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Review

Hybrid PEM Fuel Cell Power Plants Fuelled by Hydrogen for Improving Sustainability in Shipping: State of the Art and Review on Active Projects

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Abstract: The interest in hybrid polymer electrolyte membrane fuel cells (PEMFC) fuelled by hydrogen in shipping has seen an unprecedented growth in the last years, as it could allow zero-emission navigation. However, technical, safety, and regulatory barriers in PEMFC ship design and operation are hampering the use of such systems on a large scale. While several studies analyse these aspects, a comprehensive and up-to-date overview on hydrogen PEMFCs for shipping is missing. Starting from the survey of past/ongoing projects on FCs in shipping, this paper presents an extensive review on maritime hydrogen PEMFCs, outlining the state of the art and future trends for hydrogen storage and bunkering, powertrain, and regulations. In addition to the need for a clear regulatory framework, future studies should investigate the development of an efficient fuel supply chain and bunkering facilities ashore. As for the onboard power system, health-conscious energy management, low-temperature heat recovery, and advancements in fuel processing have emerged as hot research topics.

Keywords: hybrid PEMFC ship propulsion; maritime hydrogen; hydrogen storage; maritime PEMFC projects; zero emission shipping; hydrogen regulations

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Citation: Dall'Armi, C.; Pivetta, D.; Taccani, R. Hybrid PEM Fuel Cell Power Plants Fuelled by Hydrogen for Improving Sustainability in Shipping: State of the Art and Review on Active Projects. *Energies* **2023**, *16*, 2022. https://doi.org/10.3390/en16042022

Academic Editors: Vincenzo Liso and Samuel Simon Araya

Received: 7 December 2022
Revised: 12 February 2023
Accepted: 13 February 2023
Published: 17 February 2023

1. Introduction

Global emissions from maritime transport amount today to about 940 million tons of equivalent carbon dioxide ($CO_{2,eq}$), accounting for approximately 3% of global pollutant and greenhouse gas (GHG) emissions [1]. Recent projections estimate that by 2050 the total shipping emissions may increase by up to 45% with respect to the 2018 levels [2]. Recently, the International Maritime Organization (IMO) and other national/international bodies have posed new and more stringent limitations on pollutant and GHG emissions from shipping, posing new technological and regulatory challenges to the entire shipping sector. Figure 1 reports the timeline of IMO strategies to reduce shipping emissions [3], indicating that strategies identified to achieve the decarbonization of shipping are diverse and involve several aspects of ship building and operation.

Studies in the literature propose different shipping decarbonization strategies, which can be categorized as follows:

- Strategies for the improvement of existing internal combustion engine (ICE) propulsion systems in terms of fuel consumption (e.g., combustion improvement, advanced turbocharging) and emissions (e.g., water injection, intake air humidification) [4].
- Strategies for the improvement of the overall ship efficiency, e.g., hull resistance reduction [5], thrust and propeller efficiency improvement [6], route optimization [7], optimizing the load allocation among different power generators on board [8], or recovering the waste heat from the main engines [4].
- Strategies for the direct control of emissions via abatement technologies, e.g., selective catalytic reduction, or scrubbers [9].

- Strategies involving the use of alternative fuels (e.g., methanol, natural gas, ammonia, hydrogen) [10–12] and/or alternative power systems (e.g., hybrid ICE/battery, dual-fuel ICE, battery electric propulsion, fuel cells) [13,14].

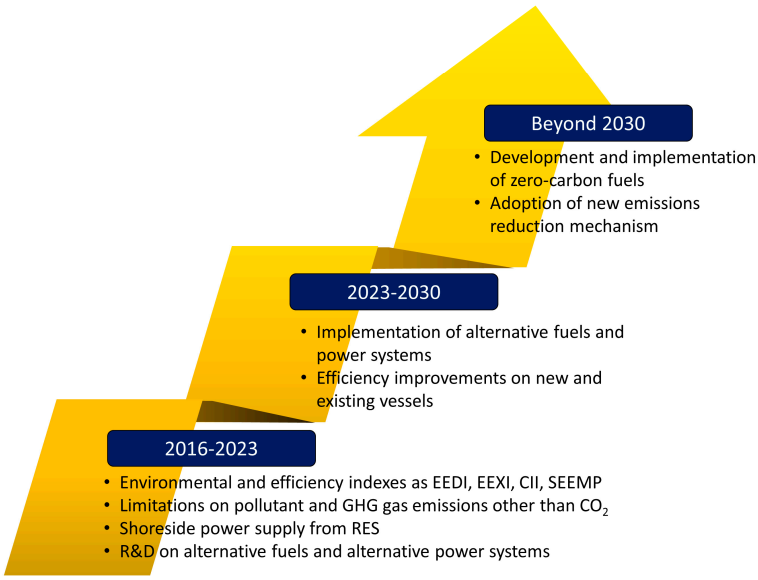


Figure 1. Timeline of IMO strategies for reducing shipping emissions. Information retrieved from [3].

The last point may be particularly promising in the long term, although it would imply an overall revolution of ship design and operation. Among different alternative power systems, fuel cells (FC) seem to be a good solution in terms of energy conversion efficiency and power density. In more detail, recent literature studies mainly refer to solid oxide fuel cells (SOFC) and polymer electrolyte membrane fuel cells (PEMFC) as promising alternative power systems for marine propulsion. Among the two, PEMFCs have higher technological maturity today, at least in sectors other than shipping, and hence seem to be more suitable for the maritime application in the short and medium term [15]. Moreover, if directly fed with hydrogen, PEMFCs could potentially guarantee zero-emission navigation, therefore respecting the most stringent limitations of emissions imposed by new regulations. Usually PEMFC-based ship propulsion systems are hybrid systems, in which PEMFC are coupled with an energy storage system (ESS) [16], i.e., hybrid PEMFC/ESS systems. Different approaches can be followed to analyse the possibility of using hybrid PEMFC ship energy systems fuelled by hydrogen. For instance, they can focus on the optimization of the operation of a single component of the energy system, or on the deep understanding and optimization of the electrochemical reactions happening in the fuel cells, or they can be directed to the understanding and improvement of the safety aspects related to this type of system, to mention a few. Nonetheless, recent studies in the literature [17–23] have proposed analyses of hybrid PEMFC ship power systems following an approach typical of the energy system engineering: rather than focusing on single aspects and components of the energy system, the ship's energy system is considered as a whole, and the analysis is carried out by accounting for the possible trade-offs that could guarantee the optimal synthesis, design, and operation of such systems under an environmental as well as economical point of view. Whilst several studies have addressed in detail some aspects of hybrid PEMFC/ESS propulsion systems [24,25], to the best of the authors' knowledge there is a lack of review studies specifically addressing hybrid PEMFC power plants in shipping. For example, van Biert et al. [13] give a general overview of the main aspects involved in the design and development of FC systems according to the type of FC and logistic fuels, while de Troya et al. [26] proposed an analysis of the main projects available in 2016 on the use of FCs on board. Moreover, both these reviews referred to projects and market scenarios as of 2016, while last years have seen a significant acceleration in the field of marine FCs, not only for the generally improved energy performances and reduced costs for FC technologies but also due to the approaching limitations on pollutant and GHG emissions imposed by the IMO [3].

To fill this gap, we present here a systematic overview of the state of the art of hybrid PEMFC/ESS propulsion systems fuelled by hydrogen. The ultimate goal is to provide the reader an insight on the main aspects to consider for the study, modelling, and design of hybrid PEMFC/ESS power systems fuelled by hydrogen, as well as to give the reader an updated and comprehensive vision of the regulatory framework of such systems in shipping. The whole analysis has been conducted from an energy system engineering perspective. Hence, it should be noticed that the terminology here proposed is the one typical of energy systems engineering. For example, *design* refers here to the determination of the energy components' sizes in the whole energy system and not to the design of the single fuel cell stacks or battery packs; *modelling* is here referred to as the energy system as a whole and not to the single electrochemical components.

The literature review here proposed has been conducted by considering the boundaries of ship energy systems as delimitations of the study. Other aspects, such as the hydrogen production and supply and the analysis of the chemical and electrochemical reactions of PEMFCs and batteries, as well as the lifecycle analysis of the environmental and social impact of the technologies, are not accounted for in this study, as there are already comprehensive reviews in the literature analysing these aspects. Figure 2 shows a simplified schematic of this paper's object and delimitations.

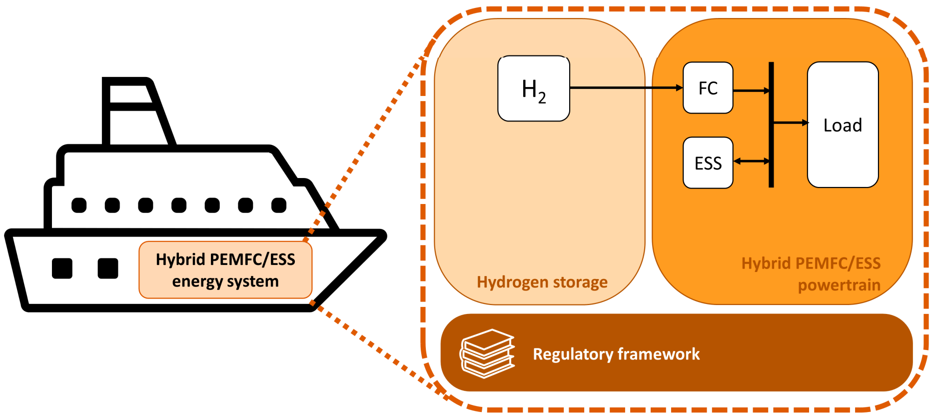


Figure 2. Simplified schematic of this paper's object and delimitations.

It can be noticed that the focus is on the hybrid PEMFC/ESS ship energy system, considered as composed by two main subsystems: the hydrogen storage system and the powertrain, which are reviewed in Sections 3 and 4, respectively. For both hydrogen storage and powertrain, a key aspect is represented by the available regulation for shipping, for which a complete overview is proposed in Section 5.

2. Review on Marine Fuel Cells Projects

The analysis of the developed and ongoing projects on the use of FCs in shipping is essential for a better definition of the object of this review. To this extent, this section reports the main findings of the review of marine and inland water FC projects developed since 2000. The review of projects was conducted starting from a previous study by the authors [16], which has been further extended and updated by adding projects for which information is freely available on the web. Reviewed projects include both feasibility studies and projects for the development of prototypes or real vessels powered by FCs. All information has been collected in a database, attached as Supplementary Material in the online version of this paper, where projects have been catalogued according to project name, ship name, project country, start and end date, state of the vessel (operating and not operating), vessel type, FC type, logistic fuel, type of ESS, funding, and project partners.

The database has been compiled by using only open-access scientific papers and technical reports, which are available through the links provided in the references section of the database. The choice of referring only to open-access scientific papers and technical reports was made to ensure that the Excel tool is accessible to the users without specific licenses or fees for access to the technical materials. The database can be a valuable resource for researchers, for example, interested in developing an advanced digital model of the complex energy system on board. Numerical models can be used to further improve a ship's overall energy performance, thus positively affecting environmental and economic sustainability.

An infographic of the data reported in the project database is shown in Figure 3, which presents information about projects' start date, vessel status, FC type, logistic fuel, and type of vessel application. To ensure quality information, the choice was made to include in the database only projects for which information was available regarding the fuel type, the fuel cell type, and the type of vessel. Existing projects for which at least one of these three data was not available have not been included in the project overview. The database is therefore not intended to provide an exhaustive overview of all projects existing at the time but aims to provide the reader with an analysis of projects for which a satisfactory number of details are available.

Firstly, it should be noticed that not all information was available for each project; hence, each chart in Figure 3 reports the number of projects responding to each criterion, so that the reader can easily retrieve the number of projects considered for each piece of information. As for *operating* and *non-operating* distinction, reference is made here to whether the vessel is currently in service/has navigated at least once (*operating* project) or not (*non-operating* project). In this case, data are available for all the 71 projects, and it emerged that only 40% of the reviewed projects can be considered operating.

As for the start date, Figure 3 indicates that the last five years have seen an increase in the development of projects in this field. This demonstrates the recent growing interests of shipowners and shipbuilders in the development of vessels with FCs fuelled by low-carbon fuel that will comply with the upcoming IMO restrictions [3]. With reference to the FC type, the analysis showed that 42 projects out of 58 for which information was available consider low-temperature PEMFCs (LT-PEMFC) as FCs, as this type is today the most mature one. It should be noticed that some projects investigated both the use of LT-PEMFC and other types of FC, e.g., MCFC. Among the 42 projects considering LT-PEMFCs, 19 projects are operating. The second most investigated FC type is the solid oxide FC (SOFC), with 8 out of 58 projects involving this type of technology. Among these, the ShipFC project [27] is planning to fuel SOFCs with ammonia. As for the logistic fuel category, reference is made here to the fuel stored onboard the vessel, used to fuel FCs either directly in its pure form or as reformate fuel (e.g., natural gas is intended as a logistic fuel in projects where it is reformed to produce hydrogen for feeding the FCs). From the review, it emerged that hydrogen is the most used logistic fuel (51 projects out of 70), mainly stored in compressed form (27 projects out of 37 for which data on the storage system are available). Lastly, the project review pointed out that most of the projects focus on small- to medium-sized ships, while projects focusing on larger ships often propose FC as auxiliary power units. In fact, FC-installed power currently does not exceed a few hundred kW. Projects that imply FC propulsion mainly focus on small- to medium-sized ships, with 33 to 71 projects considering small boats or RoPax ferries with a capacity of up to 200 passengers. Among these, 67% proposes the use of LT-PEMFCs, and 42% are operating and powered by LT-PEMFCs. In all cases, LT-PEMFCs are considered coupled with ESS, mainly batteries. Results and remarks arising from the project review here proposed clearly point out that hydrogen-fuelled LT-PEMFCs (further referred to as PEMFCs in this paper) are today the most promising alternative and hence motivated the definition of the review object proposed in this paper.

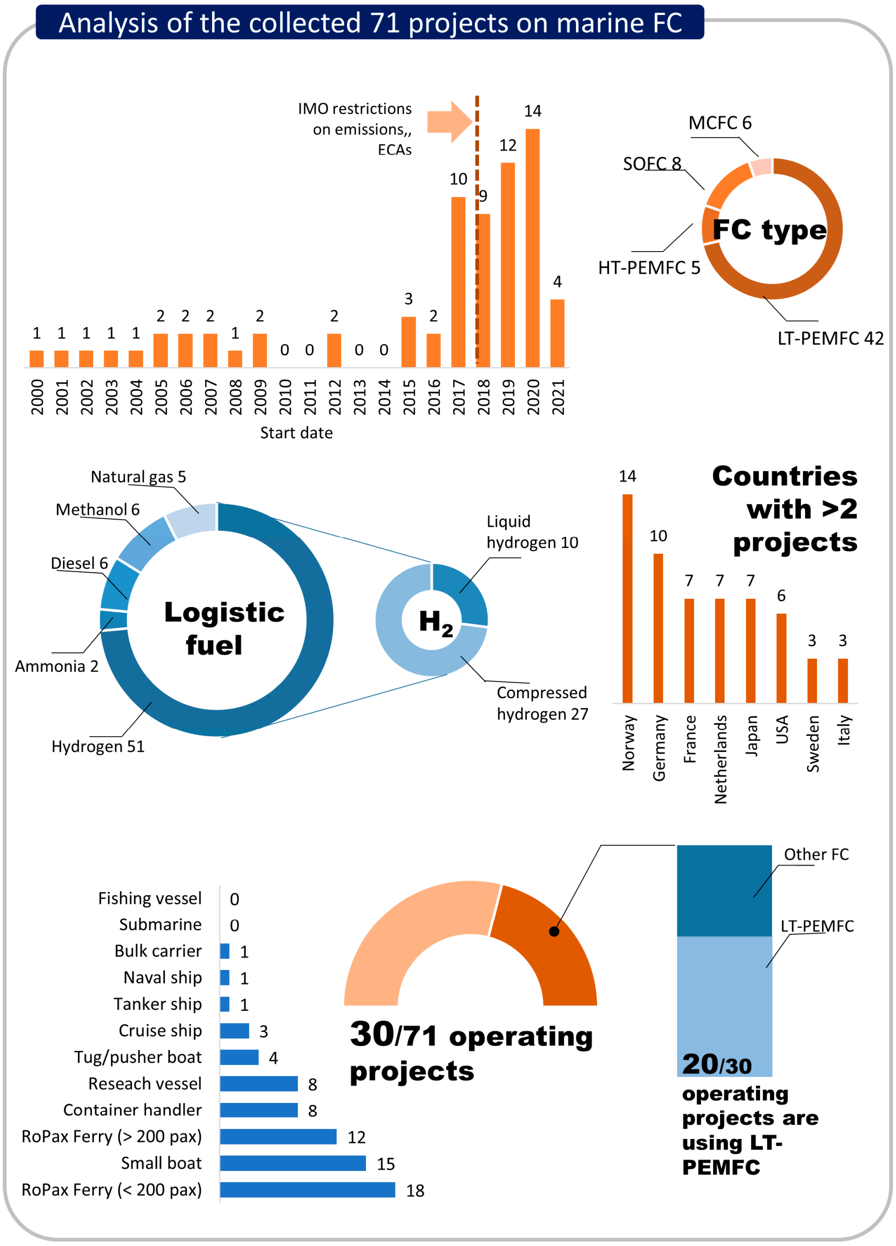


Figure 3. Infographic reporting the analysis of the 71 collected projects available in the attached database (see Supplementary Material). Numbers indicate the number of projects according to the respective criterion. *Operating* projects refer to those where the vessel is currently in service/has navigated at least once. (Acronyms used in the FC type chart: MCFC = molten carbonate FC; SOFC = solid oxide FC; HT-PEMFC = high-temperature PEMF; LT-PEMFC = low-temperature PEMFC.)

3. Hydrogen Storage

The storage of hydrogen is one of the challenges that hydrogen systems must overcome for a widespread use of hydrogen and PEMFC for ship propulsion. The choice of appropriate hydrogen storage is essential for meeting the ship's needs in terms of navigation range, space occupied, and safety. The methods to store hydrogen are usually categorized as physical-based and material-based, where the first includes cryogenic, cryo-compressed, and compressed hydrogen, and the second includes chemical absorption or physical adsorption of hydrogen as solid-state compounds [24,28–30]. In this section, the main types of hydrogen storage on board of ships are reviewed and compared, including information on the bunkering process when available.

3.1. Compressed Hydrogen

Compressed hydrogen (CH_2) storage is today the most mature technology for storing hydrogen in mobility applications [31], and thanks to the technological maturity of the storage cylinders, its cost-effectiveness, and the possibility to maintain high levels of hydrogen purity, it is also the most widely used hydrogen storage methodology for shipping applications. As reported in the Supplementary Material, several CH_2 maritime applications have been developed in recent years, ranging from small boats to medium-sized ferries, tugboats, and construction vessels. The relative ease of use and flexibility of CH_2 onboard ships are limited by its low energy density, which does not allow for adequate shipping range in vessels that require high installed power or long navigation routes. It is expected that in the future, CH_2 will play a crucial role as fuel storage for small- to medium-sized vessels that perform daily duties and have easy access to refuelling equipment.

According to the technologies and materials used to store hydrogen at different pressure levels, CH_2 cylinders are usually classified into four categories, as reported in Table 1 [28,30,32,33].

Table 1. Main characteristics of CH_2 cylinders [28,30–38]. Values of gravimetric and volumetric energy densities refer to the following pressure conditions: Type I@180–250 bar, Type II@250 bar, Type III@350–430 bar, and Type IV@250–700 bar. ++, if it has very high technological maturity, +, if high, −, if low, and − −, if very low.

Type	Materials	Maximum Pressure (bar)	Energy Density		Cost (EUR/kg$_{H2}$)	Technological Maturity
			(kWh/l)	(kWh/kg)		
I	All-metal, usually austenitic steels or aluminium alloys	≤300	0.3 ÷ 0.5	0.3 ÷ 0.6	83	++
II	Load-bearing metal liner hoop wrapped with resin-impregnated filament	≤700	0.4 ÷ 0.5	0.5 ÷ 0.8	86	+
III	Non-load-bearing metal liner axial and hoop wrapped with resin-impregnated filament	≤700	0.3 ÷ 0.8	1.1 ÷ 1.9	700	−
IV	Non-load-bearing non-metal liner axial and hoop wrapped with resin-impregnated filament	≤1000	0.3 ÷ 0.7	1.4 ÷ 2.7	600–700	− −

The choice of the cylinder suitable for a specific application should meet the best technological-cost compromise [30]. Clearly, energy density plays a key role in the choice of the suitable type of cylinder for a certain application. Figure 4 reports the range of volumetric and gravimetric energy densities of the four types of CH_2 cylinders derived from different products available on the market [34–38].

From Table 1 and Figure 4, it can be noticed that Type I and Type II cylinders have a lower energy density with respect to Type III and Type IV cylinders. Such aspects could represent an issue for their implementation in shipping applications, as it could entail loss of payload. Nevertheless, Type I and Type II cylinders have the highest technological maturity, and their costs are about nine times lower than the costs of Type III and Type IV cylinders [28].

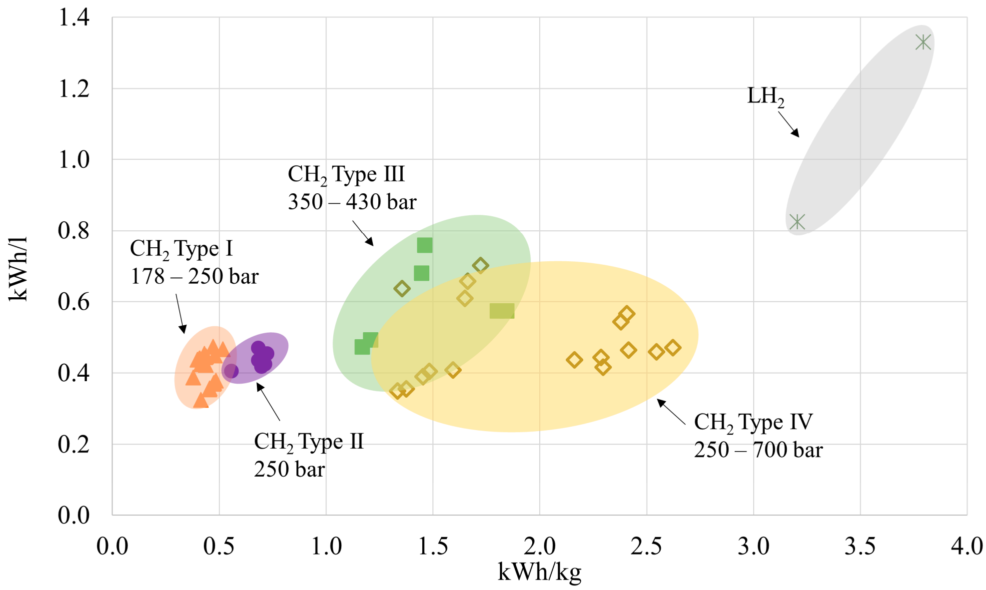


Figure 4. Energy density of different types of compressed hydrogen cylinders and liquid hydrogen tanks. Reproduced from a previous study by the authors [16].

Another key aspect to consider is the hydrogen bunkering, which requires the development of a bunkering infrastructure [39,40]. Notwithstanding whether hydrogen is stored as compressed gas or liquid, the main challenge for hydrogen bunkering is that, different from the bunkering of diesel, the hydrogen bunkering system is largely dependent on the vessel's design [40]. This is one of the reasons why there still does not exist a shared international standard for hydrogen bunkering procedures.

With reference to CH_2 bunkering, the main components of a CH_2 bunkering station are compressors, chiller unit, and pressure regulation valves. One of the main technical challenges is the long time required for the bunkering process. In fact, as in the case of land vehicles, fast filling of CH_2 cylinders may cause significant temperature rises, which must be controlled in order not to exceed 85 °C, above which there may be structural failures of the tanks [41]. Moreover, the increase in hydrogen temperature, also when expanding, would result in a decrease of the hydrogen density and hence in the underfilling of the cylinders [42]. Analysis of the CH_2 bunkering process is proposed, for example, in [33]. Another option may be the use swappable cylinders, often containerized, which can be loaded/unloaded when needed [14]. However, it should be noticed that such a solution could be feasible only for small- to medium-sized ships but might be impossible for larger ships, as this would imply too long port calls [12].

3.2. Liquefied Hydrogen

Liquefied hydrogen (LH_2) storage is already largely used as fuel for space vehicles and as feedstock in industrial plants. The liquefaction of hydrogen involves complex and energy-demanding processes (about 12 kWh/kg_{H2}) and is hence produced today in few large-scale plants [43]. Recent projects [44] are investigating the possibility of exporting LH_2 via shipping, but time is still required before such technologies are adopted on a large scale. Such limited availability of LH_2 at a global level is one of the barriers for widespread use of this fuel in the mobility sector. Moreover, the storage conditions of LH_2 (at about −253 °C) require the use of specific materials for tanks, pipelines, and valves, as well as complex safety instrumentation and technologies [31]. Nonetheless, the higher energy density of LH_2 in comparison with CH_2 (about 70 kg/m^3 at 1 bar) could guarantee higher shipping autonomy; thus, LH_2 is addressed as a promising logistic fuel for shipping [45–50]. LH_2 tanks usually proposed for shipping application are C-type tanks, similar to those used for liquefied natural gas (LNG) in ship applications. Indeed, LH_2 can somewhat take advantage of the knowledge achieved in the LNG technologies for ships, although LH_2 technologies need more performing and expensive materials for their storage construction due to the lower storage temperature than that of LNG (about −162 °C). For the other components, such as piping, ventilation, heat exchangers, and pumps, LH_2 technologies are very similar to the ones used for LNG, which are considered fully developed [51]. The essential component for the safe and economical operation of LH_2 tanks is the insulation, for which the variable density multilayer insulation with vapour-cooled shield has been shown to have the best performance among other technologies [52,53]. Such insulation technology was considered for the MF Hydra ferry [54], where an 80 m^3 C-type LH_2 tank was designed to work at a pressure of approximately 10 bar with an LH_2 capacity of 3.8 tons (with about 20% ullage) [45,46]. Another critical point in the design of LH_2-powered vessels is the positioning of the cryogenic tanks to guarantee the safe operation of the vessel. To avoid safety issues linked to the wide flammability range of hydrogen, LH_2 tanks are usually installed on the top deck of vessels [47–49].

Another critical aspect for a widespread use of LH_2 as fuel for shipping is the availability of LH_2 bunkering systems. At this time, only two LH_2 bunkering stations have been developed: one in Glasgow [55] and one in the context of the HESC project [56]. While the former, to the authors' knowledge, is not currently in operation, the latter has been operational since the beginning of 2022 to transport LH_2 from Australia to Japan. In the literature, a good contribution in the analysis of LH_2 bunkering is provided by Pratt et al. [49], who investigated the design of the infrastructures to refuel the SF-BREEZE ferry. The authors proposed two methods to transfer the LH_2 from a stationary or mobile LH_2 storage system (e.g., truck or ship) to the onboard storage tank, using a pressure-building unit (PBU) or a cryogenic pump. The PBU consists in an evaporator that vaporizes a small part of the LH_2 in the refuelling station tank and later sends it back to the gas cushion in the tank top to increase the pressure inside. The pressure difference between the refuelling station tank and the tank to be refilled allows the transfer of LH_2. The advantages of this method are the lower cost for the PBU than the cryogenic pump, and the possibility to use the generated hydrogen vapour for purging the bunkering piping and cooling them down before refuelling. Moreover, the PBU technology could allow for avoiding the transfer of LH_2 first to a stationary intermediate tank and then to the onboard tank, hence decreasing hydrogen losses by boil-off [47,48]. Cryogenic pumps are also a good option to supply hydrogen in a compressed or cryo-compressed form, resulting in less energy demands with respect to the compression of gaseous H_2 [57,58]. LH_2 refuelling via cryogenic pumps is faster than via PBU and is hence preferable for refuelling multiple vessels at a time from stationary hydrogen storage. Cryogenic pumps are usually posed below the tank or submerged to avoid cavitation phenomena [57].

Additional information on projects that use LH_2 can be found in the database attached as Supplementary Material in the online version of this paper. In general, it is observed that recent projects (after 2015) started to consider the use LH_2 as a logistic fuel on board to achieve higher installed power of the fuel cells. Nonetheless, as of today only the vessels developed under the Hystra project [59], which transport LH_2 from Australia to Japan, are operational. This is evidence of the difficulty of including cryogenic hydrogen storage on board from a technical and regulatory point of view, although the recent participation of regulatory bodies and naval registers in the research projects (e.g., [46,60,61]) somewhat shows a willingness to overcome these barriers in the near future. With regard to the ten projects on the use of LH_2 fuel analysed in this study, they feature tanks with varying LH_2 capacities, ranging from several hundreds of kilograms to thousands of kilograms. This variance is a result of the different sizes and power of the analysed ships, most of which are small- to medium-sized ferries. In general, it is expected that cryogenic hydrogen applications in the maritime sector will become more widespread in the future, particularly for larger ships that demand high power installations and increased autonomy.

3.3. Cryogenic-Compressed Hydrogen

Compressed hydrogen at a temperature below 75 K, i.e., cryogenic-compressed hydrogen (CcH_2), can reach densities up to 100 kg H_2/m^3, higher than the density of LH_2. Hence, CcH_2 could be a promising storage technology for mobility applications, although the development of a commercial solution is still far from being achieved [62–68]. To the best of the authors' knowledge, there is a lack of studies in the literature explicitly addressing the use of CcH_2 storage in ship applications. Nonetheless, the information reported hereafter could also be relevant for possible future studies and projects in the shipping sector. To this extent, an interesting contribution can be found in [62], where up to 1000 bar hydrogen pressure was reached in the tanks. Such results highlight that the developed technologies were promising in terms of energy density. The authors also concluded that the technology could potentially benefit from additional components such as re-cooling and latent heat storage systems to improve the overall CcH_2 storage energy efficiency. Indeed, an advantage of CcH_2 over LH_2 is the possibility to transfer the boil-off gas produced at high pressure from the tank to the users without requiring intermediate compression units [65,69]. For example, the BMW Group developed a prototype of a CcH_2 tank with a volumetric energy density of about 4.0 MJ/L and 3–7 g/h boil-off rate. It was found that, even after an extended idling period, a part of H_2 needed to be left inside the tank to ensure material integrity [63,68]. Meneghelli et al. [64] reported the results of the prototyping of another CcH_2 tank designed to operate at a temperature and pressure about 40–80 K and 300 bar, respectively. It was revealed that lower technical requirements were required for CcH_2 storage systems with respect to LH_2 ones, resulting in lower costs for the required isolating materials of the tanks [66,67,69]. As for the bunkering procedure, it could be possible to use cryogenic pumps that allow a lower energy demand with respect to the one required for bunkering CH_2 at an equal dispensing pressure [68]. Nonetheless, from a safety point of view, the use of CcH_2 on board would entail both the difficulties related to the high storage pressure typical of CH_2 and the ones related to the cryogenic storage temperatures typical of LH_2. This aspect, together with the still low technological maturity of CcH_2, is still hampering the use of this type of hydrogen storage on board of ships. This is also demonstrated by the fact that none of the 71 reviewed projects surveyed in this study involve the use of CcH_2. Despite this, CcH_2 holds potential as a hydrogen storage option with high energy density. With advancements in materials and engineering, CcH_2 may play a role in the mobility sector, particularly for small- to medium-sized ships, even though its energy storage capacity may eventually match that of LH_2 tanks.

3.4. Metal Hydrides

Recent years have seen a growing interest in the use of metal hydrides (MH) for hydrogen storage for mobility applications, and recent studies address the possibility to use them in shipping [70,71]. MHs store hydrogen chemically as metallic or intermetallic alloys in a parent hydride [71]. The materials that can be used to store hydrogen are different, ranging from metallic structures working as hydrogen sponges [72,73] to powders absorbing/desorbing hydrogen in relation to temperature or water concentration changes [74,75]. Among different MHs, magnesium-based H_2 storage, intermetallic compounds, and alanates have good performance in terms of high mass fraction of hydrogen to be stored and low temperature for the dehydrogenation process, i.e., the process for the extraction of hydrogen from the metal hydride [76,77]. In particular, Mg-based alloys and catalysed mixtures that have been catalysed perform well during cycling at high temperatures but are not effective for dehydriding processes at low temperatures. In contrast, composite materials made of reactive hydrides typically have poor re-hydriding performance [78,79].

In addition, boron-based hydrogen storage methods, $NaBH_4$ and NH_3BH_3 in particular, are often proposed in the literature for their hydrogen storage capacities and their characteristic of releasing hydrogen in the presence of water and specific catalysts at low temperatures [77,80]. While MHs have good characteristics in terms of volumetric energy density, a main drawback is represented by the high weight of an MH tank. Nonetheless, for shipping applications this issue can be solved by properly positioning the tanks on the vessel [81]. Another aspect to consider is the need of thermal energy for the dehydrogenation processes, which could, however, be efficiently provided by the waste heat recovered from the FCs [82]. The only ship application of MH technology was realized in the Zeus project, where eight MH cylinders were installed on board and held a total of 50 kg of hydrogen. The ship's full electric propulsion, powered by two 70 kW low-temperature PEMFCs and a 40 kWh battery, enables zero-emissions sailing for approximately 8 h at a speed of 7.5 knots. Further information can be found in the database attached as Supplementary Material on the online version of this paper. In general, MH appears to be a viable and safe option for hydrogen storage onboard ships. However, the potential for future application in large ships strongly depends on technological advancements that may occur in the coming years.

3.5. Hydrogen Carriers

To overcome the high costs related to pure hydrogen production and hence accelerate the implementation of FCs in shipping, researchers and stakeholders are investigating the possibility of storing and transporting hydrogen by means of hydrogen carriers. Among these, ammonia (NH_3), methanol (MeOH), natural gas (NG), and liquid organic hydrogen carriers (LOHC) are often proposed for FC applications in shipping, as they are characterized by storage conditions easier than those of CH_2 and LH_2, and most of them are already transported by ship [11,83].

For example, NH_3 could be a promising alternative to store hydrogen in ship applications, as it has about 18%wt hydrogen content and can be stored in liquid state at atmospheric pressure and at a temperature of about 234 K [84]. NH_3 is already produced on a large scale for industry applications, mainly in the fertilizer industry. While today NH_3 production is a carbon-intensive process, carbon-free production pathways are possible, leading to the production of the so-called green NH_3 [85]. As for NH_3 use as fuel, it could be used to feed both ICE and FC. If used in ICE, NH_3 being a carbon-free substance, NH_3 could reduce GHG emissions by up to about 90% with respect to conventional heavy fuel oil (HFO)-fuelled ships [86], while post-combustion devices would be needed to reduce nitrogen oxide (NOx) emissions [87]. As for NH_3 use in FC, it could either be used in SOFCs or to feed PEMFCs. In the first case, NH_3 could directly feed the SOFCs, as proposed in the ShipFC project [27]. In the second case, a cracking unit would be needed to obtain hydrogen from NH_3 in order to feed the PEMFCs [86]. While crackers are largely used in different industrial sectors, their use on board may be unpractical. Moreover, possible NH_3 residuals in the obtained hydrogen may poison the PEMFCs [88]. Lastly, the main drawback of NH_3 use on board is the toxicity of NH_3, which is currently hampering its inclusion in international standards as fuel for shipping [89].

Similar to NH_3, MeOH could also be used as alternative fuel in shipping both for use in ICE and FCs [87]. MeOH has a hydrogen content of about 12%wt, can be stored in liquid form in ambient conditions, and is already largely used in several industrial applications [90]. MeOH is typically produced from NG and coal, but MeOH production is also possible from biomass and agricultural waste [91,92]. Due to its chemical structure, MeOH cannot guarantee zero local emissions if used in ICE, SOFCs, or direct methanol fuel cells (DMFC). However, if produced from renewable feedstocks (e.g., biomass, municipal solid waste) it could achieve net-zero emission in the overall production-use chain [93]. A possible way to achieve zero local emissions would be the onboard carbon capture and storage (CCS), although such technologies are not yet developed for maritime applications and would increase the overall complexity and cost of the system [87,92]. MeOH could also potentially be used in PEMFC systems, both HT-PEMFCs and LT-PEMFCs [51]. In the first case, internal reforming could be possible thanks to the higher operating temperature of the FCs, while the use of MeOH in LT-PEMFCs would imply the use of an external reforming unit to obtain hydrogen for feeding the FCs. Similar to NH_3 cracking systems, MeOH reformers are also not yet available for shipping; hence, it will probably take some time before methanol-powered LT-PEMFCs are implemented on board [12,62].

Another promising solution to store hydrogen onboard ships is the use of LOHCs. LOHCs are organic substances consisting of homocyclic or heterocyclic aromatic, liquid in ambient conditions, with a hydrogen content of about 6–7%wt [94]. The choice among different types of LOHC depends not only on the capacity to store hydrogen but also on the technical and economic requirements for the process needed to enrich the organic substances with hydrogen, i.e., the hydrogenation process, and the process of extracting hydrogen from the LOHC, i.e., the dehydrogenation process [95]. Among different LOHCs, toluene, N-ethyl carbazole, and dibenzyl toluene seem to be the most suitable for the shipping industry, although the technological maturity of such systems is still relatively low [94,96,97]. If LOHCs are used in PEMFC systems, it should also be noticed that the current technologies for dehydrogenation membranes cannot meet the hydrogen purity requirements at the FC inlet, with consequent catalyst poisoning [98]. In general, it can be stated that the LOHC technology for hydrogen storage in shipping is interesting from research as well as industrial points of view, with innovative projects and companies aiming at developing this type of business in the upcoming years [99]. Nonetheless, there are no operating applications at this time. Moreover, none of the 71 projects surveyed in this study envisioned the use of LOHCs as a hydrogen storage method on board, somehow confirming the lower technological maturity of LOHCs with respect to other technologies.

Lastly, LNG could also be seen as a hydrogen carrier. LNG has a hydrogen content of 25%wt and could be reformed to obtain hydrogen. LNG ships today are a market-ready solution, and class rules are already available for LNG storage on board of ships and for the bunkering phase (IGF Code—International Code of Safety for Ship Using Gases or Other Low-flashpoint Fuels). The most critical part in this case is the reforming phase. In fact, the reformation process of LNG could lead to a residual content of carbon monoxide (CO) in the reformate gas, which could potentially poison the PEMFCs, preventing them from functioning [100]. To this extent, the use of HT-PEMFCs could avoid poisoning problems, but HT-PEMFCs still have lower technological maturity with respect to LT-PEMFCs (referred to as PEMFCs) [14]. For this reason, together with the economic convenience and technological maturity of ICE in comparison with PEMFCs, LNG is normally used in ICE, dual-fuel, and sometimes SOFCs, rather than in PEMFCs [101,102]. Lastly, it should be noticed that LNG is a fossil fuel and as such would not be able to guarantee zero-emission shipping.

3.6. Comparison among Different Hydrogen Storage Systems

A summary of the main characteristics of the hydrogen storage types presented in this section is reported in Table 2. The cost ranges reported in Table 2 are intended as cost per kg of the logistic fuel stored on board. It should be noticed that the large variability of cost ranges is related to the different production pathways, i.e., from renewable energy or from conventional fossil fuel-based technologies.

Table 2. Main characteristics of the available hydrogen storage methods. Lower and upper limits of cost ranges for physical hydrogen storage methods and metal hydrides refer to grey and green production methods, respectively (i.e., hydrogen produced from methane via steam reforming or from water via electrolysis powered by renewable energy sources) (T = temperature).

H_2 Storage Type	Storage Pressure (bar)	T (K)	H_2 Content (%wt)	Energy Density (kWh/L)	Cost Range (EUR/kg)	Remarks	Refs.
CH_2	200–1000	293	100	0.3–0.8	0.9–8.4	In total, 10% energy loss in the compression process. Limited energy density, suitable only for short-range shipping.	[28,30–38,103,104]
LH_2	1–12	20	100	2.3	2.4–9.9	Up to 40% energy loss in the liquefaction process. Limited availability. Suitable for medium–long-range shipping. Boil-off management required.	[12,31,103,104]
CcH_2	150–350	40–80	100	2.6 (@38 K and 300 bar)	2.4–9.9	Requires strict insulation. Suitable for medium–long-range shipping.	[31,103,104]
MH	20–150	260–425	>8	35–40	0.5–8 *	Requires thermal management. Could be coupled with heat recovery from PEMFCs.	[28,72,103]
LOHC	1	293	6–7	2	<1 **	Highly endo/exothermal processes. Large volumes required on board. PEMFC poisoning with current technology for dehydrogenation.	[28,94,98]
NH_3	10–17	293	17.6	3–4	0.7–0.8 **	Suitable for medium–long-distance shipping. Requires cracking process to obtain hydrogen for feeding PEMFCs. Typical cracker efficiency 75%. Main issues: toxic substance, possible poisoning of PEMFCs if no adequate hydrogen purification.	[84,86,94]
LNG	1–1.2	−162	25	6–7	0.4–0.5 **	Reforming process required for obtaining hydrogen to feed PEMFCs. Typical reformer efficiency 75%. Main issues: zero emission is not guaranteed, methane slip, PEMFC CO poisoning.	[10]
MeOH	1–81	293	12	3.64–3.92	0.4–1.2 **	Possible to use directly in HT-PEMFCs. For the use in LT-PEMFCs, reforming is required (efficiency 75%). No zero emissions, PEMFC CO poisoning.	[83,94,104]

* Cost per kg of hydrogen without taking into account the hydrogenation costs, which depends on the used technologies; ** kg of stored fuel.

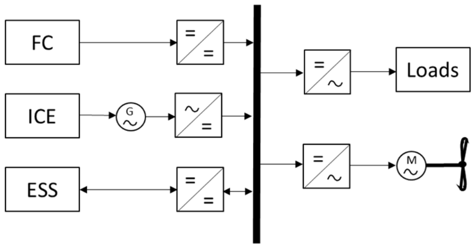
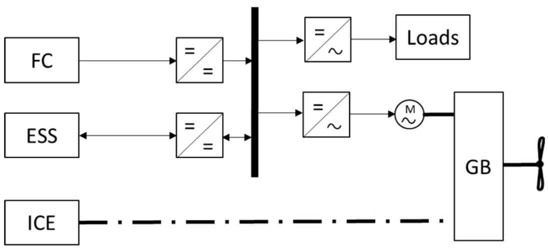
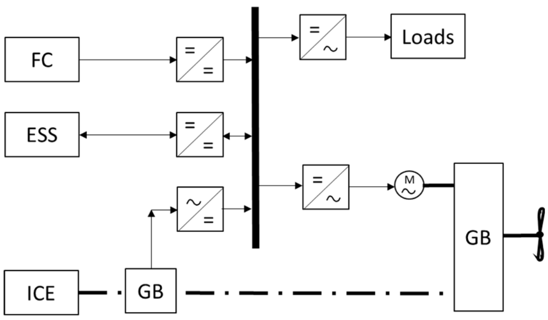
4. Powertrain

PEMFCs are commonly coupled with ESS in hybrid power systems for mobility applications, as hybrid powertrains generally allow the use of the main power generation systems (e.g., ICE, FC) under the best operating conditions. Indeed, if PEMFCs were not coupled with an ESS, the system (i) could have problems in following the power load, (ii) would work under lower energy efficiency conditions, (iii) would have larger and more frequent load changes and start-up phases, with a consequent decrease in their useful lifetime, and (iv) would need a higher FC-installed power, with consequent higher costs and safety issues for the power system [105]. In this section, the main architectures of the hybrid powertrain are outlined. Afterwards, an outlook on PEMFCs and on the different types of ESSs is presented. Lastly, the issues regarding the degradation of power units and the power allocation among PEMFCs and ESS are discussed, presenting the main outcomes from the literature analysis.

4.1. Hybrid Powertrain Architecture

A hybrid powertrain generally comprises one main power generator (e.g., ICE, FC) coupled with an ESS (e.g., battery, supercapacitors (SC)). Hybrid ICE/ESS power systems are today largely utilized for road vehicles, and in recent years they started to be utilized also in the shipping sector [106]. As for a hybrid PEMFC/ESS powertrain, they still represent a niche market in the automotive sector [107], and investigations are ongoing for their implementation in the shipping sector. Hybrid powertrains are generally classified into three main architectures according to the type of connection among the power units (i.e., the ESS and the main power generator): series, parallel, and series–parallel. Table 3 shows the simplified schematic of the three configurations for general hybrid powertrains that include both ICE and FCs, where all the electric power units are connected to a DC bus [24,106].

Table 3. Hybrid powertrain architectures for generation systems that include FCs and ICE. Elaborated from [24,106].

Hybrid Powertrain Architecture	Configuration	Legend	
Series			DC/DC Converter
			AC/DC Inverter
			Electric generator
			Electric motor
			DC bus
			Shaft
Parallel			
Series-parallel			

As shown in the figures in Table 3, the main difference between the three configurations relies on how mechanical and electrical transmission lines are connected to each other, i.e., on the presence or absence of a gearbox (GB). Hybrid PEMFC/ESS systems refer to the case of series architecture: electric power coming from both PEMFC and ESS is driven to an electric bus, from where the electric power flows to the propulsion and the auxiliary power loads of the ship. At the current state of technology, an alternating current (AC) grid with a fixed frequency is usually implemented on an all-electric ship to supply power for both auxiliary and propulsion energy demand. However, the recent development of power electronic technologies and direct current (DC) systems with high stability could lead to widespread use of a DC onboard grid in future hybrid PEMFC/ESS powertrains. This is also motivated by the easier and more efficient power distribution from the power units operating in the DC to the DC bus and then to the power loads [108,109]. The ESS is generally recharged by the PEMFCs (bidirectional electric power flow between the electric bus and the ESS). In some cases, the ESS could also be recharged by onshore electricity during ship mooring, i.e., the so-called plug-in recharge or onshore power supply [110]. In this way, it could be possible to reduce the PEMFC sizes and/or the amount of fuel stored on board [111]. However, plug-in options would require additional components not only onboard the vessel but also ashore [112]. Moreover, onshore power supply to the vessel would require the ships to stay at the quay for sufficiently long time periods; hence, the convenience of such systems should be determined in accordance with the ship's operating profile.

4.2. The Main Power Source: PEMFC

For hybrid PEMFC/ESS propulsion systems, the main power source is represented by the PEMFCs. As for marine applications, PEMFC-installed power has not exceeded, to date, hundreds of kW, but future projects aim to overcome these limitations, and MW-scale PEMFC-installed power is foreseen [113,114]. Difficulties in reaching MW-scale PEMFC-installed power involve not only space and safety requirements of the hydrogen storage system and the PEMFC stacks themselves but also the overall auxiliary equipment required to run the PEMFCs, i.e., the balance of plant (BoP). The BoP of a general PEMFC system can be divided into three subsystems: (i) fuel processing system and fuel/air supply lines, (ii) cooling circuit, and (iii) power conditioning, control, and monitoring systems. The fuel processing system includes all the components needed to ensure the correct hydrogen fuel characteristics at the PEMFC stack inlet. As for the hydrogen supply line, the main components of this category are: reformers, which produce hydrogen starting from hydrogen carriers when hydrogen is not stored in its pure form; hydrogen evaporator (if LH_2 storage); pressure reducers to ensure that hydrogen is supplied to the stack at the correct pressure (usually 3–4 bar [115]); hydrogen humidifier to ensure the correct level of hydrogen humidity at the stack inlet; condensate collector to remove any water in liquid form; hydrogen recirculation pump to allow recirculation of residual hydrogen. The main components of the air supply line are: a blower to supply atmospheric air to the stack, maintaining a sufficient air flow to the stack and potentially allowing reduced stack sizes by increasing the inlet air density [116]; an air filter to remove contaminants in the inlet air which may damage the PEMFC stack; a humidifier to maintain the performance of the electrolyte membrane; and a condensate collector; a condenser and a condensate collector may be included at the air outlet to partially recover steam which can be reused in the humidifiers. For maritime applications, it might be necessary to pre-treat the inlet air to remove sodium chloride vapour, as the exposure of the PEMFC stack to sea-air conditions may cause the degradation of the polymer membrane [116,117]. The cooling circuit system encompasses all the components that ensure the correct removal of the PEMFC waste heat, guaranteeing the operation of the stack at the correct temperature (65–70 °C) [118]. The waste heat from PEMFCs could be recovered and used to cover the heat demand of other applications. This point is particularly interesting for high PEMFC-installed power, and heat recovery at low temperature is currently a hot research topic [119]. There are mainly four ways for cooling PEMFC systems: edge cooling, air cooling, liquid cooling, and phase-change cooling [119]. Liquid cooling is often preferable due to its large cooling capability and good efficiency, and demineralized water or mixtures of demineralized water and ethylene glycol are usually implemented as refrigerants [120]. The main components of a liquid cooling system are the following: a circulating pump to guarantee a sufficient flow of refrigerant in the stack; a refrigerant reservoir; a heat exchanger to dissipate the heat either to the environment or to a heat recovery system; and a deionizer, which should be encompassed to guarantee that the refrigerant conductivity remains under set levels to avoid the short circuit of the PEMFC stack. Lastly, the power conditioning, control, and monitoring system encompasses all the measurement instrumentation necessary for data acquisition and system control, the safety valves, the control system, and the power inverter/converter to guarantee the right frequency of the generated electricity to the load. Figure 5 shows a typical configuration of a liquid-cooled PEMFC system. Typical techno-economic parameters typical of PEMFCs are reported in Table 4.

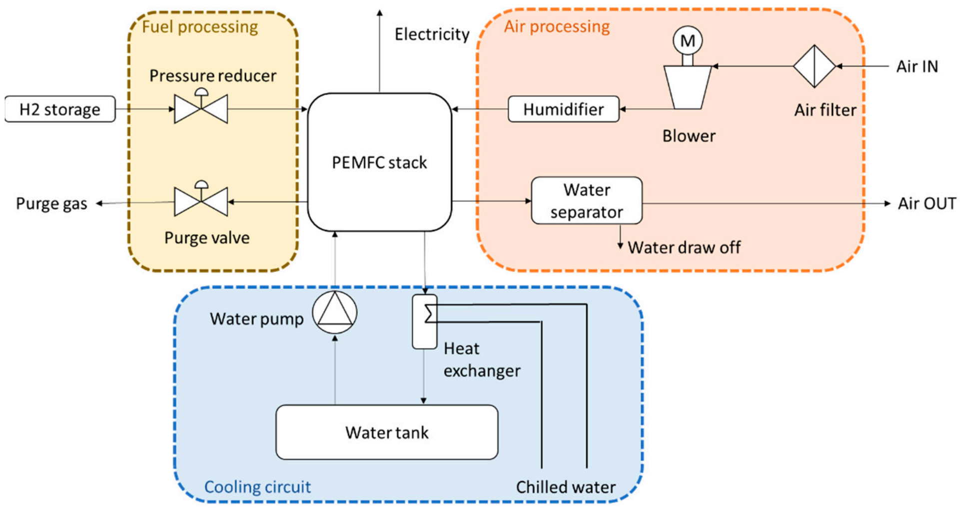


Figure 5. Simplified schematic of the typical configuration of a water-cooled PEMFC system, including the main components of the BoP. For simplicity, not all components of the power conditioning, control, and monitoring subsystem of the BoP have been reported in the schematic. Elaborated from [120].

Table 4. Techno-economic data for PEMFC stacks. Ranges extend from minimum to maximum values of the parameters found in the available literature studies. Data do not explicitly refer to maritime PEMFCs due to the lack of data for maritime PEMFCs.

LHV Maximum Design Efficiency (%)	Investment Cost (EUR/kW)	Lifetime (Operating Hours)	Refs.
50–55	830–2500	2000–10,000	[22,121,122]

4.3. The Energy Storage System

ESS plays several functions in a hybrid ship propulsion system and in particular in PEMFC/ESS ship powertrains. The European Maritime Safety Agency (EMSA) [123] points out that ESS in a hybrid marine system can (i) improve the main engine performance, allowing its operation at high efficiency, (ii) occasionally offer instant power supply when the main engine cannot guarantee it, (iii) buffer the load-changing variation, (iv) operate as energy storage for the potential renewable power plant installed on board (e.g., photovoltaic panels), and (v) operate as a backup and additional power source. With regards to the 71 projects analysed in this study and reported in the accompanying database, all the 35 projects for which information on the use of an ESS was available utilized an ESS. Of these, only two projects, namely Zemship Alsterwasser [124] and NemoH2 [125], employed the use of lead-acid batteries as their ESS, while the remaining 33 used lithium-ion batteries (LIB) as the onboard ESS. This indicates that LIBs are the most prevalent type of ESS used on-board these projects. The utilization of lead-acid batteries in the two aforementioned projects, which started in 2006 and 2008, respectively, can be attributed to the low technological maturity and high costs of LIBs at the time. The widespread use of LIBs in more recent projects demonstrates the recent advancements in the safety and regulatory aspects of maritime LIBs and the increase of commercial availability of maritime LIBs in recent years. In general, the choice of the type of ESS is fundamental for having the best operating conditions of the entire PEMFC/ESS propulsion system. Several ESSs for ship applications are available on the market, and each of them have different characteristics in terms of energy and power density, lifetime, cost, efficiency, and safety. Today, batteries, and in particular LIBs, are the most common ESS in such applications [123], as previously seen also with regard to the 71 projects analysed in this study. In fact, as shown in the Ragone plots of different ESSs for marine applications in Figure 6, batteries have good capacities in terms of specific energy in comparison with other technologies, e.g., SCs [123,126].

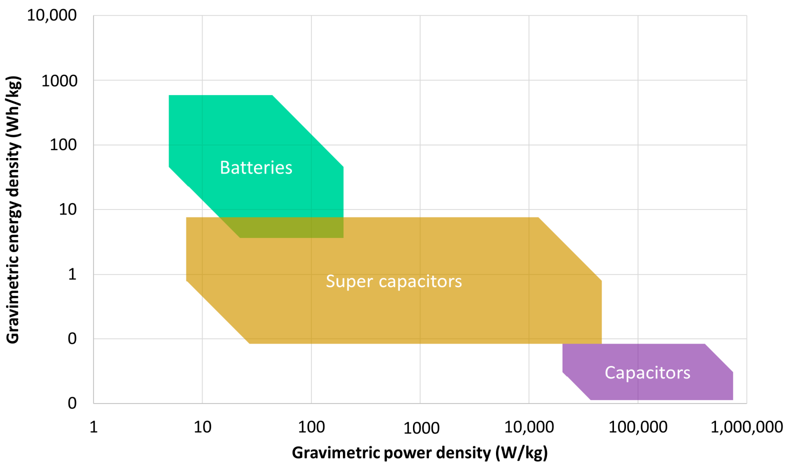


Figure 6. Ragone plot with gravimetric energy density and power density of different categories of ESS for marine applications. Elaborated from [123,126].

On the other hand, SCs may be useful in applications where low energy capacity is needed but high power density is required, for example, for peak shaving applications [123,126]. Moreover, SCs have longer lifetimes than batteries (>500,000 charging/discharging cycles) [127]. As for batteries, the most used for shipping applications are LIBs, thanks to their high specific energy with respect to other types of batteries such as, for example, lead-acid batteries [123,128]. LIBs can be composed of different materials, i.e., can have different chemistries, which determine the different performances in terms of energy and power density, efficiency, and cost. Several chemistries of LIB are available on the market, among which the most used in shipping are the nickel manganese cobalt (NMC), lithium iron phosphate (LFP), and lithium titanate oxide (LTO) [123,128]. NMC are today the most largely used chemistry in ship applications, thanks to their high flexibility in terms of energy and power performances. NMC also have a relatively high energy density and low cost. LFP are also widely used in maritime applications, particularly because of their good safety characteristics and resilience to temperature fluctuations. Their energy density is relatively low, but the power density can reach good levels if the cathode is doped appropriately [129]. A drawback of both NMC and LFP is the expected lifetimes. Hence, for applications where a very large amount of cycling is required, LTO is often preferred. LTO have also good safety feature and high power density but low energy density. It should also be noted that the investment cost of LTO is higher than those of NMC and LFP, but the total lifetime cost could become lower than the other chemistries thanks to the high lifespan achievable by LTO [123,130]. Another chemistry which could be suitable for shipping is the nickel cobalt aluminium (NCA) one, which can reach specific energy of 200–260 kWh [123]. However, its high cost is still hampering its use on a large scale. A summary of the main ESS characteristics is given in Table 5. It should be noted that Table 5 reports cost data specifically referring to ESS for marine applications, when available. Indeed, costs may be significantly lower when considering ESS for other sectors, e.g., road vehicles, and the design, redesign, or testing of the technologies in a maritime environment, the so-called *marinization*, naturally involve additional costs.

Table 5. Characteristics of the main ESSs for ship applications [123,130–134].

ESS		Energy Density (Wh/kg)	Power Density (W/kg)	Capital Cost (EUR/kWh)	Life (Cycles)	Marine Applications (-)	Refs.
LIB	NMC	150–220	520	475–960	1000–12,000	Currently the most largely used type of LIB in shipping, especially thanks to adjustable power and energy density.	[123,131,132,134]
	LFP	90–120	200	475–960	1000–12,000	Relatively low specific energy but good safety feature and resiliency to temperature characteristics; together with NMC is among the most largely used LIB in shipping.	[123,134]
	LTO	50–80	70	960–1920	6000–20,000	Suitable especially for applications where high power or large number of cycles are required.	[123,130,134]
SC		0.01–15	500–5000	96–475 *	>500,000	Suitable for applications where high power density is needed but low energy capacity is required, e.g., offshore drilling unit.	[123,133,134]

* Cost related to land application. Cost of marine SCs is likely to be at least five times higher (estimation in accordance with cost difference between LIBs for land and marine use).

4.4. Fuel Cells and Battery Degradation

One of the main drawbacks of hybrid PEMFC/ESS is the performance degradation of the power units over time, which limits their lifespan and hence results in higher overall costs.

The degradation of PEMFCs mainly results in voltage decay, which prevents the stack from working properly. Five main causes of performance degradation can be identified: load cycling, start/stop phases, idling current operation, high-power operation, and galvanostatic decay [135]. Among these, load cycling and start/stop phases have the highest impact in terms of performance degradation. Load cycling accelerates the cathode dissolution due to the increase of cathode potential and is considered the first cause of electrode oxidation, platinum dissolution, and corrosion of carbon support [136,137]. Start/stop phases cause the carbon oxidation of the anode, with consequent decrease of the active surface area and a non-uniform distribution of reactant gas [137–139]. Other degradation effects occur when PEMFCs operate at low or high current. In low current operating conditions, PEMFCs are subject to high cathode voltage, electrodes oxidation, and change of polymer decomposition mechanism [140,141]. High current operating conditions could cause not only fuel starvation when the reactant flow rate exceeds the maximum value but also the exceeding of cooling capabilities that could lead to an increased temperature of the membrane, high current density, and overcurrent, causing local hot spots [142–144]. Lastly, galvanostatic decay occurs when the FC operates at a constant current. Among the mentioned degradation mechanisms, galvanostatic decay is the one with the lowest impact on the overall PEMFC performance degradation [145,146]. PEMFC stack ageing can be modelled through different approaches: impedance estimation (based on electrochemical impedance spectrometry), remaining useful life estimation, and a stack voltage degradation model. Stack voltage degradation models are often used to limit the computational effort required in solving complex energy system models, although such a modelling approach is less accurate with respect to other degradation models and strongly depends on experimental data [147].

Differently from PEMFCs, LIBs are prone to degradation not only during cycling (i.e., cycle ageing) but also when in resting conditions (i.e., calendar ageing). Cycle ageing occurs when the battery is charged or discharged and depends on battery C-rate (i.e., power/capacity ratio), state of charge (SOC), temperature, number of performed equivalent cycles, and depth of discharge (DOD). Calendar ageing occurs when no current is flowing in the battery and depends mainly on the battery's SOC and temperature [148,149]. LIB ageing is a complex phenomenon and depends on the LIB's chemistry, but in general it is possible to identify a common degradation mechanism occurring at the anode, the electrolyte, and the cathode. At the anode side, the LIB's ageing usually involves structural disordering, graphite exfoliation, lithium plating, growth of a solid layer (solid electrolyte interface—SEI), binder decomposition, corrosion of current collectors, electrode particle cracking, and contact loss. The electrolyte is generally subject to separator dissolution and decomposition. At the cathode side, the main degradation mechanisms are commonly the dissolution of species, cracking of particle, structural disordering, passivation layer, corrosion of collector, and contact loss. Detailed explanations on how these degradation mechanisms act and what are their consequences on the LIB are explained in several papers in the literature [137,150,151], but in general it is possible to identify two main consequences of LIB degradation: voltage loss and capacity fade. The former is related to the increase of the cell's inner impedance, while the latter is linked to the conductivity loss, loss of lithium inventory, and loss of active materials [137,152]. Different degradation modelling approaches have been proposed in the literature, either based on electrochemical and equivalent circuit models (e.g., SEI thickness modelling, internal resistance models) or on empirical/semi-empirical methods (e.g., capacity fade models) [147]. Electrochemical and equivalent circuit models are usually more accurate than empirical/semi-empirical ones, but they are often unpractical due to the computational effort required for their solution. Conversely, empirical and semi-empirical models can take advantage of experimental data to limit the overall complexity of the model and thus limit its solving time [147,153].

Similar to LIBs, SCs are also subject to both cycle and calendar ageing over time, which lead to the decrease in the active area of the porous electrodes [154]. The calendar ageing is mainly related to voltage and temperature operating conditions, which cause an increase of the equivalent resistance of the system and hence result in a decrease of the energy storage capacity [155]. With reference to cycle ageing, SCs have the advantage of lower sensitivity to high charge/discharge rates than LIBs. However, it has been demonstrated that the SC degradation rate in cycle ageing is much higher than the expected calendar ageing in the same voltage and temperature conditions [156]. In fact, high charge/discharge current levels, high temperature conditions, and overvoltage conditions could start side reactions within the SC electrodes that could result in the generation of solid and gas particles in the electrolyte, with a consequent decrease of the electrode pores' accessibility and an increase in the internal pressure [157,158]. These effects, plus the effects of calendar ageing, limit the capacitance and the deliverable power of the SC [159,160]. The different approaches to model SC degradation can be mainly classified as electrochemical/equivalent circuit methods and empirical/semi-empirical methods [154]. The choice of the appropriate model should provide a compromise between accuracy and computational effort required, with empirical and semi-empirical models performing better in this last point [160,161].

4.5. Energy Management Strategy

A key yet challenging aspect for a hybrid PEMFC/ESS propulsion system is the power allocation among the PEMFCs and the ESS, i.e., the definition of the EMS. A proper EMS can guarantee the right and safe operation of the plant, managing the power sources' power output to correctly match the power demand of the vessel while avoiding potentially hazardous operating conditions. In addition, the EMS allows the power sources to work in the most efficient load ranges, while limiting possible stressful events that would decrease their lifetime [162]. In general, approaches for the definition of the EMS can be (i) rule-based or (ii) optimization-based. The former allocates the PEMFC and ESS power flows according to a set of rules based on human expertise. The main advantage of such an approach relies in their simplicity. However, the rules' formulation may be biased by human knowledge on the topic. In the literature, there are several studies on the development of rule-based EMSs. Some of these studies used deterministic methods for the definition of the EMS rules, i.e., with strategies mainly based on look-up tables [16,17,20,21,33,163], while others used fuzzy logic techniques [164]. Optimization-based EMSs usually start from the definition of the operating profile (i.e., the power demand of the vessel or the vehicle in general) and solve an optimization problem to find the optimal value of a set objective function (e.g., the daily operation cost of the ferry). Depending on how the operating profile is taken into account, optimization-based EMSs can be divided into two classes: global optimization EMSs and real-time optimization EMSs. The former aim to find the global optimum solution based on the overall operating profile, which needs to be known in advance [22,23,110,165–171]. The latter define instantaneous objective functions which can be updated in real time and do not require knowing the operating profile in advance [18,19,172–174]. The choice among global optimization and real-time optimization usually depends on the availability of data for training and testing the real-time algorithms and on the degree of complexity considered acceptable for a specific application. A summary of some of the most recent and relevant literature studies on the definition of EMS for hydrogen-fuelled PEMFC/ESS ship propulsion systems is given in Table 6. The studies are classified according to the type of EMS (rule-based/optimization-based) and to the degradation mechanism considered and modelled. EMSs that account for the power sources' degradation and include strategies to mitigate it are defined as health-conscious EMS and today represent one of the key research areas for hybrid PEMFC/ESS systems, not only in the shipping sector but also for other vehicles [147,175].

Table 6. Overview of the main scientific contributions in the literature addressing the analysis of EMS for hybrid PEMFC ships, including and not including PEMFC and ESS degradation phenomena in the definition of strategies. (●= considered; ○ = not considered).

Ref.	Authors	Year	EMS Proposed		Degradation Considered	
			Rule-Based	Optimization-Based	PEMFC	ESS
[20]	Han, J., et al.	2014	●	○	○	○
[164]	Zhu, L., et al.	2014	●	○	○	○
[163]	Bassam A.M., et al.	2016	●	○	●	●
[176]	Bassam A.M., et al.	2017	●	○	●	●
[165]	Tang, D., et al.	2017	○	●	○	○
[166]	Rivarolo, M., et al.	2018	○	●	○	○
[167]	Chen, H., et al.	2020	○	●	○	●
[172]	Hasanvand, S., et al.	2020	○	●	○	●
[168]	Letafat, A., et al.	2020	○	●	○	○
[169]	Rivarolo, M., et al.	2020	○	●	○	○
[33]	Taccani, R., et al.	2020	●	○	○	○
[173]	Vafamand, N., et al.	2020	○	●	○	○
[110]	Wu, P., et al.	2020	○	●	●	●
[174]	Zhang, Z., et al.	2020	○	●	●	●
[17]	Balestra, L., et al.	2021	●	○	●	●
[21]	Balestra, L., et al.	2021	●	○	●	○

Table 6. *Cont.*

Ref.	Authors	Year	EMS Proposed		Degradation Considered	
			Rule-Based	Optimization-Based	PEMFC	ESS
[170]	Banaei, M., et al.	2021	○	•	○	•
[16]	Dall'Armi, C., et al.	2021	•	○	○	○
[22]	Pivetta, D., et al.	2021	○	•	•	•
[23]	Dall'Armi, C., et al.	2021	○	•	•	•
[171]	Dall'Armi, C., et al.	2021	○	•	•	•
[18]	Wu, P., et al.	2021	○	•	•	•
[19]	Wu, P., et al.	2021	○	•	•	•

5. Regulatory Framework

This section presents an up-to-date overview of the regulatory framework for hydrogen PEMFC/ESS ship propulsion systems. Hydrogen-fuelled PEMFC/ESS systems are still relatively new in the maritime sector, and as such each application needs to undergo an alternative design process to assess the compliance with classification safety standards [177]. While key knowledge can be taken from available standards on land-based hydrogen PEMFC/ESS systems, maritime regulations need to ensure safe and reliable operation of the system in maritime conditions, e.g., guaranteeing adequate redundancy levels to ensure that the power generation system does not have single points of failure [124]. To this extent, PEMFC/ESS systems have few mechanical moving parts, which makes them less prone to failures with respect to ICEs [178]. However, the chemical and physical characteristics of hydrogen pose important challenges for its storage on board. Similar considerations can be performed for other low-flashpoint fuels that can be used as a hydrogen carrier on board, e.g., NH_3, NG, or MeOH [14]. Indeed, while rules and classification guidelines start to be available for the installation of PEMFC on board of ships, rules and regulations on the safe handling of hydrogen and hydrogen carriers used as fuel and on the bunkering procedures are not yet available. To this extent, it is important to stress how regulatory bodies and ship registers are making efforts to improve their knowledge on hydrogen as a maritime fuel and on hybrid PEMFC/ESS ship power plants, as demonstrated by the participation of such bodies in national and international projects on the use of hydrogen and FCs in shipping. For example, among the 71 projects surveyed in this study and available in the attached database, 19 projects (the majority of which in the last 10 years) count regulatory bodies among the main partners. Such efforts are likely to translate to an increased availability of rules and regulation on the topic in upcoming years.

Table 7 reports the rules and class requirements available as of January 2022 for both the PEMFCs and batteries of marine installations. The institutions that have already published guidelines for PEMFCs are the American Bureau of Shipping (ABS), the Bureau Veritas (BV), the Det Norske Veritas—Germanischer Lloyd (DNV-GL), and the Korean Register of Shipping (KS). IMO does not have any shared guidelines yet, although interim guidelines for the use of FCs in shipping are expected in May 2022 [179]. To date, IMO only provides recommendations for the use of an alternative design procedure for FC systems in the IGF Code—Part A (International Code of Safety for Ships using Gases or other Low-flashpoint Fuels), according to the guidelines for alternative design [180] and to the International Convention for the Safety of Life at Sea (SOLAS) requirements. As for marine battery installations, Table 7 shows that in addition to ABS, BV, and DNV-GL, the Lloyd's Register (LR) also published guidelines for the installation of large batteries in shipping [181]. Updates on hydrogen and PEMFC regulations for maritime use in a specific European Country can be found in the HyLaw online database website [182], while the Fuel Cells and Hydrogen Energy Association (FCHEA) provides updates on hydrogen and FC standards worldwide on the Hydrogen/Fuel Cell Codes and Standards website [183]. Other useful information on hydrogen policies (not specifically on shipping) can be retrieved from [184]. Lastly, it should be noticed that some national and international standards for on-land hydrogen and PEMFC technologies have been recognized as relevant for maritime applications, as they could give useful insights on safety aspects to consider for obtaining the approval of alternative design systems [14,123]. Hence, a list of international standards on PEMFCs, hydrogen technologies, and batteries available today, which is also for applications other than shipping, is provided in Table 8.

Table 7. Rules and class requirements for maritime PEMFCs and batteries or ESS installations. Information updated as of January 2022.

Institution	Document	Year	Notes	Refs.
		Fuel cells		
ABS	Guide for fuel cell power systems for marine and offshore applications	2019	\	[185]
BV	Ships using Fuel cells	2022	\	[186]
DNV-GL	Rules for classification of ships: Part 6 Ch. 2 Sec. 3 Fuel cell installation—FC	2019	\	[187]
KS	Guidance for fuel cell systems on board of ships	2015	\	[188]
		Batteries and ESS		
ABS	Guide for the use of lithium batteries in the marine and offshore industries	2022	\	[189]
BV	Rules for classification of steel ships	2021	Pt. F Ch. 11 Sec. 22, Electric hybrid	[190]
DNV-GL	Rules for classification of ships	2019	Pt. 6, Ch. 2 Sec. 1, Battery power	[187]
LR	Large battery installations	2015	\	[181]

Table 8. International standards on PEMFC, hydrogen technologies, and batteries available for both shipping applications and sectors other than shipping that could be relevant for use in maritime applications. (u.d. = under development; n.a. = not applicable; amd. = amendment.)

Standard Number/Series	Title	Year	Notes
	PEMFC and hydrogen technologies		
ISO/TC 197	Hydrogen technologies	n.a.	Cover hydrogen production, storage, transportation, measurement, and use. Note yet used in the maritime sector, but packages under development (ISO 19885 series) on hydrogen fuelling could be useful for bunkering of maritime vessels. Packages of ISO/TC 197 considered particularly relevant also for maritime applications are reported in the following lines.
ISO 19880	Gaseous hydrogen—Fueling stations	2020 (Pt.1) 2018 (Pt.3) 2019 (Pt.5) u.d. (Pt.6) 2019 (Pt.8)	Part of ISO/TC 197. Part 1 (General requirements). Part 3 (Valves). Part 5 (Dispenser hoses and hose assemblies). Part 6 (Fittings). Part 8 (Fuel quality control).

Table 8. *Cont.*

Standard Number/Series	Title	Year	Notes
ISO 16110	Hydrogen generators using fuel processing technologies	2007 (Pt.1) 2010 (Pt.2)	Part of ISO/TC 197. Part 1 (Safety). Part 2 (Test methods for performance).
ISO/TR 15916	Basic considerations for the safety of hydrogen systems	2018	Part of ISO/TC 197. Includes considerations on hydrogen embrittlement, material compatibility, low-temperature hydrogen effects on materials.
ISO 26142	Hydrogen detection apparatus—Stationary applications.	2010	Part of ISO/TC 197. Standard intended to be used for certification purposes. Covers hydrogen detection apparatus, useful for the requirements in terms of hydrogen leaks detection.
ISO 14687	Hydrogen fuel—product specification	2019	Part of ISO/TC 197. Part 3 (Proton exchange membrane (PEM) fuel cell applications for stationary appliances).
ISO 19881	Gaseous hydrogen—Land vehicle fuel containers	2018	Part of ISO/TC 197. Referred to compressed hydrogen cylinders for land vehicles. Volume up to 1000 L and pressure up to 70 MPa. Only cylinders permanently attached to the vehicles are addressed.
ISO 19882	Gaseous hydrogen—Thermally activated pressure relief devices for compressed hydrogen vehicle fuel containers	2018	Part of ISO/TC 197. Minimum requirements for pressure relief devices of hydrogen vehicles compliant with ISO 19881, IEC 62282-4-101, ANSI HGV 2, CSA B51 Part 2, EC79/EU406, SAE J2579, or the UN GTR No. 13.
ISO 19884	Gaseous hydrogen—Cylinders and tubes for stationary storage	u.d.	Part of ISO/TC 197. Information can also be found at the previously available ISO 15399:2012—"Gaseous hydrogen. Cylinders and tubes for stationary storage" for cylinders and tubes up to 110 MPa, 10,000 L.
IEC 62282	Fuel cell technologies	n.a.	IEC 62282-2-100:2020 "Fuel cell modules—Safety" IEC 62282-3-100:2019 "Stationary fuel cell power systems—Safety" IEC 62282-3-200:2015 "Stationary fuel cell power systems—Performance test methods" IEC 62282-3-300:2012 "Stationary fuel cell power systems—Installations" IEC 62282-3-400:2016 "Small stationary fuel cell power systems with combined heat and power output" IEC 62282-7-1:2017 "Single cell test methods for polymer electrolyte fuel cell (PEFC)" IEC 62282-8-101:2020 "Energy storage systems using fuel cell modules in reverse mode"
IEC 60050-485	International Electrochemical Vocabulary (IEV)—Part 485: Fuel cell technologies.	2020	Replaces the withdrawn IEC 62282-1:2013 "Terminology".

Table 8. *Cont.*

Standard Number/Series	Title	Year	Notes
ISO/TC 220	Cryogenic vessels	n.a.	Land-based cryogenic vessels (vacuum or non-vacuum). Could be useful for the maritime as it addresses also design and safety of the cryogenic vessels, gas/materials compatibility, insulation, operational requirements. Packages of ISO/TC 220 also considered particularly relevant for maritime applications are reported in the following lines.
ISO 20421	Cryogenic vessels—Large transportable vacuum-insulated vessels	2019 (Pt.1) 2017 (Pt.2)	Part of ISO/TC 220. Part 1 (Design, fabrication, inspection and testing). Part 2 (Operational requirements). Static vessels regulation available in ISO 21009.
ISO 21011	Cryogenic vessels—Valves for cryogenic service	2008	Part of ISO/TC 220. Manufacturing and tests of valves for rated temperatures < −40 °C.
ISO 21029	Cryogenic vessels—Transportable vacuum insulated vessels of not more than 1000 L volume	2018 (Pt. 1) 2015 (Pt. 2)	Part of ISO/TC 220. Part 1 (Design, fabrication, inspection, and tests). Part 2 (Operational requirements).
ISO 24490	Cryogenic vessels—Pumps for cryogenic service.	2016	Applicable to centrifugal pumps but could be applied also to other types of cryogenic pumps, e.g., reciprocating pumps.
ISO/TC 58	Gas cylinders	n.a.	Technical committee for the standardization of gas cylinders. Of relevance for hydrogen cylinders is the package ISO 11114.
ISO 15649	Petroleum and Natural gas industry	2001	Often used as a guidance in hydrogen piping systems.
UNI EN 13480	Industrial metallic piping	2020	Specifies design and calculation methods for industrial piping systems and relative supports.
ISO 23273	Fuel cell road vehicles—Safety specifications—Protection against hydrogen hazards for vehicles fuelled with compressed hydrogen	2013	Part 2 (Protection against hydrogen hazards for vehicles fuelled with compressed hydrogen). Part 3 (Protection of persons against electric shock, etc.).
NFPA 2	Hydrogen Technologies Code	2016	Fundamentals for generation, installation, storage, piping, use, and handling of compressed and cryogenic hydrogen.
NFPA 55	Compressed Gases and Cryogenic Fluids Code	2020	Guidelines for protection against physiological, explosive, over-pressurization, and flammability hazards associated with compressed and cryogenic gases.
NFPA 221	Standard for High Challenge Fire Walls, Fire Walls, and Fire Barrier Walls	2021	Prescriptions for design and construction of fire protection structures for use in protecting life and property from fire.

Table 8. *Cont.*

Standard Number/Series	Title	Year	Notes
NFPA 853	Standard for the Installation of Stationary Fuel Cell Power Systems	2020	Related to stationary systems, provides fire prevention and proception measures for the safeguarding of life and buildings.
SAE J2578	Recommended Practice for General Fuel Cell Vehicle Safety	2014	Related to the design, construction, operation, and maintenance of fuel cell vehicles.
SAE J2579	Standard for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles	2018	Design, construction, operational, and maintenance requirements of hydrogen fuel storage and handling systems (road vehicles).
SAE J2600	Compressed Hydrogen Surface Vehicle Fueling Connection Devices	2015	Design and testing of fuelling connectors, nozzles, and receptacles.
SAE J2601/2	Fuelling Protocol for Gaseous Hydrogen Powered Heay Duty Vehicles	2014	Independent document from SAE J2601 related to light-duty vehicles. Provides performance requirements for hydrogen-dispensing systems for heavy-duty vehicles with hydrogen storage pressures up to 35 MPa.
EN 1626	Cryogenic vessels—Valves for cryogenic service	2008	Design, fabrication, and testing of valves for cryogenic use. Valid for valves diameters up to DN150.
EN 60079	Explosive atmosphere	n.a.	Regulation series for explosive atmospheres (ATmosphere EXplosive—ATEX).
	Batteries and ESS		
EN 50110	Operation of electrical installations	2013	Part 1—General requirements (documentation for batteries and electrical testing).
IEC 61508	Functional safety of electrical/electronic/programmable electronic safety-related systems	2010	\
IEC 61511	Safety instrumented systems for the process industry sector	2016 (2017 amd.)	Amendment 1: 2017. Prescription on requirements for specification, design, installation, operation, and maintenance of Safety Instrumented Systems (SIS).
IEEE 45	Recommended practice for electrical installation on shipboard	2017 (Pt.1) 2020 (Pt.2)	Part 1 (Design of electrical power generation, distribution, propulsion, loafs systems, and equipment on merchant, commercial, and naval vessels). Part 2 (Controls, control applications, control apparatus, automation on shipboards).
IEC 62619	Secondary cells and batteries containing alkaline or other non-acid electrolytes—Safety requirements for secondary lithium cells and batteries, for use in industrial applications	2017	Requirements and tests or safe operation of secondary lithium cells and batteries in industrial applications, including marine applications.

Table 8. *Cont.*

Standard Number/Series	Title	Year	Notes
IEC 62620	Secondary cells and batteries containing alkaline or other non-acid electrolytes—Secondary lithium cells and batteries for use in industrial applications	2014	Marking, tests, and requirements of secondary lithium cells and batteries in industrial applications, including marine applications.
DOT/UN 38.3	UN Manual of tests and criteria, Transport of Dangerous goods	2019	Chapter on lithium metal and lithium-ion batteries.
IEC 62281	Safety of primary and secondary lithium cells and batteries during transport	2019 (2021 amd.)	Test methods and requirements for batteries (rechargeable and non-rechargeable) for safety during transport.
UL 9540	Energy storage systems and equipment	2020	Safety standard for grid connected or standalone ESS (battery system safety, fire detection and suppression, environmental performance, etc.).
IEC 60529	Degrees of protection provided by enclosures (IP Code)	2020	\
IEC 60092	Electrical installations in ships	2022	Part 504: Special features—control and instrumentation.
IEC 62061	Safety of machinery—Functional safety of safety-related control systems.	2021	Year 2021 version still not harmonized. The harmonized version is still the one of 2015.

6. Concluding Remarks and Future Research Trends

This paper provides a comprehensive overview of past, ongoing, and future projects related to the implementation of fuel cell technology onboard ships. The study begins by surveying past and current projects, highlighting their objectives and progress to date. The focus then shifts to the current state of the art of hydrogen fuel cell technology in the shipping industry, with a particular emphasis on proton exchange membrane fuel cells (PEMFC), which are the most widely used fuel cells for mobility applications. The paper includes a review of existing technologies and their capabilities, as well as an examination of the challenges that must be overcome for a widespread adoption of hybrid PEMFC powertrains in the shipping industry. Finally, the paper provides recommendations for future research and development in this field.

The main outcomes and the future research trends that arose from this analysis are outlined and discussed for five macro research areas.

1. Projects on fuel cell ships. The current focus of projects in the field of fuel cell ships is primarily on the installation of PEMFCs on small- and medium-sized vessels. The preferred method of hydrogen storage for these projects is compressed hydrogen, although liquid hydrogen storage is gaining traction for larger vessels. It is expected that future projects will involve the installation of fuel cell systems on larger vessels and an increase in the installed power of fuel cell systems.
2. Hydrogen storage. One of the main challenges facing the implementation of FC ships is the storage of hydrogen on board. This includes technical, economic, and safety considerations not only for onboard storage but for the entire hydrogen supply chain, from production to bunkering facilities. Currently, hydrogen carriers are not a viable

option for PEMFC/energy storage system (ESS) ship propulsion systems, but they may be promising for other types of powertrains such as solid oxide fuel cells (SOFC). Advances in technology for both PEMFC and reforming/cracking units may change this trend.

3. Powertrain. Hybrid PEMFC/ESS powertrains are still more expensive than conventional ship propulsion systems. Additionally, the degradation of PEMFCs and ESSs over time can result in shorter lifespans and higher costs. As such, researching ways to optimize the health-conscious management of these systems and using data-driven approaches for real-time optimization are important areas of study. Additionally, future studies should also explore the possibility of recovering heat from PEMFCs to increase the overall plant energy efficiency.
4. Onshore infrastructure. Onshore infrastructure for hydrogen and hydrogen carrier supply chains is a crucial area of research not only for academia but also for industry. Future studies should also focus on analysing the onshore power supply infrastructure for vessels at berth, with a specific emphasis on renewable energy systems.
5. Regulatory framework. The lack of international rules and standards for PEMFC and hydrogen use in shipping is a significant barrier to the widespread adoption of these technologies. However, guidelines are starting to become available and significant advancements in this area are expected in the coming years.

The information provided by the review can hence be beneficial for researchers in academia and industrial actors looking to expand their business in this new market sector. It is important to note that the advantages of this type of ship propulsion system are dependent on the use of green hydrogen or hydrogen carriers. Using grey hydrogen or fossil hydrogen carriers may provide short-term economic competitiveness, but it may not be sustainable in the long-term due to changing geopolitical and market conditions, and it would not support the transition towards cleaner shipping.

Finally, it is worth emphasizing that the large-scale use of fuel-cell-based low-emission ship energy systems depends on a variety factors. Aside from the bottlenecks related to the still incomplete regulatory framework, the limited hydrogen availability, and the lack of an established hydrogen infrastructure, other economic, environmental, and social aspects may also play a critical role in the deployment of this type of technology and, more generally, in defining optimal decarbonization strategies for the maritime transport sector. With this in mind, it is believed that the analysis proposed in this paper may help in enhancing the research and development on low-to-zero-emission PEMFC systems in shipping from an energy-system engineering perspective.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en16042022/s1, Database of FC projects in shipping.

Author Contributions: Conceptualization, C.D. and D.P.; methodology, C.D. and D.P.; formal analysis, C.D. and D.P.; investigation, C.D. and D.P.; resources, C.D. and D.P.; data curation, C.D. and D.P.; writing—original draft preparation, C.D. and D.P.; writing—review and editing, C.D., D.P. and R.T.; visualization, C.D., D.P. and R.T.; supervision, R.T.; project administration, R.T.; funding acquisition, R.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available in Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

ABS	American Bureau of Shipping
AC	Alternating Current
ATEX	ATmosphere EXplosive
BoP	Balance of Plant
BV	Bureau Veritas
CcH_2	Cryo-compressed hydrogen
CH_2	Compressed hydrogen
CO_2	Carbon dioxide
DC	Direct Current
DMFC	Direct Methanol Fuel Cells
DNV-GL	Det Norske Veritas—Germanischer Lloyd
DOD	Depth Of Discharge
EMS	Energy Management Strategy
EMSA	European Maritime Safety Agency
ESS	Energy Storage System
FC	Fuel Cells
FCHEA	Fuel Cell and Hydrogen Energy Association
GB	Gearbox
GHG	Greenhouse Gas
H_2	Hydrogen
HFO	Heavy Fuel Oil
HT-PEMFC	High-Temperature Polymer Electrolyte Membrane Fuel Cells
ICE	Internal Combustion Engine
IGF	International Code of Safety for Ships using Gases or other Low-flashpoint Fuels
IMO	International Maritime Organization
LFP	Lithium iron phosphate
LH_2	Liquid hydrogen
LIB	Lithium-Ion Batteries
LNG	Liquified Natural Gas
LOHC	Liquid Organic Hydrogen Carriers
LR	Lloyd's Register
LTO	Lithium Titanate Oxide
LT-PEMFC	Low-Temperature Polymer Electrolyte Membrane Fuel Cells
MCFC	Molten Carbonate Fuel Cells
MeOH	Methanol
MH	Metal Hydrides
NCA	Nickel Cobalt Aluminium
NG	Natural Gas
NH_3	Ammonia
NMC	Nickel Manganese Cobalt
NO_x	Nitrogen oxides
Pax	Passengers
PBU	Pressure-Building Unit
PEMFC	Proton Exchange Membrane Fuel Cells
SC	Supercapacitors
SEI	Solid Electrolyte Interface
SOC	State Of Charge
SOFC	Solid Oxide Fuel Cells
SOLAS	International Convention for the Safety of Life at SEA

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