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Thermal Shock Resistance of Solid Oxide Fuel Cells in Hybrid Electric Ships

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Abstract: This paper explores contemporary trends and developments in the field of green shipping, with particular emphasis on the use of various types of fuel cells in hybrid-powered ships. The focus is on the thermal shock resistance of solid oxide fuel cells (SOFCs) and their specific application in hybrid ship propulsion systems. The effects of thermal shock on SOFCs are thoroughly examined, and a comprehensive summary of the various proposed and implemented solutions to mitigate these effects is provided. It is shown that the thermal shock resistance of SOFCs can be significantly improved through optimized design, which, in turn, extends the overall lifespan of the fuel cells. Enhancing the reliability of SOFCs in marine environments is critically dependent on appropriate material selection and structural optimization. This paper serves as an important reference for the sustainable development of hybrid-powered ships, offering insights into how the performance of SOFCs can be effectively managed and improved under the challenging conditions of the marine environment.

Keywords: Hybrid Ship Propulsion Systems, Solid Oxide Fuel Cells (SOFCs), Thermal Shock Resistance, Marine Environmental Sustainability

1. Introduction

With the continuous development of the shipping industry, the problems of environmental pollution and energy consumption have become increasingly prominent, which have a significant impact on the ecological environment and resource utilization. The International Maritime Organization (IMO) introduced a mandatory Energy Efficiency Design Index (EEDI) regulation in 2011. Initially, most ships can meet the required first phase of emission reduction requirements by improving or lowering the speed with traditional technology. However, as the second and third phase regulations approach, shipbuilding companies face severe technical challenges [1]. To address this challenge, China has issued a series of policies to emphasize the importance of energy conservation and emission reduction in the shipping industry, and has set new environmental standards for ship technology. In this context, the promotion and application of hybrid electric ships have become the key focus of industry research [2-3].

The NOx emission limits for marine diesel engines corresponding to different construction periods are listed in Table 1. Specifically, for marine diesel engines with an output power exceeding 130 kW, NOx emission limits must be implemented according to the construction period. These limits are

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divided into three stages to gradually reduce NOx emissions and achieve environmental protection goals.

Additionally, the IMO fuel sulfur content limits and their implementation dates are shown in Table 2. By limiting the sulfur content in marine fuels, the aim is to reduce sulfur oxide (SOx) emissions, further improve air quality, and protect the marine environment.

For marine diesel engines with an output power exceeding 130 kW installed on each ship, corresponding NOx emission limits shall be implemented based on the construction period, divided into three stages (Table 1).

Table 1: Limitations on NOx emissions

NOx emission limit	n<130 r/min	Speed 130 r/min ≤n< 2000 r/min	n≥2000 r/min
From January 1, 2000, to January 1, 2011 (Phase 1 Standard Requirements)	17.0 g/(kW ·h)	45 ·n(-0.2)g/(kW · h)	9.8 g/(kW ·h)
From January 1, 2011, to January 1, 2016 (Phase 2 Standard Requirements)	14.4 g/(kW ·h)	44 ·n(-0.23)g/(kW ·h)	7.7 g/(kW ·h)
After January 1, 2016, navigation within emission control areas (complying with Stage III requirements)	3.4 g/(kW ·h)	9 ·n(-0.2)g/(kW · h)	2.0 g/(kW ·h)

Table 2: Limiting Sulphur Content of IMO Fuels and Implementation Dates

Implementation time	S0x Emission Control Area	Global
Before July 1, 2010	1.50%	4.50%
After July 1, 2010	1.00%	
2012		3.50% Review of global fuel conditions in 2018
2015	0.10%	
2018		
2020		0.50%
2025		

Hybrid electric vessels are ships powered by various types of engines or electric motors, with more than one source of electricity. By coordinating and complementing different energy sources, hybrid electric vessels can significantly improve overall energy efficiency, thereby achieving the goals of energy conservation and emission reduction [4]. Modern hybrid electric vessels differ from traditional ships, which were driven by a combination of wind and manpower, or from modern ships that rely on both wind and steam turbines. Contemporary hybrid electric vessels typically achieve propulsion through the coupling of diesel engines (or gas engines) with electric motors, or by using multiple

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sources of electricity (such as diesel generators, gas engine generators, fuel cells, solar energy, wind power, lithium batteries, supercapacitors, etc.) to power the electric motors [5].

Currently, various types of hybrid electric vessels exist. Common types include diesel-electric hybrid vessels, where diesel engines and electric motors work alternately to meet different navigation needs; wind-power-electric hybrid vessels, which combine wind and electric power to reduce fuel consumption; and solar-power-electric hybrid vessels, which integrate solar panels with electric motors to improve energy efficiency and reduce emissions. Additionally, there are fuel cell-electric hybrid vessels under development, which provide a cleaner and more efficient energy solution by combining fuel cells with electric motors.

Compared to traditional ships that rely on diesel engines, which have mature technology, low maintenance costs, and high reliability, diesel engines are less fuel-efficient, resulting in high fuel consumption, high operating costs, and the emission of large amounts of harmful gases, contributing to significant environmental pollution. Hybrid electric vessels, on the other hand, combine the advantages of diesel engines and electric motors, intelligently selecting the optimal energy combination for different navigation conditions. This not only improves fuel efficiency and reduces emissions but also effectively lowers operating costs. However, hybrid vessels may have some disadvantages compared to traditional vessels. For example, while they offer significant improvements in fuel efficiency and environmental impact, they may incur higher initial capital costs, more complex maintenance requirements, and face current limitations in energy storage and fuel cell technology, which could affect their long-term operational stability and range. In certain operational conditions, hybrid vessels may also struggle to achieve the same speed and power output as conventional diesel-powered vessels. Therefore, although hybrid electric ships offer clear advantages in reducing environmental pollution and operational costs, they are still in the process of overcoming challenges related to energy density and system reliability.

Among all possible hybrid power systems, fuel cells have become an increasingly popular solution due to their high efficiency and clean characteristics. Fuel cells offer advantages such as no combustion, zero emissions, low noise, and a stable power output unaffected by environmental conditions, making them especially suitable for ships that need to operate for long periods or navigate in areas with strict emission controls. Furthermore, fuel cells have higher thermal efficiency and better overall energy efficiency, providing significant advantages over traditional power systems. Therefore, researching and applying fuel cell technology, and exploring its potential in hybrid electric vessels, is of great importance for addressing increasingly stringent environmental regulations and improving the operational efficiency of ships [6],The working principle of hybrid electric ships is shown in Figure 1.

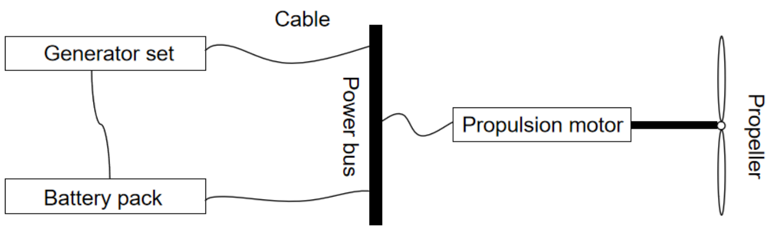

Figure 1: Structure of Ship Hybrid Power System.

2. Challenges

2.1. Fuel Cells for Hybrid Propulsion Ships

Fuel cells, as an indispensable component of hybrid propulsion ships, are gradually becoming the key technological pillar for the future development of the shipping industry due to their high efficiency, cleanliness, and versatility. Through a unique electrochemical reaction mechanism, they directly convert the chemical energy of fuel into electricity, effectively avoiding the heat loss and pollutant emissions generated during the combustion process of traditional internal combustion engines, thus achieving the goals of efficient energy conversion and low emissions.

Currently, in the field of fuel cells, several types—such as alkaline fuel cells (AFC), proton exchange membrane fuel cells (PEMFC), solid oxide fuel cells (SOFC), phosphoric acid fuel cells (PAFC), and molten carbonate fuel cells (MCFC)—are particularly common and demonstrate unique advantages in practical applications(Table 3) [7]. In marine applications, PEMFC and SOFC have become the mainstream choice, not only excelling in domestic and international demonstration ship projects but also indicating their vast prospects for the future shipping industry.

Table 3: Types and Characteristics of Fuel Cells

Type	Alkaline Fuel Cell	Proton Exchange Membrane Fuel Cell	Phosphoric Acid Fuel Cell	Molten Carbonate Fuel Cell	Solid Oxide Fuel Cell
Abbreviation	AFC	PEMFC	PAFC	MCFC	SOFC
Electrolyte	Potassium Hydroxide Solution	Polymer Electrolyte	Phosphoric Acid	Potassium Carbonate	Solid Oxide
Fuel	Pure Hydrogen	Hydrogen, Methanol, Natural Gas	Natural Gas, Hydrogen	Natural Gas, Biogas, Hydrogen	Natural Gas, Biogas, Hydrogen
Oxidant	Pure Oxygen	Air	Air	Air	Air
Efficiency	60%~90%	43%~58%	37%~42%	>50%	50%~65%
Operating Temperature (°C)	60-120	80-100	160-220	600-700	600-800
Applications	Military, Aerospace, Marine Transport, Backup Power	Marine Transport, Stationary Applications	Distributed Power Generation	Distributed Power Generation, Power Equipment	Power Generation, Cogeneration, Marine Transport, Space Exploration

Alkaline fuel cells (AFC) utilize an alkaline electrolyte (usually potassium hydroxide solution). These cells are favored in aerospace and other fields for their efficiency and reliability. However, they face limitations in long-distance marine transportation applications due to the sensitivity of alkaline electrolytes to carbon dioxide in seawater. The carbon dioxide reacts with the electrolyte to form carbonates, leading to performance degradation of the cell [8].

Phosphoric acid fuel cells (PAFC) use phosphoric acid as the electrolyte, and this type of fuel cell is commonly used in medium-sized equipment. Compared to other types of fuel cells, PAFCs have lower efficiency, especially under high load or low-temperature conditions, where their performance deteriorates more significantly. This poses a challenge for the long-term, efficient operation of ships, which is why PAFCs are not widely used in the maritime industry.

Molten carbonate fuel cells (MCFCs) offer high efficiency and flexibility in stationary power generation and industrial applications. However, issues such as material corrosion, large volume and weight, complex maintenance requirements, fuel storage problems, and poor adaptability to marine environments restrict their use in marine applications. These factors make MCFCs less suitable for the long-term, stable, and efficient operation of ships, particularly in the shipping industry, where frequent sailing and harsh environmental conditions must be addressed [9].

Proton exchange membrane fuel cells (PEMFC) have gained widespread recognition in the industry due to their low-temperature operation, rapid start-stop capability, high power-to-weight ratio, and relatively mature technological system [10]. Low-temperature operation enables fuel cells to start and stop more quickly, reducing startup time and enhancing emergency response capability in uncertain environments for ships. For example, in situations where fast departure or temporary parking is needed, PEMFCs can quickly provide stable power without requiring long preheating or cooling periods, as seen in internal combustion engines. This efficient and flexible feature significantly improves operational efficiency and safety for ships. Additionally, the high power-to-weight ratio of PEMFCs allows for a more lightweight design, optimizing space and weight distribution. Furthermore, the high energy conversion efficiency of PEMFCs enhances the conversion of chemical energy into effective mechanical energy, improving the fuel utilization of ships. This is crucial for improving navigation efficiency, reducing fuel consumption, and lowering operating costs.

However, the limitations of PEMFCs cannot be ignored: the high cost of using precious metal catalysts, strict requirements for fuel purity (especially hydrogen purity), and low tolerance for impurities such as sulfur and CO all present challenges to the widespread application of PEMFCs [11]. Moreover, current mainstream hydrogen storage technologies, such as high-pressure hydrogen storage, metal alloy hydrogen storage, and methanol reforming hydrogen production, still face efficiency bottlenecks, which further limit the increase in energy density of PEMFC systems. Despite these challenges, the application prospects of PEMFCs in the shipping sector remain broad. With the optimization of catalyst materials and improvement in hydrogen storage efficiency, it is expected that costs will decrease and system stability will increase, ultimately overcoming existing limitations and promoting the widespread adoption of PEMFCs in marine power systems.

Solid oxide fuel cells (SOFC) have demonstrated significant advantages in the maritime sector.

2.2. SOFCs

First, the high fuel adaptability of SOFCs makes them particularly suitable for the diverse fuel needs of ships. Vessels can utilize a variety of fuel types, including hydrogen, liquefied natural gas (LNG), methanol, and even diesel, ensuring flexible energy choices for ships. This adaptability is especially critical in the context of the global shipping industry's gradual transition to low-carbon emissions, with SOFC technology providing essential support for the use of low-carbon fuels [12].

Second, the high waste heat recovery efficiency of SOFCs is particularly important in ship applications. Ships typically require a large amount of energy to operate both for navigation and onboard systems. SOFCs can efficiently recover and utilize waste heat, improving overall energy efficiency, while also helping to reduce energy consumption and emissions [13]. In addition, the long lifespan and stable performance of SOFCs make them highly reliable and durable in the demanding maritime environment, particularly during long-duration voyages and under harsh sea conditions, thereby reducing maintenance and replacement costs [14]. Furthermore, the high operating temperature of SOFCs aligns well with the high-efficiency thermal energy conversion systems required by ships, enabling efficient operation in the ship's propulsion system and maintaining stable power output during long-term operation [15].

When integrated into a hybrid power system on ships, SOFCs offer further benefits by complementing other energy sources, such as diesel engines, batteries, or wind turbines. The SOFC

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hybrid system typically operates by using the SOFC to supply continuous and stable power for the ship's electrical needs, while the diesel engine or other power sources handle peak load demands or provide backup power. During periods of low energy demand or cruising at lower speeds, the SOFC can operate at optimal efficiency, while the diesel engine can be used for higher power outputs when needed, such as during acceleration or heavy-duty operations. This dynamic energy management significantly improves overall system efficiency and reduces fuel consumption and emissions. Moreover, the integration of SOFCs with energy storage systems, such as lithium batteries or supercapacitors, allows the ship to optimize its energy use based on operating conditions, providing flexibility in fuel usage and further reducing the environmental footprint.

Therefore, the SOFC hybrid power system not only enhances energy utilization efficiency on ships but also provides a reliable technological pathway for achieving greener and more sustainable maritime operations.

2.3. Analysis of SOFC Thermal Shock Resistance Performance

Thermal shock refers to the mechanical stress caused by rapid temperature changes during the start-up, shut-down, or load variations of solid oxide fuel cells (SOFCs). These stresses arise from the differences in thermal expansion coefficients between various materials inside the cell. When the temperature changes too quickly, different parts of the materials cannot adapt synchronously to the temperature variations, resulting in stress. When these stresses exceed the material's tolerance, they may lead to crack formation or structural damage, thereby affecting the long-term stability and reliability of SOFCs [16].

In the lifecycle of SOFCs, thermal shock typically occurs at several stages: during the initial start-up, when the battery needs to be rapidly heated to its operating temperature; during shutdown or power outages, when the temperature drops rapidly; and during load changes, when the battery temperature fluctuates. Each abrupt temperature change may cause cumulative damage to the battery materials. Especially under frequent thermal cycling conditions, this thermal shock effect can accelerate battery degradation. Therefore, optimizing the thermal management system of the SOFC to slow the rate of temperature change is an important means of extending its service life and improving reliability [17]. The impact of thermal shock on SOFCs is mainly reflected in the following aspects:

(1) Reduction of Interface Strength: High temperature fluctuations weaken the interface strength between various components of the SOFC. For example, the interface between the electrolyte and the electrode may develop microcracks under thermal shock, leading to a decrease in interface strength and, consequently, affecting the overall performance of the cell.

(2) Thermal Fatigue of Materials: Due to frequent temperature changes during the start-up and shutdown processes of SOFCs, materials experience thermal fatigue. This thermal fatigue gradually weakens the mechanical performance of the materials and shortens the lifespan of the battery components [18].

(3) Electrode Degradation Caused by Thermal Stress: Thermal shock can lead to changes in the microstructure of electrode materials, thereby affecting their electrochemical performance. For example, anode materials may undergo particle coarsening or changes in chemical composition under high-temperature variations, resulting in a decrease in electrode activity [19].

(4) Chemical Instability: High temperature changes can not only cause mechanical stress but may also lead to chemical instability of materials. For instance, electrolyte materials may undergo phase transitions or chemical reactions under thermal shock, resulting in a decrease in their ion conduction performance.

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(5) Degradation of Sealing Materials: The sealing materials in SOFC systems are prone to aging or degradation under thermal shock, resulting in decreased gas tightness. This can lead to fuel and oxidant leakage, affecting the efficiency and safety of the cell [20].

(6) Structural Deformation and Distortion: SOFC components may undergo structural deformation or distortion under thermal shock, affecting the geometric integrity and sealing performance of the cell. This deformation not only leads to stress concentration but also influences the gas flow and reaction efficiency inside the cell [21].

The impact of thermal shock on SOFCs involves multiple aspects. Among these, the first two factors (reduction of interface bonding strength and material thermal fatigue) primarily manifest as the degradation of the mechanical properties of the materials themselves, while the following four factors (electrode degradation, chemical instability, sealing material degradation, and structural deformation) are secondary effects triggered by the thermal shock response of the materials. For example, the reduction of interface bonding strength may lead to electrode degradation and seal failure, while material thermal fatigue may accelerate structural deformation. These effects not only affect the short-term performance of SOFCs, but also their long-term stability and reliability throughout their lifecycle. Overall, the impact of thermal shock on SOFCs is a multi-layered, multi-dimensional process that is closely related not only to the characteristics of the materials themselves but also to their coordination and interactions within the structure.

Currently, numerous studies focus on improving the thermal shock resistance of SOFCs.

Guan et al. proposed a planar-tube anode-supported cell structure with a double-sided cathode, which effectively reduced thermal stress during thermal cycling and alleviated the problem of decreased interfacial bonding strength. By optimizing the structure, the mechanical strength and redox tolerance of the cell were enhanced, significantly improving its thermal cycling performance. However, this design did not consider the impact of thermal cycling on the durability of the SOFC system, especially under constant current operation, where internal temperature increases could lead to screw loosening, thereby affecting interfacial bonding strength. Therefore, potential issues with this approach remain in practical operations.

Jiawen Pan et al. [22] conducted a stability study on the electrical performance of an SOFC stack with an external manifold structure after 15 thermal cycles. They found that a reasonable choice of cathode contact materials and optimization of interconnect materials could significantly enhance the thermal cycling stability of the SOFC stack and alleviate thermal fatigue of the materials. This study fills the gap in the verification research under actual complex SOFC stack operating conditions and provides an effective optimization path for the electrical performance stability of SOFCs during thermal cycling. However, this study does not address the impact of material degradation on the overall performance during long-term operation, particularly the long-term stability of sealing materials and the cumulative effect of structural deformation in high-temperature environments. Further research is required.

M. Faisal Riyad D et al. [23] used the freeze-casting process to prepare porous YSZ ceramics, and by optimizing the pore structure and morphology, they effectively improved the thermal shock resistance of the material, alleviating electrode degradation due to thermal stress and chemical instability at high temperatures. Although this method significantly enhanced the thermal shock resistance of the material, they did not consider the potential negative impact of uneven defect distribution in the YSZ samples on the mechanical strength, which affected the reliability of the test results. In addition, the study should focus on the impact of changes in the material's microstructure on performance during long-term operation, further optimizing the design to improve the overall durability of the SOFC.

Gurbinder Kaur et al. [24] addressed the problem of sealing material degradation by mixing different glass compositions and ball milling for 5 hours to prepare glass composite sealing materials,

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improving their chemical compatibility and reducing thermal stress between SOFC components. This method alleviated the problem of cracks in the sealing material at high temperatures, thus improving the mechanical and structural integrity of the battery stack. However, the thermal treatment conditions in the experiment were only at 850°C for 1000 hours, which could not fully represent the long-term performance under actual SOFC operating conditions, potentially leading to performance degradation in practical applications. Moreover, only seven glass composite materials were tested for compatibility with the solid oxide electrolyte YSZ, which is insufficient to cover all possible material combinations. Further research needs to expand the range of material testing and simulate a thermal treatment process closer to actual operating conditions to ensure the long-term reliability of the sealing material and the overall stability of the SOFC system.

Hagay Hayun et al. [25] adopted multiphase materials to solve the problems of structural deformation and warping. This strategy successfully reduced the coefficient of thermal expansion (CTE) mismatch between SOFC components and improved thermal shock resistance (TSR). However, although the multiphase materials effectively improved thermal expansion matching, this study did not perform performance simulation and testing under actual operating conditions, limiting its application potential in practical operations. Further research should combine actual operating environments, simulate extreme conditions such as high temperature and high humidity, and verify the long-term performance of multiphase materials under complex conditions to ensure their stability and reliability in SOFC systems, thereby enhancing their overall application prospects.

3. Conclusion

In conclusion, the exploration of thermal shock resistance in solid oxide fuel cells (SOFCs) for hybrid electric ships underscores the pivotal role these systems play in advancing green shipping technologies. Our study has thoroughly examined the impact of thermal shock on SOFCs and identified several key strategies for mitigating these effects. Optimized cell design, appropriate material selection, and structural enhancements are crucial for improving the thermal shock resistance and overall reliability of SOFCs in marine environments.

The findings indicate that SOFCs, with their high fuel adaptability and efficiency, represent a viable and sustainable solution for hybrid electric vessels, offering significant advantages over traditional diesel engines. These advantages include lower emissions, higher thermal efficiency, and better energy utilization, which are essential for addressing the pressing environmental and energy challenges facing the shipping industry.

However, while our research provides valuable insights into the optimization of SOFC performance during thermal cycling, it also highlights the need for further studies on long-term material degradation and the cumulative effects of structural fatigue. Addressing these issues is critical for ensuring the long-term stability and efficacy of SOFCs in maritime applications.

Overall, this study contributes to the sustainable development of hybrid-powered ships and offers practical guidance for enhancing SOFC performance under challenging marine conditions. Continued research and innovation in this field are essential for realizing the full potential of SOFC technology and achieving greener, more efficient maritime transport solutions.

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