costs related to increased complexity in the design phase, extensive certification process, limited availability of materials and components and auxiliary systems. These costs will

fall as marine engineers and naval architects become more familiar with the technology, standards are developed and prescriptive guidelines become available.

3.7. Experience and future outlook

Despite a long standing interest to apply fuel cells in the maritime sector the technology is not commercially applied yet, with the exception of specific niche markets like air independent propulsion systems for submarines. However, maritime fuel cell products are maturing thanks to a vast number of research and demonstration projects. An overview of relevant experience in several research and demonstration projects is presented in this section, together with a future outlook.

3.7.1 Experience with fuel cell application in ships

The application of fuel cells for air independent propulsion in submarines by Howaldswerke-Deutsche Werft is probably a maritime premiere. The development program of the fuel cell-based propulsion systems is believed to have started in the eighties, and was first applied in the Class 212 submarines from 1998 [5,111]. Many research and demonstration projects have been carried out since then, both military and commercial.

Early notable research projects date from the beginning of century. In most cases, fuel cells were intended to use the existing maritime diesel fuels. The MCFC and LT-PEMFC were most commonly investigated, with fuel processing an important aspect of fuel cell system development. Diesel-fuelled MCFCs were, for example, studied in the *ship service fuel cell* (SSFC) [112–114], *fuel cell technology for ships* (FCSHIP) [115] and *molten-carbonate fuel cells for waterborne application* (MC-WAP) [116,117] research projects. A diesel reformer for LT-PEMFCs was developed in the *diesel reforming with fuel cell* (DESIRE) project [118].

Later on the research has focused towards the use of alternative bunker fuels combined with fuel cells. A 330 kW LNG-fueled MCFC was installed on-board of the offshore supply vessel ‘Viking Lady’ in the *fuel cells for low emissions ships* (Fellow-SHIP) project [119,120], and in the *zero emission ship* (ZEMSHIP) project the passenger vessel *FCS Alsterwasser* was equipped with a hydrogen-fueled LT-PEMFC system in 2010 [121,100].

The majority of maritime fuel cell projects has increased further in the last decade. Notable projects include the *ship-integrated fuel cell* (SchIBZ) project [122,123], where an SOFC system was developed using low-sulfur diesel, and the Pa-X-ell project where a small methanol-fueled HT-PEMFC system was marinized and demonstrated on a cruise ship [123]. The MARANDA project validated a 165 kW fuel cell system on a research vessel in arctic conditions.

Many research and demonstration projects are still ongoing at the moment. The majority is focused on the application of LT-PEMFCs in combination with hydrogen,

Table 3.2 An overview of notable research & development projects on maritime fuel cell application.

Program	Period	Fuel cell type	Fuel	Application
Class 212	1980–1998	LT-PEMFC	Hydrogen	Submarine
SSFC	1997–2003	MCFC/PEMFC	Diesel	Naval ship
DESIRE	2001–2004	LT-PEMFC	Diesel	
FCSHIP	2002–2004	MCFC	Diesel	
FellowSHIP	2003–2013	MCFC	LNG	Offshore support
MC-WAP	2005–2011	MCFC	Diesel	RoPax, RoRo
ZEMSHIP	2006–2010	LT-PEMFC	Hydrogen	Passenger
SchIBZ	2009–2016	SOFC	Diesel	Multipurpose
Pa-X-cell	2009–2016	HT-PEMFC	MeOH	Cruise ship
ELEKTRA	2017–2019	LT-PEMFC	Hydrogen	Push boat
MARANDA	2017–2021	LT-PEMFC	Hydrogen	Research vessel
ISHY	2019–2022	LT-PEMFC	Hydrogen	Miscellaneous
H2SHIPS	2019–2022	LT-PEMFC	Hydrogen	Passenger
FLAGSHIPS	2019–2023	LT-PEMFC	Hydrogen	Ferry & inland
PACBOAT	2019–2022	SOFC	LNG	Cruise ship
NAUTILUS	2020–2024	SOFC	LNG	Cruise ship
ShipFC	2020–2025	SOFC	Ammonia	Offshore support
SH2IPDRIVE	2021–2025	PEMFC/SOFC	Hydrogen	Inland & coastal

partly due to the relatively high maturity and low cost of this fuel cell technology. The FLAGSHIPS project, for example, develops both a ferry for passengers and cars and a river push boat powered by hydrogen and LT-PEMFCs. Such a push boat is also developed in the ELEKTRA project [123]. Other notable projects developing and implementing maritime solutions based on hydrogen and LT-PEMFCs are the *Implementation of Ship Hybridisation* (ISHY) and H2SHIPS projects.

Although the smaller in number and ambitions, the application of SOFCs is investigated in research and demonstration projects as well. LNG-fueled SOFCs are developed in both the PACBOAT and *Nautical Integrated Hybrid Energy System for Long-haul Cruise Ships* (NAUTILUS) project to be demonstrated for large cruise ships, be at kW scale still. The ShipFC project has significantly higher ambitions and aims to demonstrate a 2MW SOFC system fueled with ammonia on-board of the offshore support vessel *Viking Energy*. Table 3.2 present an overview of notable research & development projects on maritime fuel cell application.

3.7.2 Future outlook

The ambitions to reduce emissions from shipping are increasing, which is reflected by the uptake of any emission reduction technology. Fuel cells offer an important piece of

future proof solutions, enabling on-board power generation with high efficiencies and zero emissions using a variety of fuels.

No prescriptive standards for maritime fuel cell systems are available as of today. Developing those will require extensive practical experience, accepted engineering practices and iterative system design efforts. Therefore, research, demonstration and pilot projects remain an inevitable necessity of maritime fuel cell development for the years to come. The same holds for bunkering, storage and use of associated logistic fuel, especially for hydrogen and ammonia.

Fuel cell technology has been continuously developing in the last decades. Generally speaking, important barriers for wide spread adoption remain:

- Scaling of products and production
- Limited experience in the maritime sector
- Lack of standards and a regulatory framework
- Challenges associated with bunkering, storage and use new fuels
- High capital and operating cost.

Scaling fuel cell production is an important bottle neck for large scale application and an important aspect to bring down costs through economics of scale. However, production can only be scaled once a reasonably steady market volume is achieved and requires dedicated long term investment. Recently, a number of large original equipment manufacturers have entered the market, expressing ambitions to set up scaled production lines for fuel cell systems, some tailored to the maritime sector [124].

LT-PEMFC technology is maturing rapidly, which is reflected in the number of demonstration and pilot projects is increasing. LT-PEMFC technology itself is close to commercialization, but the availability of affordable hydrogen remains an issue in many cases. However, the technology may take off rapidly in smaller applications once incentives are in place to push for zero emission alternatives.

The pathway towards commercialization is longer for high temperature fuel cell technology. HT-PEMFCs fulfill many technical requirements, but require significant lifetime improvements still. SOFCs have modest success in land-based distributed power generation, data centers in particular, but maritime application remains challenging [125]. However, they may use LNG which is increasingly adopted by ships and available in many ports. Moreover, SOFCs hold the potential to achieve significant reductions of both emissions and fuel consumptions, especially when combined with bottoming cycles. For now, however, low power density and high capital cost remain hurdles for the application in most ship types.

Fuel cells provide many advantages over conventional power generation technology, such as high electrical efficiency, reliability and flexibility with low emissions, noise and vibrations. However, some aspects of fuel cell technology need further development for maritime application. Standards and regulations need to be developed based on vast experience with the operation fuel cells in various maritime environments. In addition,

products and production needs to be scaled and cost need to be reduced. However, the increasing societal pressure to eliminate all greenhouse gas and hazardous emissions, combined with the increasing availability of renewable fuels, will drive the adoption of fuel cell systems in ships in the next decades.

References

- [1] O.Z. Sharaf, M.F. Orhan, An overview of fuel cell technology: fundamentals and applications, *Renewable and Sustainable Energy Reviews* 32 (2014) 810–853.
- [2] Z. Yan, J.L. Hitt, J.A. Turner, T.E. Mallouk, Renewable electricity storage using electrolysis, *Proceedings of the National Academy of Sciences* 117 (2020) 12558–12563.
- [3] A.J. Appleby, *Fuel Cell Handbook*, 1988.
- [4] A.E. Lutz, R.S. Larson, J.O. Keller, Thermodynamic comparison of fuel cells to the Carnot cycle, *International Journal of Hydrogen Energy* 27 (2002) 1103–1111.
- [5] G. Sattler, Fuel cells going on-board, *Journal of Power Sources* 86 (2000) 61–67.
- [6] T. Tronstad, H.H. Åstrand, G.P. Haugom, L. Langfeldt, Study on the use of fuel cells in shipping, EMSA European Maritime Safety Agency (2017) 1–108.
- [7] S. Kandlikar, M. Garofalo, Z. Lu, Water management in a pemfc: water transport mechanism and material degradation in gas diffusion layers, *Fuel Cells* 11 (2011) 814–823.
- [8] J. Chen, T. Matsuura, M. Hori, Novel gas diffusion layer with water management function for pemfc, *Journal of Power Sources* 131 (2004) 155–161.
- [9] H. Wang, J. Turner, Reviewing metallic pemfc bipolar plates, *Fuel Cells* 10 (2010) 510–519.
- [10] B. Wang, H. Deng, K. Jiao, Purge strategy optimization of proton exchange membrane fuel cell with anode recirculation, *Applied Energy* 225 (2018) 1–13.
- [11] M.H. Bargal, M.A. Abdelkareem, Q. Tao, J. Li, J. Shi, Y. Wang, Liquid cooling techniques in proton exchange membrane fuel cell stacks: a detailed survey, *Alexandria Engineering Journal* 59 (2020) 635–655.
- [12] A. Guo, W. Chen, Q. Li, Z. Liu, H. Que, Air flow control based on optimal oxygen excess ratio in fuel cells for vehicles, *Journal of Modern Transportation* 21 (2013) 79–85.
- [13] X. Cheng, Z. Shi, N. Glass, L. Zhang, J. Zhang, D. Song, Z.-S. Liu, H. Wang, J. Shen, A review of PEM hydrogen fuel cell contamination: impacts, mechanisms, and mitigation, *Journal of Power Sources* 165 (2007) 739–756.
- [14] R. Halseid, P.J. Vie, R. Tunold, Effect of ammonia on the performance of polymer electrolyte membrane fuel cells, *Journal of Power Sources* 154 (2006) 343–350.
- [15] D. Imamura, D. Ebata, Y. Hishimasa, M. Akai, S. Watanabe, Impact of hydrogen fuel impurities on pemfc performance, *SAE Transactions* (2007) 621–626.
- [16] Y. Zhao, Y. Mao, W. Zhang, Y. Tang, P. Wang, Reviews on the effects of contaminations and research methodologies for pemfc, *International Journal of Hydrogen Energy* (2020).
- [17] G. Liu, H. Zhang, J. Hu, Y. Zhai, D. Xu, Z.-g. Shao, Studies of performance degradation of a high temperature pemfc based on h₃po₄-doped pbi, *Journal of Power Sources* 162 (2006) 547–552.
- [18] R. Rosli, A. Sulong, W. Daud, M. Zulkifley, T. Husaini, M. Rosli, E. Majlan, M. Haque, A review of high-temperature proton exchange membrane fuel cell (ht-pemfc) system, *International Journal of Hydrogen Energy* 42 (2017) 9293–9314.
- [19] S.K. Das, A. Reis, K. Berry, Experimental evaluation of co poisoning on the performance of a high temperature proton exchange membrane fuel cell, *Journal of Power Sources* 193 (2009) 691–698.
- [20] Y.H. Jeong, K. Oh, S. Ahn, N.Y. Kim, A. Byeon, H.-Y. Park, S.Y. Lee, H.S. Park, S.J. Yoo, J.H. Jang, et al., Investigation of electrolyte leaching in the performance degradation of phosphoric acid-doped polybenzimidazole membrane-based high temperature fuel cells, *Journal of Power Sources* 363 (2017) 365–374.
- [21] C. Hartnig, T.J. Schmidt, On a new degradation mode for high-temperature polymer electrolyte fuel cells: how bipolar plate degradation affects cell performance, *Electrochimica Acta* 56 (2011) 4237–4242.

- [22] J. Supra, H. Janßen, W. Lehnert, D. Stolten, Temperature distribution in a liquid-cooled ht-pefc stack, *International Journal of Hydrogen Energy* 38 (2013) 1943–1951.
- [23] S.S. Araya, F. Zhou, V. Liso, S.L. Sahlin, J.R. Vang, S. Thomas, X. Gao, C. Jeppesen, S.K. Kær, A comprehensive review of pbi-based high temperature pem fuel cells, *International Journal of Hydrogen Energy* 41 (2016) 21310–21344.
- [24] N. Mahato, A. Banerjee, A. Gupta, S. Omar, K. Balani, Progress in material selection for solid oxide fuel cell technology: a review, *Progress in Materials Science* 72 (2015) 141–337.
- [25] J. Fleig, On the width of the electrochemically active region in mixed conducting solid oxide fuel cell cathodes, *Journal of Power Sources* 105 (2002) 228–238.
- [26] L. Mahmud, A. Muchtar, M. Somalu, Challenges in fabricating planar solid oxide fuel cells: a review, *Renewable and Sustainable Energy Reviews* 72 (2017) 105–116.
- [27] P. Aguiar, C.S. Adjiman, N.P. Brandon, Anode-supported intermediate-temperature direct internal reforming solid oxide fuel cell: II. Model-based dynamic performance and control, *Journal of Power Sources* 147 (2005) 136–147.
- [28] X. Wu, J. Jiang, W. Zhao, X. Li, J. Li, Two-dimensional temperature distribution estimation for a cross-flow planar solid oxide fuel cell stack, *International Journal of Hydrogen Energy* 45 (2020) 2257–2278.
- [29] J.-H. Lee, J.-W. Heo, D.-S. Lee, J. Kim, G.-H. Kim, H.-W. Lee, H. Song, J.-H. Moon, The impact of anode microstructure on the power generating characteristics of sofc, *Solid State Ionics* 158 (2003) 225–232.
- [30] M.C. Tucker, Progress in metal-supported solid oxide fuel cells: a review, *Journal of Power Sources* 195 (2010) 4570–4582.
- [31] Z. Yang, K.S. Weil, D.M. Paxton, J.W. Stevenson, Selection and evaluation of heat-resistant alloys for sofc interconnect applications, *Journal of the Electrochemical Society* 150 (2003) A1188.
- [32] Y. Wang, K.S. Chen, J. Mishler, S.C. Cho, X.C. Adroher, A review of polymer electrolyte membrane fuel cells: technology, applications, and needs on fundamental research, *Applied Energy* 88 (2011) 981–1007.
- [33] M. Ni, Modeling of SOFC running on partially pre-reformed gas mixture, *International Journal of Hydrogen Energy* 37 (2012) 1731–1745.
- [34] T. Okanishi, K. Okura, A. Srifa, H. Muroyama, T. Matsui, M. Kishimoto, M. Saito, H. Iwai, H. Yoshida, M. Saito, et al., Comparative study of ammonia-fueled solid oxide fuel cell systems, *Fuel Cells* 17 (2017) 383–390.
- [35] L. van Biert, K. Visser, P.V. Aravind, Intrinsic methane steam reforming kinetics on nickel-ceria solid oxide fuel cell anodes, *Journal of Power Sources* 443 (2019) 227261.
- [36] R.J. Kee, H. Zhu, D.G. Goodwin, Solid-oxide fuel cells with hydrocarbon fuels, *Proceedings of the Combustion Institute* 30 (2005) 2379–2404.
- [37] L. van Biert, Solid oxide fuel cells for ships: system integration concepts with reforming and thermal cycles, Ph.D. thesis, Delft University of Technology, 2020.
- [38] L. van Biert, P. 't Hart, K.M. Mrozewski, Public final report: Inventory of the application of fuel cells in the maritime sector (fcmar), 2021.
- [39] R. Peters, E. Riensche, P. Cremer, Pre-reforming of natural gas in solid oxide fuel-cell systems, *Journal of Power Sources* 86 (2000) 432–441.
- [40] J. Xu, G.F. Froment, Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics, *AIChE Journal* 35 (1989) 88–96.
- [41] M. Mitchell, P.J.A. Kenis, et al., Ceramic microreactors for on-site hydrogen production from high temperature steam reforming of propane, *Lab on a Chip* 6 (2006) 1328–1337.
- [42] C. Pan, R. He, Q. Li, J.O. Jensen, N.J. Bjerrum, H.A. Hjølmand, A.B. Jensen, Integration of high temperature PEM fuel cells with a methanol reformer, *Journal of Power Sources* 145 (2005) 392–398.
- [43] C.O. Colpan, I. Dincer, F. Hamdullahpur, Thermodynamic modeling of direct internal reforming solid oxide fuel cells operating with syngas, *International Journal of Hydrogen Energy* 32 (2007) 787–795.
- [44] Y. Yi, A.D. Rao, J. Brouwer, G.S. Samuelsen, Fuel flexibility study of an integrated 25 kW SOFC reformer system, *Journal of Power Sources* 144 (2005) 67–76.

- [45] R. Peters, R. Dahl, U. Klüttgen, C. Palm, D. Stolten, Internal reforming of methane in solid oxide fuel cell systems, *Journal of Power Sources* 106 (2002) 238–244.
- [46] D. Dissanayake, M.P. Rosynek, K.C. Kharas, J.H. Lunsford, Partial oxidation of methane to carbon monoxide and hydrogen over a Ni/Al₂O₃ catalyst, *Journal of Catalysis* 132 (1991) 117–127.
- [47] A. Lindermeir, S. Kah, S. Kavurucu, M. Mühlner, On-board diesel fuel processing for an SOFC–APU—Technical challenges for catalysis and reactor design, *Applied Catalysis B, Environmental* 70 (2007) 488–497.
- [48] F. Yagi, A. Nagumo, Y. Wada, M. Shimura, S. Asaoka, S. Wakamatsu, Process for preparing synthesis gas by autothermal reforming, 2002, US Patent 6,340,437.
- [49] A. Ersoz, H. Olgun, S. Ozdogan, C. Gungor, F. Akgun, M. Tiris, Autothermal reforming as a hydrocarbon fuel processing option for PEM fuel cell, *Journal of Power Sources* 118 (2003) 384–392.
- [50] V. Kyriakou, I. Garagounis, A. Vourros, E. Vasileiou, M. Stoukides, An electrochemical Haber–Bosch process, *Joule* 4 (2020) 142–158.
- [51] S. Yin, B. Xu, X. Zhou, C. Au, A mini-review on ammonia decomposition catalysts for on-site generation of hydrogen for fuel cell applications, *Applied Catalysis A, General* 277 (2004) 1–9.
- [52] C. Wheeler, A. Jhalani, E.J. Klein, S. Tummala, L.D. Schmidt, The water–gas–shift reaction at short contact times, *Journal of Catalysis* 223 (2004) 191–199.
- [53] A.F. Ghenciu, Review of fuel processing catalysts for hydrogen production in PEM fuel cell systems, *Current Opinion in Solid State and Materials Science* 6 (2002) 389–399.
- [54] M. Echigo, T. Tabata, Development of novel Ru catalyst of preferential CO oxidation for residential polymer electrolyte fuel cell systems, *Catalysis Today* 90 (2004) 269–275.
- [55] A. Manasilp, E. Gulari, Selective CO oxidation over Pt/alumina catalysts for fuel cell applications, *Applied Catalysis B, Environmental* 37 (2002) 17–25.
- [56] R.A. Dagle, Y. Wang, G. Xia, J.J. Strohm, J. Holladay, D.R. Palo, Selective CO methanation catalysts for fuel processing applications, *Applied Catalysis A, General* 326 (2007) 213–218.
- [57] C. Galletti, S. Specchia, V. Specchia, CO selective methanation in H₂-rich gas for fuel cell application: microchannel reactor performance with Ru-based catalysts, *Chemical Engineering Journal* 167 (2011) 616–621.
- [58] G. Ercolino, M.A. Ashraf, V. Specchia, S. Specchia, Performance evaluation and comparison of fuel processors integrated with PEM fuel cell based on steam or autothermal reforming and on CO preferential oxidation or selective methanation, *Applied Energy* 143 (2015) 138–153.
- [59] P. Djinić, C. Galletti, S. Specchia, V. Specchia, Ru-based catalysts for CO selective methanation reaction in H₂-rich gases, *Catalysis Today* 164 (2011) 282–287.
- [60] S. Sircar, T.C. Golden, Purification of hydrogen by pressure swing adsorption, *Separation Science and Technology* 35 (2000) 667–687.
- [61] S.-I. Yang, D.-Y. Choi, S.-C. Jang, S.-H. Kim, D.-K. Choi, Hydrogen separation by multi-bed pressure swing adsorption of synthesis gas, *Adsorption* 14 (2008) 583–590.
- [62] X. Zhu, S. Li, Y. Shi, N. Cai, Recent advances in elevated-temperature pressure swing adsorption for carbon capture and hydrogen production, *Progress in Energy and Combustion Science* 75 (2019) 100784.
- [63] N.W. Ockwig, T.M. Nenoff, Membranes for hydrogen separation, *Chemical Reviews* 107 (2007) 4078–4110.
- [64] M. Rahimpour, F. Samimi, A. Babapoor, T. Tohidian, S. Mohebi, Palladium membranes applications in reaction systems for hydrogen separation and purification: a review, *Chemical Engineering and Processing: Process Intensification* 121 (2017) 24–49.
- [65] G.Q. Lu, J.C.D. da Costa, M. Duke, S. Giessler, R. Socolow, R.H. Williams, T. Kreutz, Inorganic membranes for hydrogen production and purification: a critical review and perspective, *Journal of Colloid and Interface Science* 314 (2007) 589–603.
- [66] M. Shahbaz, T. Al-Ansari, M. Aslam, Z. Khan, A. Inayat, M. Athar, S.R. Naqvi, M.A. Ahmed, G. McKay, A state of the art review on biomass processing and conversion technologies to produce hydrogen and its recovery via membrane separation, *International Journal of Hydrogen Energy* 45 (2020) 15166–15195.
- [67] M. Rhandi, M. Trégaro, F. Druart, J. Deseure, M. Chatenet, Electrochemical hydrogen compression and purification versus competing technologies: Part i. pros and cons, *Chinese Journal of Catalysis* 41 (2020) 756–769.

- [68] F. Huang, A.T. Pingitore, B.C. Benicewicz, Electrochemical hydrogen separation from reformat using high-temperature polybenzimidazole (pbi) membranes: the role of chemistry, *ACS Sustainable Chemistry & Engineering* 8 (2020) 6234–6242.
- [69] L. Vermaak, H.W. Neomagus, D.G. Bessarabov, Recent advances in membrane-based electrochemical hydrogen separation: a review, *Membranes* 11 (2021) 127.
- [70] I. Staffell, D. Scamman, A.V. Abad, P. Balcombe, P.E. Dodds, P. Ekins, N. Shah, K.R. Ward, The role of hydrogen and fuel cells in the global energy system, *Energy & Environmental Science* 12 (2019) 463–491.
- [71] H. Malerød-Fjeld, D. Clark, I. Yuste-Tirados, R. Zanón, D. Catalán-Martínez, D. Beeaff, S.H. Morejudo, P.K. Vestre, T. Norby, R. Haugsrud, et al., Thermo-electrochemical production of compressed hydrogen from methane with near-zero energy loss, *Nature Energy* 2 (2017) 923–931.
- [72] L. van Biert, M. Godjevac, K. Visser, P.V. Aravind, A review of fuel cell systems for maritime applications, *Journal of Power Sources* 327 (2016) 345–364.
- [73] A. Dicks, D.A.J. Rand, *Fuel Cell Systems Explained*, Wiley Online Library, 2018.
- [74] F. Curletti, M. Gandiglio, A. Lanzini, M. Santarelli, F. Maréchal, Large size biogas-fed solid oxide fuel cell power plants with carbon dioxide management: technical and economic optimization, *Journal of Power Sources* 294 (2015) 669–690.
- [75] Q. Fang, L. Blum, R. Peters, M. Peksen, P. Batfalsky, D. Stolten, Sofc stack performance under high fuel utilization, *International Journal of Hydrogen Energy* 40 (2015) 1128–1136.
- [76] F. Mueller, F. Jabbari, J. Brouwer, On the intrinsic transient capability and limitations of solid oxide fuel cell systems, *Journal of Power Sources* 187 (2009) 452–460.
- [77] J. Cho, H.-S. Kim, K. Min, Transient response of a unit proton-exchange membrane fuel cell under various operating conditions, *Journal of Power Sources* 185 (2008) 118–128.
- [78] C. Gentner, *Einbindung von Brennstoffzellenanlagen in schiffstechnische Systeme*, Ph.D. thesis, Technische Universität Hamburg, 2018.
- [79] G. D'Andrea, M. Gandiglio, A. Lanzini, M. Santarelli, Dynamic model with experimental validation of a biogas-fed SOFC plant, *Energy Conversion and Management* 135 (2017) 21–34.
- [80] X. Wu, D. Gao, Fault tolerance control of sofc systems based on nonlinear model predictive control, *International Journal of Hydrogen Energy* 42 (2017) 2288–2308.
- [81] P. Leone, A. Lanzini, Experimental modeling of transients in large sofc systems, *Journal of Fuel Cell Science and Technology* 10 (2013) 011004.
- [82] T.M. Gür, Comprehensive review of methane conversion in solid oxide fuel cells: prospects for efficient electricity generation from natural gas, *Progress in Energy and Combustion Science* 54 (2016) 1–64.
- [83] H. Ozcan, I. Dincer, Performance evaluation of an SOFC based trigeneration system using various gaseous fuels from biomass gasification, *International Journal of Hydrogen Energy* 40 (2015) 7798–7807.
- [84] F. Baldi, L. Wang, F. Maréchal, Integration of solid oxide fuel cells in cruise ship energy systems, in: *Proceedings of the 31st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, CONF*, 2018.
- [85] L. van Biert, T. Woudstra, M. Godjevac, K. Visser, P.V. Aravind, A thermodynamic comparison of solid oxide fuel cell-combined cycles, *Journal of Power Sources* 397 (2018) 382–396.
- [86] L.K.C. Tse, S. Wilkins, N. McGlashan, B. Urban, R. Martínez-Botas, Solid oxide fuel cell/gas turbine trigeneration system for marine applications, *Journal of Power Sources* 196 (2011) 3149–3162.
- [87] Y. Kobayashi, K. Tomida, M. Nishiura, K. Hiwatashi, H. Kishizawa, K. Takenobu, Development of next-generation large-scale sofc toward realization of a hydrogen society, *Mitsubishi Heavy Industries Technical Review* 52 (2015) 111.
- [88] D.V. Singh, E. Pedersen, A review of waste heat recovery technologies for maritime applications, *Energy Conversion and Management* 111 (2016) 315–328.
- [89] H. Sapra, J. Stam, J. Reurings, L. van Biert, W. van Sluijs, P. de Vos, K. Visser, A.P. Vellayani, H. Hopman, Integration of solid oxide fuel cell and internal combustion engine for maritime applications, *Applied Energy* 281 (2021) 115854.
- [90] F. Baldi, F. Ahlgren, T.-V. Nguyen, M. Thern, K. Andersson, Energy and exergy analysis of a cruise ship, *Energies* 11 (2018) 2508.

- [91] J. Markowski, I. Pielecha, The potential of fuel cells as a drive source of maritime transport, in: IOP Conference Series: Earth and Environmental Science, vol. 214, IOP Publishing, 2019, p. 012019.
- [92] P. Nehter, B. Wildrath, A. Bauschulte, K. Leites, Diesel based SOFC demonstrator for maritime applications, *ECS Transactions* 78 (2017) 171–180.
- [93] M. Rivarolo, D. Rattazzi, L. Magistri, Best operative strategy for energy management of a cruise ship employing different distributed generation technologies, *International Journal of Hydrogen Energy* 43 (2018) 23500–23510.
- [94] M. Pehnt, Life-cycle analysis of fuel cell system components, in: *Handbook of Fuel Cells*, 2003.
- [95] R.F. Stapelberg, *Handbook of Reliability, Availability, Maintainability and Safety in Engineering Design*, Springer Science & Business Media, 2009.
- [96] K. Åström, E. Fontell, S. Virtanen, Reliability analysis and initial requirements for FC systems and stacks, *Journal of Power Sources* 171 (2007) 46–54.
- [97] E. Rillo, M. Gandiglio, A. Lanzini, S. Bobba, M. Santarelli, G. Blengini, Life cycle assessment (LCA) of biogas-fed solid oxide fuel cell (SOFC) plant, *Energy* 126 (2017) 585–602.
- [98] R. Islam, H. Yu, R. Abbassi, V. Garaniya, F. Khan, Development of a monograph for human error likelihood assessment in marine operations, *Safety Science* 91 (2017) 33–39.
- [99] F. Vogler, G. Würsig, D. Stolten, T. Grube, New developments for maritime fuel cell systems, *Schriften des Forschungszentrums Jülich/Energy & Environment* (2010).
- [100] F. Vogler, G. Würsig, Fuel cells in maritime applications challenges, chances and experiences, in: *The 4th International Conference on Hydrogen Safety (ICHS)*, 2011.
- [101] F. Vogler, G. Sattler, Hydrogen-fueled marine transportation, in: *Compendium of Hydrogen Energy*, Elsevier, 2016, pp. 35–65.
- [102] Draft interim guidelines for ships using fuel cells agreed by Sub-Committee, <https://www.imo.org/en/MediaCentre/Pages/WhatsNew-1636.aspx>. (Accessed 15 March 2022).
- [103] M. Wei, S.J. Smith, M.D. Sohn, Experience curve development and cost reduction disaggregation for fuel cell markets in Japan and the US, *Applied Energy* 191 (2017) 346–357.
- [104] S. Atilhan, S. Park, M.M. El-Halwagi, M. Atilhan, M. Moore, R.B. Nielsen, Green hydrogen as an alternative fuel for the shipping industry, *Current Opinion in Chemical Engineering* 31 (2021) 100668.
- [105] V. Eyring, H. Köhler, A. Lauer, B. Lemper, Emissions from international shipping: 2. Impact of future technologies on scenarios until 2050, *Journal of Geophysical Research: Atmospheres* (1984–2012) 110 (2005).
- [106] C.M. Milkie, A.N. Perakis, Statistical methods for planning diesel engine overhauls in the US coast guard, *Naval Engineers Journal* 116 (2004) 31–42.
- [107] P. Pei, Q. Chang, T. Tang, A quick evaluating method for automotive fuel cell lifetime, *International Journal of Hydrogen Energy* 33 (2008) 3829–3836.
- [108] M. Knowles, D. Baglee, A. Morris, Q. Ren, The state of the art in fuel cell condition monitoring and maintenance, *World Electric Vehicle Journal* 4 (2010) 487–494.
- [109] H. Tu, U. Stimming, Advances, aging mechanisms and lifetime in solid-oxide fuel cells, *Journal of Power Sources* 127 (2004) 284–293.
- [110] N. Brandon, *Solid Oxide Fuel Cell Lifetime and Reliability: Critical Challenges in Fuel Cells*, Academic Press, 2017.
- [111] V.P. McConnell, Now, voyager? The increasing marine use of fuel cells, *Fuel Cells Bulletin* 2010 (2010) 12–17.
- [112] S. Allen, E. Ashey, D. Gore, J. Woerner, M. Cervi, Marine applications of fuel cells: a multi-agency research program, *Naval Engineers Journal* 110 (1998) 93–106.
- [113] R.M. Privette, T.A. Flynn, M.A. Perna, R. Holland, S. Rahmani, C. Wood-burn, S.W. Scoles, R.C. Watson, 2.5 MW PEM fuel cell system for navy ship service power, 2002.
- [114] C. Bourne, T. Nietsch, D. Griffiths, J. Morley, Application of Fuel Cells in Surface Ships, Harwell Laboratory, 2001.
- [115] S. Alkaner, P. Zhou, A comparative study on life cycle analysis of Molten carbon fuel cells and diesel engines for marine application, *Journal of Power Sources* 158 (2006) 188–199.
- [116] S. Specchia, G. Saracco, V. Specchia, Modeling of an APU system based on MCFC, *International Journal of Hydrogen Energy* 33 (2008) 3393–3401.

- [117] S. Bensaid, S. Specchia, F. Federici, G. Saracco, V. Specchia, MCFC-based marine APU: comparison between conventional ATR and cracking coupled with SR integrated inside the stack pressurized vessel, *International Journal of Hydrogen Energy* 34 (2009) 2026–2042.
- [118] S. Krummrich, B. Tuinstra, G. Kraaij, J. Roes, H. Olgun, Diesel fuel processing for fuel cells—DESIRE, *Journal of Power Sources* 160 (2006) 500–504.
- [119] K.B. Ludvigsen, E. Ovrum, Fuel Cells for Ships, DNV Research and Innovation, Position Paper, 2012.
- [120] Fuel cell system on FellowSHIP supply vessel is hybridised, *Fuel Cells Bulletin* 2012 (2012) 3–4.
- [121] J. Schneider, S. Dirk, D. Stolten, T. Grube, ZEMShip, in: 18th World Hydrogen Energy Conference, 2010, pp. 16–21.
- [122] K. Leites, A. Bauschulte, M. Dragon, S. Krummrich, P. Nehter, SchIBZ—design of different diesel based fuel cell systems for seagoing vessels and their evaluation, *ECS Transactions* 42 (2012) 49–58.
- [123] e4ships – brennstoffzellen im maritimen einsatz, <http://www.e4ships.de>. (Accessed 15 March 2022).
- [124] H.F. Fure, Sustainable shipping: exploring the feasibility of investments in hydrogen-powered vessels for the short-sea sector, Master's thesis, 2020.
- [125] M. Gandiglio, A. Lanzini, M. Santarelli, Large stationary solid oxide fuel cell (SOFC) power plants, in: *Modeling, Design, Construction, and Operation of Power Generators with Solid Oxide Fuel Cells*, Springer, 2018, pp. 233–261.