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RESEARCH ARTICLE

COGENERATION VIA SOLID OXIDE FUEL CELLS

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ABSTRACT

Although employment of fossil fuels for power generation may have seemed inevitable, fuel cells since have emerged; however, have been a sustainable energy means. Thanks to their several types, different characteristics and great performance, fuel cells have found a wide range of applications. Among fuel cells, solid oxide fuel cells have been harnessed for the synthesis of valuable chemicals without compromising energy production in a cogeneration setup. It is possible to generate electricity while simultaneously producing syngas with different compositions. This is accomplished through the dry reforming of various fuels, such as CH_4-CO_2, pure CH_4, and other hydrocarbon fuels, aided by selective oxidation. Although that being said, solid oxide fuel cells not only demand difficult operating conditions, but their components such as the cathode, electrolyte, anode, interconnects and sealants must also exhibit several essential bespoke properties. Another significant hurdle to the wider adoption of fuel cells, especially solid oxide fuel cells that utilize hydrogen as a key fuel, is the absence of a comprehensive infrastructure for the production, storage and distribution of hydrogen.

KEYWORDS

Fuel cell, electrolyte, cogeneration, reforming, syngas.

1. INTRODUCTION

The limited nature of fossil fuel sources, along with their harmful effects on the environment and climate, underscores the need for the development of alternative sustainable energy sources (Arshad, et al., 2018; Abd Aziz, et al., 2020; Zakaria, et al., 2020a). In this context, fuel cells have emerged as a promising technology not only for power generation, but also for valuable chemicals production through cogeneration, offering high efficiency, fuel versatility, combustion-free operation and nearly zero nasty carbonaceous emissions (Arshad, et al., 2018; Fan, et al., 2018; Song, et al., 2019). Additionally, fuel cells play a crucial role in a hydrogen-based energy system, which has become an essential element in energy production due to its capacity to decarbonize the energy sector by offering carbon-free fuel alternatives and possessing a high energy density.

A fuel cell directly converts the chemical energy from fuels like hydrogen, ammonia and hydrocarbons such as methane, etc. into electricity. This process is similar to that of batteries; however, fuel cells utilize gaseous electrodes and do not require recharging, operating continuously as long as both fuel and oxidant are supplied to these electrodes (Stambouli, AB. and Traversa, E., 2002; Kirubakaran, et al., 2009; Mahato, et al., 2015). Furthermore, their efficiency is not constrained by the Carnot cycle, unlike internal combustion heat engines (Chan, SH., 2004; Abdalla, et al., 2018).

Recently, fuel cells, which were first developed in 1838, have attracted a tremendous global interest as effective and eco-friendly source of energy (Steele and Heinzel, 2001; Winter and Brodd, 2005). A fuel cell is a device that produces electricity via an electrochemical reaction rather than through combustion. It continuously transforms chemical energy from a fuel (hydrogen) into its electrical equivalent energy through redox reactions, provided that both the fuel and oxidant (oxygen/air) are supplied to the electrodes of the cell (Yuan, et al., 2021; Stambouli, and Traversa, 2002; Kirubakaran, et al., 2009; Mahato, et al., 2015; Rashidi, et al., 2022; Si, et al., 2022). Essentially, a fuel cell is made up of three closely positioned components, an anode with a catalyst from certain material(s) depending on the fuel cell type with certain reactive characteristics, an electrolyte membrane, that facilitates the movement of ions between the electrodes, and a cathode (Ogawa, et al., 2018).

Generally, fuel cells work by typically combining hydrogen, although other fuels such as methane, ammonia and other hydrocarbons, etc., can also be used, and oxygen to produce electricity, heat and water. Fundamentally, in a typical fuel cell during system operation, hydrogen is introduced at the anode and oxygen is introduced at the cathode. A catalyst at the anode breaks down the hydrogen molecules, via an oxidation reaction, into protons and free electrons ($H_2 \rightarrow 2H^+ + 2e^-$). The protons (positive hydrogen particles) move through the electrolyte, which depending on the fuel cell type as would be demonstrated later can be a solution of a certain type or a porous membrane with bespoke characteristics, towards the cathode side, while the electrons are directed through an external circuit, creating an electric current and generating excess heat. On the contrary, at the cathode, the protons, electrons and oxygen, via a reduction reaction, react to form water molecules ($4H^+ + O^2 + 4e^- \rightarrow 4H_2O$) (Ralph et al., 1998; Fan, et al., 2021; Osman, et al., 2021).

Fuel cells are exceptionally clean due to their chemical processes. Those

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that utilize pure hydrogen fuel produce no carbon emissions, generating only electricity, heat and water as byproducts. Additionally, although certain fuel cell systems can operate on different types of fuel such as hydrocarbon fuels, natural gas, biogas, chemical hydrides and methanol, using hydrogen in fuel cells; however, is environmentally-friendly since it produces no emissions of pollutants (Psoma and Sattler 2002). Unlike traditional energy production methods such as steam turbines and internal combustion engines, which rely on combustion, fuel cells generate electricity through chemical reactions, allowing them to achieve significantly higher efficiencies producing no carbon dioxide and other greenhouse gases as the case with steam turbines and internal combustion.

One of the main reasons fuel cells could achieve higher efficiencies, in comparison to steam turbines and internal combustion engines, is that they do not operate on the Carnot cycle (Liebhafsky, 1959; Lutz, et al., 2002; Chan, 2004; Abdalla, et al., 2018). Also, operational temperatures in fuel cells are extremely lower than those encountered in internal combustion engines (Xu, et al., 2021). To further enhance efficiency, a fuel cell can be integrated with a combined heat and power (CHP) system that utilizes the waste heat from the cell for heating or cooling purposes. It is beyond the scope of this review; however, to further discuss this topic discussed elsewhere (Bagherian and Mehranzamir, 2020; Kwan, et al., 2020; Sinha, et al., 2023).

Moreover, fuel cells offer significant advantages over traditional batteries and combustion-based technologies used in critical sectors such as electronics, residential power, power generation, passenger vehicles and military applications. Furthermore, fuel cells are advantageous over other renewable energy sources. Unlike traditional batteries, which require regular electrical recharging, fuel cells generate electricity continuously as long as they have a supply of fuel. Moreover, batteries have the capability to store hydrogen, whereas fuel cells can deliver a continuous supply of electricity as long as hydrogen (the fuel) and oxygen (the oxidizing agent) are accessible from external source(s). Along with the previously mentioned differences, the electrodes in batteries gradually wear out over time with prolonged use, a phenomenon that is not present in fuel cells (Spingler, et al., 2017; Aydın, et al., 2018).

They operate with greater efficiency than combustion engines, achieving an electrical energy conversion efficiency of 60% or higher while producing lower emissions. Also, unlike other clean renewable energy technologies sources, e.g., wind turbines and solar panels, etc., fuel cell systems occupy significantly less space. Fuel cell systems offer a clean, efficient and reliable power source with a fuel flexibility including ammonia, methane and hydrogen, etc. The only byproduct of hydrogen fuel cells during power generation is water, meaning there are no carbon dioxide emissions or air pollutants that contribute to smog and health issues. Additionally, fuel cells operate quietly due to having fewer moving parts. While there are various types of fuel cells, they all function in a similar fashion (Fan, et al., 2021).

Fuel cells offer scalability, allowing individual units to be connected to create stacks. These stacks can then be integrated into larger systems. The size and power of fuel cell systems can vary significantly, ranging from replacements for combustion engines in electric vehicles to extensive multi-megawatt setups that supply electricity directly to the utility grid. Furthermore, fuel cells today are utilized in various applications, including powering homes and businesses, ensuring the operation of essential facilities such as hospitals, grocery stores and data centers, as well as driving a diverse array of vehicles, including cars, buses, trucks, forklifts and trains. To this end, this paper aims to provide an overview of fuel cells; in general, with a particular emphasis on cogeneration via solid oxide fuel cells.

2. TYPES OF FUEL CELLS

According to the type of electrolyte material used as well as the operating conditions, fuel cells can be categorized into alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), protonic ceramic fuel cells (PCFCs), molten carbonate fuel cells (MCFCs), bio-electrochemical fuel cells or microbial fuel cells (MFCs), direct carbon fuel cells (DCFCs), direct methanol fuel cells (DMFCs), proton exchange membrane fuel cells (PEMFCs) and solid oxide fuel cells (SOFCs) (Fan, et al., 2021; Zhang, et al., 2024; Osman, et al., 2021). This wide spectrum of fuel cell types present multiple opportunities for hydrogen use in transportation, power generation and other fields in accordance to the necessary power output range (Fan, et al., 2021). AFCs are a category of fuel cells that utilize a liquid alkaline solution, such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) as their electrolyte, with hydroxide ions (OH^-) acting as the mobile ions at lower oxygen reduction over-potentials (Seetharaman, et al., 2013; Kapoor, et al., 2020). These cells function at moderate temperatures, typically between 20 °C to 60 and 250 °C, making them ideal for applications in spacecraft, submarines and certain stationary power generation systems (Fan, et al., 2021; Zhang, et al., 2024). PAFCs utilize liquid phosphoric acid as their electrolyte (Oh, et al., 2023). These fuel cells function at moderate temperatures between 150 and 220 °C, making them ideal for applications like stationary power generation stations and CHP systems, due to their wide output range (Fan, et al., 2021; Zhang, et al., 2024). In addition, PCFCs are a category of fuel cells that utilize a proton-conducting ceramic electrolyte, like barium cerate or barium zirconate (Tsvetkov, et al., 2022). These cells function at elevated temperatures, typically between 500 and 700 °C, which makes them ideal for uses in stationary power generation stations and CHP systems (Fan, et al., 2021).

MCFCs are a variety of fuel cells that utilizes a molten mixture of carbonate salts, including lithium and potassium carbonates, as the electrolyte (Ghorbani, et al., 2021). These cells function at elevated temperatures, typically between 600 and 700 °C, which makes them ideal for applications such as large-scale stationary power generation stations and CHP systems, due to their wide output range as well (Fan, et al., 2021; Zhang, et al., 2024). Bioelectrochemical fuel cells, commonly referred to as microbial fuel cells (MFC), harness different types of electrolytes, such as polymeric membranes and ionic liquids, to produce electricity (Yaqoob, et al., 2023). They function effectively at ambient to moderately high temperatures, making them ideal for applications like wastewater treatment, remote sensing and small-scale power generation stations (Zhang, et al., 2024).

DCFCs are a category of fuel cells that utilize solid yttria stabilised zirconia, molten carbonate or molten hydroxide as the electrolyte. These cells function at elevated temperatures, typically between 600 and 900°C, which makes them ideal for CHP systems. DMFCs are a category of fuel cells that utilize solid polymeric membranes such as Nafion as the electrolyte. They function at low temperatures, typically between 60 and 120 °C, which makes them ideal for mobile applications (Edwards, et al., 2008; Wilberforce, et al., 2016; Ogawa, et al., 2018). PEMFCs are a category of fuel cells that use a polymeric membrane, like Nafion, as the electrolyte, with protons ions (H^+) serve as the mobile ions using either oxygen or air as an oxidant at the cathode (Lan, et al., 2023). They function at relatively a broad range of operating temperatures, typically between -40 °C to 50 and 100 °C, enabling rapid start-up times and making them ideal for a range of applications, such as in transportation for fuel cell electric-vehicles, portable power solutions and small-scale stationary power generation stations (Fan, et al., 2021; Zhang, et al., 2024). This has set PEMFCs along with their high specific energy apart from other fuel cell types (Fan, et al., 2021).

SOFCs are a category of fuel cells that utilize a solid ceramic material, such as yttria-stabilized zirconia (Y_2O_3-ZrO_2), as the electrolyte (Jeon, DH., 2018; Fan et al., 2021). The electrolyte, as schematically shown in Figs. (1a-b); respectively, can be an oxide ion-conductor ($O2^-$) or a proton-conductor (H^+). The materials used for oxygen ion conductors and proton conductors along with the operating conditions and fuel(s) used are available elsewhere (Si, et al., 2022). These cells function at elevated temperatures, typically between 600 and 1000 °C, which makes them ideal for applications such as large-scale stationary power generation stations, CHP systems and auxiliary power units (APUs) (Singhal, 2000; Shao, et al., 2004; Sundmacher, et al., 2005; Chalakov, et al., 2007; Zhang, et al., 2024).

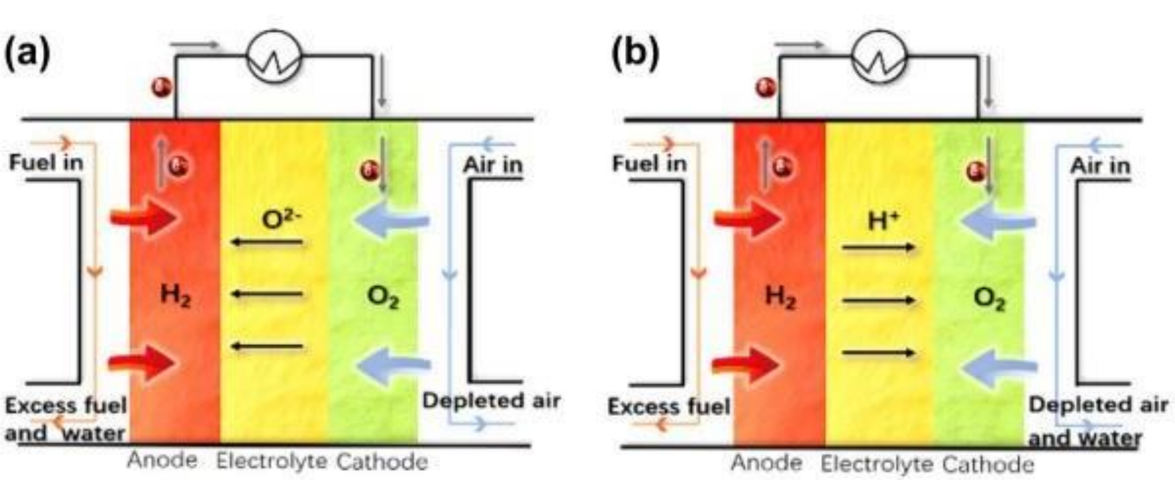

Figure 1: A Schematic Diagram of a SOFC, a- An Oxide Ion-Conducting Electrolyte and b- A Proton Conducting (Si et al., 2022).

A comparison of these various fuel cell types in terms of their advantages and disadvantages can be found in Table (1), along with some other approximate operational conditions, catalysts and fuels used and obtained electrical efficiencies.

Table 1: Types of Fuel Cell with their Approximate Operational Conditions, Catalysts and Fuels Used and Obtained Electrical Efficiencies as well as some of their Advantages and Disadvantages. Reproduced from (Qiang, 2005; Edwards et al., 2008; Fu, et al., 2010; Wilberforce, et al., 2016; Ogawa et al., 2018; Ghorbani, et al., 2021; Si, et al., 2022; Lan, et al., 2023; Zhang, et al., 2024).

Fuel Cell Type	Electrolyte	Conductible Ions	Fuel	Oxidant	Catalyst	Operating Temperature, °C	Theoretical Voltage, %	System Electrical Efficiency, %	Applications	Advantages	Disadvantages	Development
AFC	KOH solution	OH^-	Hydrogen	O_2	Nickel/ silver supportedon carbon	70-130	1.18	40-70	Military and aerospace	Cost-effective materials with high efficiency and proven technology	Sensitivity to CO_2, requirement for pure hydrogen and oxygen and restricted commercial availability	Rapid, 1-100 KW
PAFC	Liquid phosphoric acid or phosphoric acid in silicon carbide	H^+	Hydrogen	Air	Platinum supportedon carbon	175-210	1	40-55	Combined heat and regional power generation and medium to large-scale power generation	Moderate operating temperature, excellent impurity tolerance and readily available in the market	Reduced efficiency in comparison to other types, restricted fuel flexibility and comparatively high costs	Rapid, 1-200 KW
PCFC	Proton conducting ceramic material	-	-	-	-	-	-	-	-	Reduced operating temperature in comparison to SOFC, enhanced efficiency and versatile fuel flexibility	Emerging technology, restricted market presence and issues with material stability	-

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MCFC	Molten carbonate salt mixture such aslithium and potassium carbonates or alkali carbonatein lithium aluminate	$CO3^2$	Methane	Air	Lithiated nickel or nickel-chromium	550-650	1.116	50-65	Large scale power generation	Enhanced efficiency, fuel versatility and cogeneration capabilities	Elevated operating temperatures, intricate system design, material deterioration dueto corrosion and short lifespan	250-2000 KW
SOFC	Solid ceramic material such as YSZ and Y2O3-ZrO2.	O^2	Methane, ammonia and hydrogen	Air	Nickel-yttria-stabilized zirconia composite or strontium-doped lanthanm manganite	500-1000	1.13	40-72	CHP production andsmall to large- scale power generation.	Enhanced efficiency, versatile fuel flexibility and cogeneration capabilities	Elevated operating temperatures, material deterioration, and extended start-up times	1-200 KW
MFC	Polymeric membrane or ionic exchange liquid membranes	-	Organic materials	-	Carbon supports on biocatalysts or platinum	20-60	-	15-65	Wastewater treatment and biosensors	Direct conversion of waste to electricity, renewable energy sources and environmental advantages	Low power density, restricted commercial availability and system complexity	-
DCFC	solid yttria stabilized zirconia, molten carbonate or molten hydroxide	-	Carbonaceous materials	-	Carbon-based materials or lanthanum manganite doped with strontium	600-900	-	70-85	CHP generation	-	-	-
DMFC	solid polymeric membranes such as Nafion	-	Liquid methanoll-water solution		Carbon supports on platinum or a combination of platinum and ruthenium	60-120	-	50-70	Mobile applications	-	-	-

Table 1 (Cont.) : Types of Fuel Cell with their Approximate Operational Conditions, Catalysts and Fuels Used and Obtained Electrical Efficiencies as well as some of their Advantages and Disadvantages. Reproduced from (Qiang, 2005; Edwards et al., 2008; Fu, et al., 2010; Wilberforce, et al., 2016; Ogawa et al., 2018; Ghorbani, et al., 2021; Si, et al., 2022; Lan, et al., 2023; Zhang, et al., 2024).

PEMFC	Solid polymeric membrane such as low temperature Nafion or high temperature Nafionpolybenz imidazole doped in phosphoric acid	H^+	Hydrogen	Air	Low temperature carbon-supported platinum or high temperature platinum ruthenium	60-110	1.18	40-68	Mobile applications such as electric vehicles, submarine and mobile power source	Rapid startup, high power density and low operating temperature	Sensitivity to contaminants, requirement for moisture and high material costs	Rapid, 1-300 KW

3. COGENERATION VIA SOFCS

Among various fuel cell technologies referred to herein, SOFCs stand out as one of the most efficient options for power generation as well as cogeneration applications. SOFCs offer flexibility in fuel selection, operate quietly, produce low carbonaceous emissions and possess a potential lifespan of 40,000 to 80,000 hours (Stambouli and Traversa, 2002). A SOFC typically utilizes a yttrium-stabilized zirconia electrolyte. In the SOFC, the cathode absorbs oxygen molecules from the oxidant gas (air) and converts them into negative oxygen ions. These ions then migrate through the electrolyte to the anode, which is supplied with fuel, driven by a chemical potential gradient. At the anode, the oxygen ions catalytically oxidize the incoming fuel, resulting in the generation of electrons. The released electrons are; then, transferred to the cathode via an external circuit, completing the discharge process (Gou, et al., 2021). The high operating temperature of SOFCs, essential for achieving sufficient ionic conductivity, also produces significant heat byproducts that can be utilized for cogeneration of energy and valuable chemicals, as discussed in this section. Additionally, the solid-state electrolyte is advantageous as it is durable and does not lead to corrosion or handling complications. Moreover, SOFCs are cost-effective for mass production since they do not require expensive noble metals (Stambouli and Traversa, 2002; Mahato, et al., 2015; Zakaria, et al., 2020b).

Fuel cells can play a significant role in enhancing the efficiency of various power systems while also lowering the overall production costs via cogeneration. In this context, in contrary to traditional fuel cell systems, where energy density is primarily influenced by the type of fuel and operating conditions, in cogeneration systems; however, oxidizing agents supplied to the cathode are utilized for two purposes: generating value-added chemicals and producing electrical energy (Murphy, et al., 1998; Shao, et al., 2005; Stoukides, 2006; Ren, et al., 2014). In this situation, fuel cells can be categorized as electro-synthesis devices, functioning as electrochemical fuel cell reactors that produce chemical compounds in addition to the main production task of power generation (Li, et al., 2009; Amar, et al., 2011; Turygin, and Tomilov, 2015). Consequently, prioritizing the control of both the type of input and the operating conditions is essential for achieving higher value and purity in chemicals production. In this regard, energy density or power density should be considered secondary evaluation criteria, following conversion efficiency and selectivity (Yamanaka, et al., 2003; Shao, et al., 2011; Hua, et al., 2016a). By manipulating factors such as cell potential, catalyst composition, surface structure and reagent concentration, electro-synthesis offers significant advantages over traditional fuel cell redox reactions. These benefits include adjustable reaction rates and selectivity, reduced waste heat and improved selectivity and yield (Navarro, 2017). Electro-synthesis has been a highly researched area of science and holds economic advantages in industrial applications, such as wastewater treatment (Martínez-Máñez, and Sancenón, 2003; Logan, et al., 2006; Frontana-Uribe, et al., 2010; Schäfer, 2011; Francke, and Little, 2014).

To simultaneously extract value-added chemicals and electrical energy via SOFC reactors as electro-synthesis devices, HSC chemistry software, that is concerned with enthalpy, entropy and heat capacity and is mainly used as a static process simulator, is used (Holler, 1996). Research has indicated that, the conversion process, specifically the selective oxidation of the fuel, is significantly influenced by the current passed through the fuel cell reactor (Ji et al., 2009). This current can be adjusted by modifying the load (resistance) in the external circuit of the fuel cell reactor, resulting in increased conversion rates with higher current levels. In such reactors, the anodic side is primarily utilized for the production of value-added chemicals through selective oxidation of the fuels. In this context, selective oxidation refers not only to the selective groups present in the fuel, but also to the selective and distinct compositions of the mixed gaseous fluid that undergoes oxidation during the cogeneration process. By this manner, the selective oxidation of the used fuels can help adjust the components to align with a theoretical ideal, which is crucial for practical applications and realizing economic benefits.

A potential approach for a cogeneration system involves a CH_4–CO_2 dry reforming process, followed by the selective oxidation of the hydrogen produced in-situ within high-performance proton-conducting SOFCs. This method aims to simultaneously generate CO-rich syngas and electricity, effectively utilizing the heat produced during the selective hydrogen oxidation phase (Si et al., 2022). This selective oxidation process predominantly relies on O-2 ions transferred from the cathodic side or involves the dehydrogenation of the fuel to remove hydrogen atoms and create unsaturated bonds (Huang and Huang, 2008; Alexander, et al., 2011; Fu, et al., 2011a; Liu, et al., 2015). Specifically, O2-conducting and H+-conducting electrolyte membranes are employed in these reactors, respectively. However, the latter system exhibits significantly higher selectivity due to its limited controllability over the degree of oxidation (Osseo-Asare, et al., 1989; Zawodzinski, et al., 1993; Otsuka, et al., 1996; Sone, et al., 1996; Skou, et al., 1997; Baerns, M. and Buyevskaya, O., 1998; Lee, et al., 1998; Ren, et al., 2000; Chen, et al., 2005; Tao, et al., 2006; Zuo, et al., 2006; Cavani, et al., 2007; Azizi, et al., 2008; Guo, et al., 2009; Ji, et al., 2009; Fabbri, et al., 2010; Fu, et al., 2010; Fu, et al., 2011a; Fu, et al., 2011b; De Schepper, et al., 2012; Zhang, et al., 2013).

Similarly, dry reforming process can be achieved by an additional layered structure integrated to create an anode support within a layered SOFC reactor utilizing a $Ni_{0.8}Co_{0.2}$-$La_{0.2}Ce_{0.8}O_{1.9}$ (NiCo-LDC) composite. Employing scanning electron microscopy for the layered proton-conducting SOFC reactor used, indicted the successfulness of the implemented designed structure (Hua, et al., 2016b). Elsewhere, a feed stream consisting of CH_4 and CO_2 was completely reformed using a high-performance NiCo-LDC catalyst layer, producing syngas (CO and H_2 in a 1:1 ratio) during the anode reactions. In this process, some of the H_2 in the syngas underwent selective oxidation on the anodic catalyst Ni-BaZr0.1Ce0.7Y0.1Yb0.1O3−δ (BZCYYb). This selective oxidation not only generated electrical power and CO-enriched syngas, but also supplied the total heat required for internal dry reforming. It was found that thermal independence can be achieved when H_2 utilization exceeds 52%, which corresponds to a total fuel utilization of 26%. As a result, the energy input needed for conventional methane reforming can be significantly counterbalanced (Rosen, 1991; Edwards and Maitra, 1995).

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In a manner similar to the previously mentioned method of selectively oxidizing the sweep gas right after the reactions in the reforming layer, an alternative structure can be developed in a reverse order, focusing on the sequence of successive reactions. This involves reforming the off-gas from a fuel cell reactor, where partial oxidation occurs concurrently with the extraction of electrical energy derived from the difference in Gibbs free energy between the feed gas and the selectively oxidized products. Shao et al. incorporated a downstream catalyst within a single-chamber SOFC reactor to enhance its cogeneration capabilities using methane as a fuel. A bilayer electrolyte SOFC reactor operating in a CH_4:O_2 ratio of 2:1 achieved an open circuit voltage of 1.07 V and a peak power density of around 1,500 mW/cm^2 at 700 °C, while also facilitating the partial oxidation of methane into CO, CO_2, H_2 and also H_2O. Subsequently, the exhaust gas was combusted via a GdNi/Al_2O_3 catalyst at a temperature of 850 °C, resulting in the production of syngas. Additionally, a portion of this combustion energy is transformed into electrical energy. Throughout the entire process of converting methane to syngas, the conversion rate exceeded 95%, with selectivities for CO and H_2, due to the reduction of the overly oxidized CO_2 and H_2O, surpassing 98% and a H_2:CO ratio of approximately 2:1 (Si et al., 2022). It was also observed that the polarization current density had no impact on either the rate of syngas formation or the H_2:CO molar ratio (Shao et al., 2011).

To clarify and direct the design of SOFC reactors, several theoretical modeling studies have been published. Zhu et al. investigated methods for scaling electrochemical partial oxidation processes from laboratory settings to practical applications using computational models. Their work has focused on the partial oxidation of hydrocarbon fuel streams to simultaneously generate syngas composed of H_2 and CO and electrical energy using a tubular SOFC reactor that internally reforms methane within its anode structure. A key challenge identified in this reaction was the tendency for carbon to accumulate on Ni-based anode catalysts. To address this issue, they examined the implementation of barrier layers to mitigate carbon deposition. A list of additional anodic catalysts utilized for this purpose can be found elsewhere (Si et al., 2024). The designed tubular cell was capable of producing syngas and electricity from methane as the primary fuel source. Although fuel flow rates are so elevated that not all of the produced syngas can be oxidized through electrochemical means (Zhu et al., 2008). A similar work has been conducted by Xu et al. in which a 2D model designed for a tubular direct carbon SOFC reactor aimed at the cogeneration of CO and electricity to comprehend the physical and chemical processes occurring in this process. They took into account various factors, such as the distance between the carbon chamber and the anode electrode, the operating temperature and the length of the fuel cell. Additionally, they compared electrolyte- supported and anode-supported direct carbon SOFCs to analyze how the type of support influences cogeneration of CO and electrical power output. It was found that direct carbon SOFC demonstrates strong performance even when there is a significant distance between the carbon bed and the porous anode, suggesting its potential for large-scale applications. However, the performance was found to decline as the temperature decreases, primarily due to reduced kinetics of the Boudouard reaction. It has also been observed that the molar fraction of CO at the anode can be effectively regulated by modifying the operating conditions, making this SOFC suitable for simultaneous electricity and CO production. Additionally, the current density within the fuel cell reactor used shows a slight increase along the length of the cell, which contrasts with the behavior demonstrated in H_2-fueled SOFCs. Furthermore, while the anode-supported configuration enhances the electrical output of the fuel cell used, it is less favorable for CO production. This model can be utilized for system-level design optimization of direct carbon SOFCs (Xu et al., 2016).

Cogeneration also refers to the simultaneous production of heat and power or cold and power. Accordingly, tri-generation systems refer to the simultaneous production of cold, heat and power. Cogeneration refers to the simultaneous production of two distinct forms of useful energy from a single primary source, such as fuel cells. In this process, the electricity generated by a fuel cell is utilized to satisfy electrical demand(s), while the heat produced is harnessed for heating purposes. This approach can achieve an overall efficiency of approximately 95%. Fuel cell systems cogeneration applications are composed of various components, including fuel processors, power suppliers, heat recovery units, electrochemical and thermal energy storage units, control devices and additional equipment like pumps and stacks. Numerous facilities have been established commercially to enhance the performance of these cogeneration systems, with various projects implemented globally.

In Japan, the ENE-FARM project has installed around 300,000 units as of 2018, providing homes with the necessary electricity and heat for daily activities through the use of PEMFCs, which range from 0.3 to 1 kilowatt. The process begins with liquefied petroleum gas being fed into a reformer, where it is converted into hydrogen. This hydrogen is; then, combined with oxygen in the fuel cell(s) to generate water, electricity and heat for various residential applications (Yue et al., 2021). Furthermore, the production of micro-cogeneration fuel cells has seen significant growth in Europe. Between 2012 and 2017, over 1,000 micro-combined heat and power fuel cells were deployed across ten European countries. A life cycle assessment conducted for such projects has demonstrated that cogeneration fuel cells are more environmentally friendly compared to traditional gas boilers and heat pump systems, primarily due to their lower greenhouse gas emissions (Osman et al., 2021).

In addition to cogeneration, tri-generation which is an advanced form of cogeneration that utilizes a single primary energy source to provide the necessary cooling through thermally driven systems. Heat pumps operate on the principle of generating cooling from a thermal source, typically employing condenser and evaporator equipment. In this process, the gas released from the absorbent or adsorbent is cooled in the condenser, transforming it into a liquid by releasing heat (the refrigeration process). The cooled liquid; then, moves to the evaporator, where it evaporates by absorbing heat from its surroundings. Notably, tri-generation fuel cells contribute to a reduction in carbon emissions while improving energy efficiency (Yue et al., 2021). It was reported that the use of a 593-kilowatt SOFC in conjunction with absorption chillers led to a significant reduction in carbon emissions by approximately 50%, while energy efficiency increased to 75% (Fong and Lee, 2014). Additionally, a simulated 339-kilowatt SOFC, when paired with a combustor and heat recuperation system, effectively recovered around 267 kilowatts of heat with an efficiency of 84%. Furthermore, it was noted that the 339-kilowatt SOFC, when equipped with an absorption chiller, produced approximately 303.6 kilowatts of cooling with an efficiency of 89% (Yu et al., 2011).

To this end, SOFC reactors can be regarded capable to offer several advantages over traditional catalytic reactors. Firstly, when fuel cells are employed as reactors, the internal reactions occur continuously (Stoukides 2006; Garagounis, et al., 2011), for which the overall reaction conversion and the instantaneous conversion are identical (Si et al., 2022). Also, the separate feeding of reactants into the reaction system minimizes competition between oxidation and reduction reactions at the same sites, thereby reducing the risk of explosions. Thirdly, fuel cell reactors can be smaller and experience less corrosion. Additionally, by leveraging electrochemical reactions, they can operate at significantly lower temperatures. Fourthly, by adjusting the electrode potential or the external load, it is possible to change the type of product and the associated chemical selectivity. Furthermore, the diversity in particle sizes and the surface characteristics of the catalysts in the electrodes are crucial for optimizing selectivity and efficiency. Fifthly, the recyclability of the reactants makes their use cost-effective, enabling fuel cell reactors to fulfill all operational requirements while also generating additional power (Liebhafsky, 1959; Lutz, et al., 2002; Martínez-Máñez, and Sancenón, 2003; Zeng, et al., 2008; Li, et al., 2009; Chen, et al., 2010; Frontana-Uribe, et al., 2010; Jiang, et al., 2010; Amar, et al., 2011; Garagounis, et al., 2011; Schäfer, 2011; Yao, et al., 2011; Ferreira, et al., 2013; Francke, and Little, 2014; Turygin, and Tomilov, 2015; Bao, et al., 2017; Navarro, 2017; Djerioui, et al., 2019, Si, et al., 2022).

Moreover, in SOFC reactors, both oxidation reactions (occurring at the anode) and reduction reactions (occurring at the cathode), which are essential for a traditional fuel cell, can be employed, often involving radical intermediates. These intermediates can form during initial reactions at the electrode surface, subsequently diffusing into the solution to engage in further reactions (Amar, et al., 2011; Navarro, 2017). This process allows for an expanded range of reactions beyond mere direct redox reactions at the electrode of a traditional SOFC. Drawing inspiration from these fuel cell reactors, they can be customized to simultaneously produce value-added chemicals with high conversion efficiency and generate high-density power within the same reactor. This process requires no external electrical energy and results in minimal emissions of carbonaceous or other pollutants (Steele, and Heinzel, 2001; Winter, and Brodd, 2005; Garagounis, et al., 2011; Ferreira, et al., 2013; Pan, et al., 2017). The remarkable characteristics of SOFC reactors promote energy efficiency when used for electricity generation.

Furthermore, the flexibility to select specific oxidation and reduction reactions at the separate anode and cathode enables the synthesis of various value-added chemicals. Additionally, using membranes in a sandwich configuration to separate the anode and cathode components ensures the purity of the final product (Garagounis, et al., 2011; Djerioui, et al., 2019). Furthermore, this process requires no external electrical energy and results in minimal emissions of carbonaceous or other pollutants (Steele, and Heinzel, 2001; Winter, M. and Brodd, 2005; Garagounis, et al., 2011; Ferreira, et al., 2013; Pan, et al., 2017). As a result, these innovative reactors can significantly contribute to a low-carbon economy, aligning with the idea of carbon neutrality. Collaborative efforts among multinational teams of scientists have focused on clean energy solutions that go beyond carbon neutrality by actively removing CO_2 from the atmosphere. These distinctive reactors offer the potential to either reduce CO_2 emissions or capture CO_2, presenting a viable strategy for meeting carbon neutrality objectives (Zeng, et al., 2008; Chen, et al., 2010; Jiang, et al., 2010; Yao, et al., 2011; Ma, et al., 2017).

Fuel cells are devices that transform the chemical energy of hydrogen, and possibly additional fuels such as hydrocarbon fuels, natural gas, biogas, chemical hydrides and methanol, into electrical energy through an electrochemical process. They can be more energy-efficient than conventional combustion-based power generation methods, as they directly convert chemical energy into electrical energy (Chehrmonavari, et al., 2023). When hydrogen is used as fuel, fuel cells produce only water and heat as byproducts, leading to low greenhouse gas emissions and decreased air pollution. Available in various sizes and capacities, fuel cells are suitable for a wide array of applications, ranging from portable electronics to large-scale power generation (Zakaria, et al., 2021). Additionally, fuel cells operate quietly, making them an appealing choice for residential and urban environments (Acha, et al., 2020).

Nevertheless, fuel cells in general, PEMFCs; in particular, can be costly due to the use of expensive materials such as platinum and the requirement for specialized components (Sajid, et al., 2022). Additionally, certain types of fuel cells may have limited lifespans or experience performance decline over time, which can affect their long-term reliability and cost-effectiveness, such as MCFCs; for instance (Abdelkareem, et al., 2019). Moreover, given the challenging operating conditions of SOFCs, which include high temperatures, redox reactions and thermal cycling, as well as a toxic atmosphere, their components (cathode, electrolyte, anode, interconnects and sealants) must possess several essential properties (Price et al., 2021). These include suitable conductivity in a way the electrolyte should act as an electronic insulator while providing excellent ionic conductivity, and the that electrodes must demonstrate both strong electronic and ionic conductivity. Also, the components of a SOFC ought to exhibit acceptable chemical, thermal, morphological and mechanical stability. Among these various components, there should be a good chemical, thermal and mechanical compatibility. The electrodes; in particular, should be of a porous structure to facilitate adequate gas transport to the reaction sites, although the electrolyte should be dense to prevent gas mixing. Also, the interconnects of a SOFC must have high electrical conductivity, excellent gas tightness and strong resistance to oxidation, sulfation and carbon deposition. Finally, the sealants should possess hermetic properties and insulating characteristics (Fergus, 2006; Sun, et al., 2010; Kendall, and Kendall, 2015; Mahato, et al., 2015). Besides, the broader adoption of fuel cells; in general, is contingent upon the establishment of hydrogen infrastructure for production, storage and distribution (Mohideen, et al., 2023). Ongoing research in materials science; however, may lead to the identification and development of newer materials with enhanced hydrogen storage capabilities. Further studies could also optimize the integration of solid- state hydrogen storage materials with fuel cells and other energy conversion systems. As solid-state hydrogen storage technologies advance, they may become commercially viable, paving the way for newer applications and industries (Zhang, et al., 2024).

4. CONCLUSIONS

In this paper, a comparison has been made among various types of fuel cells, highlighting their advantages and disadvantages, along with approximate operational conditions, the catalysts and fuels utilized and the electrical efficiencies achieved. Fuel cells clearly demonstrate greater energy efficiency compared to traditional combustion-based power generation methods, as they convert chemical energy directly into electrical energy. When hydrogen serves as the fuel, the only byproducts are water and heat, resulting in minimal greenhouse gas emissions and reduced air pollution. Fuel cells come in a variety of sizes and capacities, making them ideal for numerous applications, from portable electronics to large-scale power generation. Furthermore, their quiet operation makes them an attractive option for residential and urban settings.

However, fuel cells, especially PEMFCs, can be expensive because they utilize costly materials like platinum and require specialized components. Furthermore, some fuel cell types, such as MCFCs, may have limited lifespans or experience a decline in performance over time, impacting their long-term reliability and cost-effectiveness.

Inspired by the ability of SOFCs to be tailored for the simultaneous production of value-added chemicals with high conversion efficiency while generating high-density power within a single reactor, this paper has also emphasized on SOFCs as one of the most efficient options amongst other fuel cells for power generation as well as cogeneration applications. This process requires no external electrical energy and results in minimal emissions of carbonaceous or other pollutants. By utilizing SOFCs in various configurations as electro-synthesis reactors for cogeneration, researchers have found that it is feasible to generate electricity while simultaneously producing syngas with varying compositions. This is achieved through the dry reforming of multiple fuels, including CH_4-CO_2, pure CH_4 and other hydrocarbon fuels, facilitated by selective oxidation.

Nevertheless, in addition to the challenging harsh operating conditions faced by SOFCs which include high temperatures, redox reactions and thermal cycling, as well as a toxic environment, their components (cathode, electrolyte, anode, interconnects and sealants) must possess several critical properties. The electrolyte should function as an electronic insulator while exhibiting excellent ionic conductivity, while the electrodes need to demonstrate strong electronic and ionic conductivity. Additionally, all SOFC components should maintain acceptable levels of chemical, thermal, morphological and mechanical stability, with good compatibility among these various elements. Specifically, the electrodes should have a porous structure to facilitate effective gas transport to the reaction sites, whereas the electrolyte must be dense to prevent gas mixing. The interconnects must offer high electrical conductivity, excellent gas tightness and robust resistance to oxidation, sulfation, and carbon deposition. Furthermore, sealants should have hermetic properties and insulating characteristics. The broader adoption of fuel cells, in general, relies on the development of a hydrogen infrastructure for production, storage and distribution. However, ongoing research in materials science may lead to the discovery and development of new materials with improved hydrogen storage capabilities. Additional studies could also focus on optimizing the integration of solid-state hydrogen storage materials with fuel cells and other energy conversion systems. As solid-state hydrogen storage technologies progress, they may become commercially viable, opening up new applications and industries.

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