Research Article

Composite Cathode Development for Solid Oxide Fuel Cells at Low Temperatures Using Gadolinium-Doped Ceria as Electrolyte

Mohammad Fikrey Roslan[1,*], and Rafidah Abd Karim[2]

[1] Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia; fikrey.roslan@gmail.com; ORCID ID: 0000-0003-4010-5790

[2] Department of English and Linguistics, Universiti Teknologi MARA Cawangan Perak, Tapah Campus, Malaysia; feida16@uitm.edu.my; ORCID ID: 0000-0001-9147-6191

* Correspondence: fikrey.roslan@gmail.com; 0103838170.

Abstract: *This paper examines the development and characterization of composite cathodes for low-temperature solid oxide fuel cells (SOFCs) utilizing gadolinium-doped ceria (GDC) as the electrolyte material. The advantages of operating SOFCs at low temperatures include increased durability, decreased material costs, and improved start-up characteristics. The composite cathodes seek to optimize the electrochemical performance of SOFCs operating at low temperatures. The focus of this study is on combining GDC with other cathode materials to improve the overall efficacy of composite cathodes. Due to its high ionic conductivity at low temperatures, chemical stability, and compatibility with a variety of cathode materials, GDC is chosen as the electrolyte material. Using techniques such as co-precipitation, solid-state mixing, and electrodeposition, composite cathodes are fabricated, and their structural and electrochemical properties are characterized by scanning electron microscopy, X-ray diffraction, and electrochemical analysis. In low-temperature SOFCs, performance evaluations reveal that composite cathodes with GDC electrolyte exhibit enhanced power density, cell voltage, and stability. Combining GDC with other cathode materials produces synergistic effects that result in enhanced electrochemical activity, reduced polarization losses, and improved compatibility with the low-temperature operation. This study contributes to the development of composite cathodes for low-temperature SOFCs by shedding light on their design and optimization for enhanced performance and durability. Utilizing GDC as an electrolyte material provides benefits in terms of its ionic conductivity and chemical stability. Exploring additional cathode materials and optimizing the composite cathode design for improved performance at low temperatures requires additional research.*

Keywords: solid oxide fuel cells; low temperature; composite cathode; gadolinium-doped ceria (GDC).

1.0 INTRODUCTION

Solid oxide fuel cells (SOFCs) are electrochemical energy conversion devices that have attracted considerable attention due to their potential for highly efficient and environmentally friendly energy conversion. They directly convert the chemical energy contained in fuels into electric power without the limitation of the Carnot cycle, resulting in a higher energy conversion efficiency (around 60 percent) than traditional combustion engines (30-40%) (Adams et al., 2013; Liu & Duan, 2021). Hydrogen is regarded as the purest fuel, but it is not abundant in nature, and its production and storage are difficult.

Therefore, based on Figure 1, SOFCs are being developed to efficiently convert energy from other fuels, such as hydrocarbons (Leng et al., 2004).

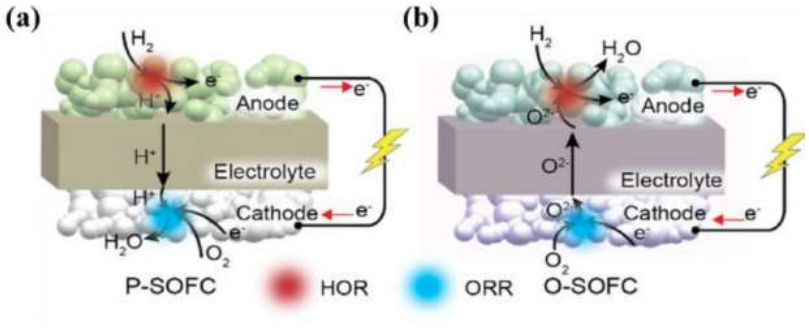

Figure 1. Schematic illustration of SOFCs with (a) a proton-conducting electrolyte; (b) an oxygen on conductor (Leng et al., 2004)

Electrochemical devices, such as fuel cells, batteries, and electrolysers, have demonstrated tremendous potential for large-scale applications involving the conversion and storage of clean energy. These technologies are considered pure and have the potential to mitigate climate change issues brought on by the intensive use of fossil fuels. However, electrode efficiency, membrane costs, and electrolyte stability continue to impede the widespread commercialization of electrochemical energy conversion/storage devices (Appetecchi, 2020).

It is essential to increase the performance of batteries, supercapacitors, and fuel cell electrodes by developing new and improved electrocatalytic materials (Costa et al., 2021). Recent advances in electrocatalysts/electrode development for energy conversion and storage devices (Hussain & Yangping, 2020) have yielded promising results, making research and development of efficient catalysts crucial to achieving this goal.

SOFCs shown in Figure 2, and other electrochemical energy conversion and storage devices have the potential to revolutionise how renewable energy is generated and stored. By overcoming current limitations in electrode efficacy, membrane costs, and electrolyte stability, these devices can play a significant role in the transition to a low-carbon and sustainable future (Hussain & Yangping, 2020).

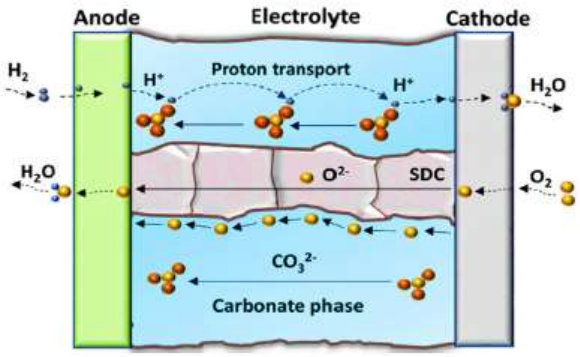

Figure 2. Diagram of ionic & proton conductions (Hussain & Yangping, 2020)

1.1 Significance of Developing Low-Temperature SOFCS

Due to their numerous benefits and prospective applications, the development of low-temperature solid oxide fuel cells (LT-SOFCS) is significant. LT-SOFCS can operate at temperatures between 400-600°C, which is lower than conventional SOFCS shown in Figure 3, which typically operate at 800-1000°C (Vostakola & Horri, 2021). This decreased operating temperature has numerous advantages, including reduced material degradation, enhanced durability, and a quicker start-up (Xia & Liu, 2001).

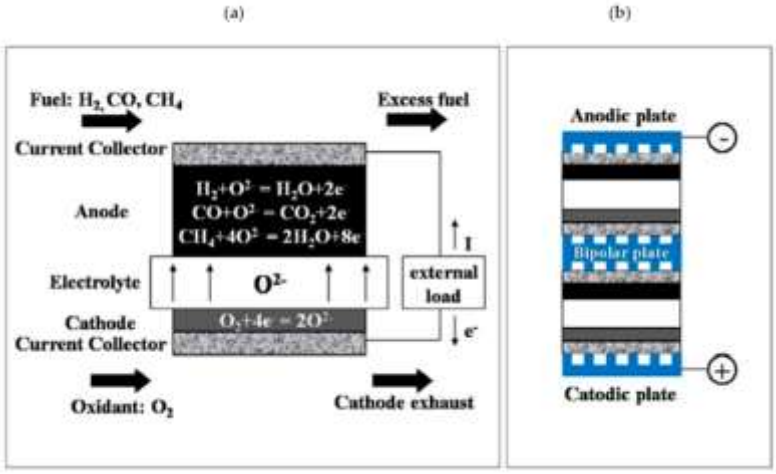

Figure 3. Schematic of (a) Solid oxide fuel cells (SOFC) operation and (b) Single cells assembly in-series (Vostakola & Horri, 2021)

One of the primary benefits of LT-SOFCs is their compatibility with a wide variety of fuels, such as hydrogen, natural gas, propane, butane, ethanol, and methanol (E. D. Wachsman & Lee, 2011). This fuel versatility enables the use of generally available and renewable fuels, making LT-SOFCs a desirable option for sustainable energy conversion. In addition, the lower operating temperature reduces the need for costly materials and complex thermal management systems, resulting in reduced fabrication expenses (Vostakola & Horri, 2021).

LT-SOFCs have prospective applications in numerous industries, including combined heat and power (CHP) systems, stationary and mobile power plants, hybrid vehicles, distributed power sources, and even spacecraft [3]. Hydrogen and liquid fuels such as petrol and methanol are preferred for light vehicles and low-temperature applications (E. D. Wachsman & Lee, 2011). Heavy vehicles, jets and military applications can use diesel with a high sulphur content, while natural gas is the preferable fuel for small and stationary plants (E. D. Wachsman & Lee, 2011).

1.2 Composite Cathode Development using Gadolinium-Doped Ceria as the Electrolyte

Because of its high ionic conductivity and compatibility with other materials, composite cathode development with gadolinium-doped ceria (GDC) as the electrolyte has been an area of interest in low-temperature solid oxide fuel cells (LTSOFCs). There has been research done to see if improving the performance and stability of LTSOFCs with GDC-based composite cathodes is possible.

Combining GDC with perovskite materials, such as lanthanum strontium cobalt ferrite (LSCF), is one strategy for generating composite cathodes (Baharuddin et al., 2013). Another strategy is to combine GDC with other materials. This combination has the potential to improve the cathode's electrochemical performance by enhancing the kinetics of the oxygen reduction process (ORR) and lowering the polarization resistance. In terms of power density and stability at moderate to low

temperatures, the LSCF-GDC composite cathode has demonstrated some encouraging results (Baharuddin et al., 2013).

Another strategy is to use GDC as a barrier layer between the cathode and the electrolyte to prevent unwanted reactions and improve the fuel cell's overall performance. Before applying the material that makes up the cathode, it is necessary to first deposit a very thin layer of GDC onto the surface of the electrolyte. Both the cathode and the electrolyte's ability to adhere to one another and the interfacial resistance can be lowered with the help of the GDC layer (Baharuddin et al., 2013) shown in Figure 4.

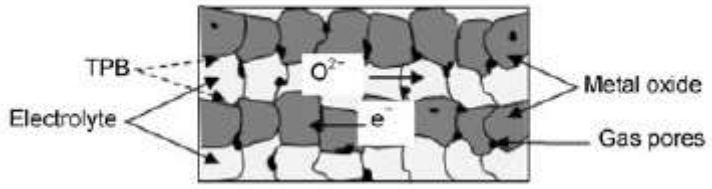

Figure 4. Simplified schematic of the mechanism of electronic and ionic conductions in a composite cathode (Baharuddin et al., 2013)

In conclusion, the development of composite cathodes that use GDC as the electrolyte has concentrated on enhancing the electrochemical performance of LTSOFCs as well as their stability and compatibility. Researchers have been able to improve the performance of these fuel cells while also lowering the temperatures at which they must be operated by mixing GDC with other materials or utilizing it as a barrier layer.

2. FUNDAMENTALS OF SOLID OXIDE FUEL CELLS, INCLUDING THEIR OPERATING PRINCIPLES, COMPONENTS, AND ELECTROCHEMICAL REACTIONS

Electrochemical devices known as solid oxide fuel cells (SOFCs) convert the chemical energy that is contained in fuels into direct electrical energy through a series of electrochemical reactions. The generation of an electric current is the result of the transfer of oxygen ions (O2-) from the cathode to the anode in a SOFC, which takes place in an electrolyte. (Tsipis & Kharton, 2008) This process is known as the fundamental operating principle of SOFCs.

An SOFC is comprised of three primary parts: the anode, the cathode, and the electrolyte. The anode is often constructed out of a porous ceramic material, such as nickel-yttria-stabilized zirconia (Ni-YSZ). This type of material allows for the conduction of electrons as well as the diffusion of fuel (Vostakola & Horri, 2021). The cathode is also built out of a porous ceramic material, such as lanthanum strontium manganite (LSM) or lanthanum strontium cobalt ferrite (LSCF), which makes it easier for the reduction of oxygen and the conduction of oxygen ions (E. Wachsman et al., 2014). The electrolyte is a dense ceramic substance, such as yttria-stabilized zirconia (YSZ) or gadolinium-doped ceria (GDC), which conducts oxygen ions while impeding the flow of electrons. This ensures that electrochemical reactions only take place at the interfaces between the electrodes and the electrolyte (Yamamoto, 2000).

The oxidation of fuel takes place at the anode, and the reduction of oxygen takes place at the cathode, in the electrochemical reactions that take place in a SOFC. At the anode, the fuel (such as hydrogen) combines with oxygen ions (O2-) to make water and release electrons. These electrons then

flow through an external circuit, which results in the generation of electricity. The comprehensive reaction that takes place at the anode can be depicted as follows:

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$ (Fan et al., 2015)

At the cathode, oxygen molecules from the surrounding air are accepted as electrons from the external circuit, which results in the production of oxygen ions (O^{2-}). The comprehensive reaction that takes place at the cathode can be represented as follows:

$1/2\ O_2 + 2e^- \rightarrow O^{2-}$ (Fan et al., 2015)

In a nutshell, the operation of SOFCs is predicated on the movement of oxygen ions through an electrolyte, which results in the production of an electric current. The anode, the cathode, and the electrolyte are the primary elements that make up SOFC. The electrochemical reactions that take place in a SOFC involve the oxidation of fuel at the anode and the reduction of oxygen at the cathode.

2.1 Challenges Associated with High-Temperature SOFCS and the Motivation for Developing Low-Temperature Alternatives

Electrochemical devices known as solid oxide fuel cells (SOFCs) convert the chemical energy that is contained in fuels into direct electrical energy through a series of electrochemical reactions. The generation of an electric current is the result of the transfer of oxygen ions (O^{2-}) from the cathode to the anode in a SOFC, which takes place in an electrolyte. (E. Wachsman et al., 2014) This process is known as the fundamental operating principle of SOFCs.

There are several obstacles that must be overcome by high-temperature solid oxide fuel cells (SOFCs), which is what drives the research and development of low-temperature alternatives. The following are some of the most significant difficulties related with high-temperature SOFCs:

1. Material compatibility: High operating temperatures (800-1000°C) can lead to undesirable reactions between the electrolyte, cathode, and anode materials, causing performance degradation and limiting the choice of materials (E. Wachsman et al., 2014).
2. Thermal stress: high temperatures can cause thermal stress and mechanical failure in the cell components due to differences in thermal expansion coefficients (Vostakola & Horri, 2021).
3. Sealing: Achieving a hermetic seal between the cell components at high temperatures is difficult, leading to gas leakage and reduced performance (Tsipis & Kharton, 2008).
4. Cost: High-temperature SOFCs require expensive materials, such as interconnects and seals, that can withstand the harsh operating conditions, increasing the overall cost of the system (Zha et al., 2004).
5. Durability: High operating temperatures can accelerate the degradation of cell components, reducing the lifetime of the fuel cell (Xia & Liu, 2001).

As an alternate solution, low-temperature solid oxide fuel cells, or LTSOFCs, have been developed because of these issues. Operating at lower temperatures (400-600°C) than high-temperature SOFCs allows LTSOFCs to address many of the challenges that are associated with high-temperature SOFCs. This can result in improved material compatibility, reduced thermal stress, simplified sealing,

reduced costs, and increased durability (Wang et al., 2019). The development of low temperature solid oxide fuel cells, or LTSOFCs, has primarily focused on enhancing the performance and stability of these fuel cells while continuing to preserve the benefits of conventional SOFCs.

2.2 Existing Literature on Gadolinium-Doped Ceria (GDC) as an Electrolyte Material and its Potential Advantages in Low-Temperature SOFCS

Due to its high ionic conductivity and compatibility with other materials, gadolinium-doped ceria, also known as GDC, has been the subject of a significant amount of research as an electrolyte material for low-temperature solid oxide fuel cells, also known as LTSOFCs (Tsoga et al., 2000). When compared to the yttria-stabilized zirconia (YSZ) electrolytes that are typically utilized, the ionic conductivity of GDC electrolytes is significantly higher (by a factor of 4-5) in the temperature range of 600-800 degrees Celsius (Li et al., 2016). Furthermore, materials based on CeO2, such as GDC, are thermodynamically stable in the presence of water and hydrocarbon vapors, and they are chemically compatible with perovskite oxide cathodes containing cobalt (Li et al., 2016). In BZY -H-SOFCs, the reduced oxygen ion may only meet the proton carried from the anode through BZY at the TPB lines at the interface between Pt cathode and BZY (in Figure 5), and these are the likely places where the water evolution process happens. In addition, the reduced oxygen ion may only meet the proton near the TPB lines near the interface between Pt cathode and BZY.

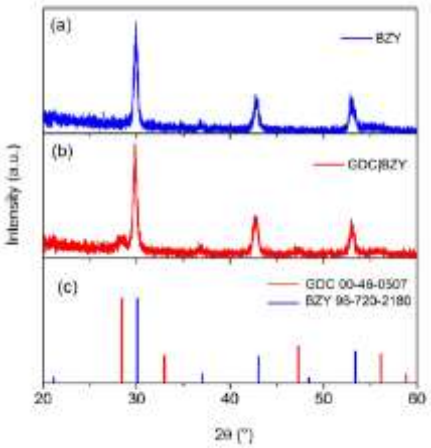

Figure 5. XRD patterns of BZY thin film electrolytes (a) with and (b) without GDC interlayer, with the reference peaks indices for BZY and GDC in (c) (Li et al., 2016)

The development of long-term solid oxide fuel cells (LTSOFCs) employing GDC as the electrolyte has mostly focused on enhancing the fuel cells' electrochemical performance as well as their compatibility and stability. It has been observed that proton-conducting micro-solid oxide fuel cells (-SOFCs) with a nanoscale thin film GDC interlayer can boost cathode reactions as well as overall cell performance (Vostakola & Horri, 2021).

However, there are issues connected with GDC electrolytes, such as the reduction of Sm-doped ceria in the reducing environment of the SOFC anode. This reduction can bring additional electrical conductivity to the system, which can result in a large loss of power (Choolaei et al., 2018). Another difficulty related with GDC electrolytes is that they are not as stable as other electrolytes. Despite these drawbacks, GDC shown in Figure 6, continues to be a potential electrolyte material for LTSOFCs due to the high ionic conductivity it possesses as well as its compatibility with the various other components of the cell.

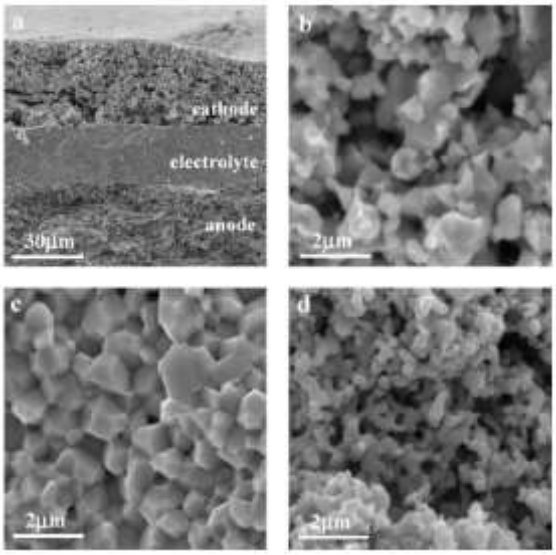

Figure 6. Cross-sectional views (SEM micrographs) of (a). a single cell, (b). the porous Ni–GDC anode, (c). the dense GDC electrolyte, and (d). the porous SSC–GDC cathode (Choolaei et al., 2018)

2.3 Previous Studies on Composite Cathodes, Focusing on the Use of GDC-Based Materials and Their Performance Characteristics

In previous research on composite cathodes, the emphasis was placed on the use of GDC-based materials as a means of enhancing the performance characteristics of low-temperature solid oxide fuel cells, also known as LTSOFCs. Combining GDC with perovskite materials, such as lanthanum strontium cobalt ferrite (LSCF), is one method of approaching this problem. In terms of power density and stability at moderate to low temperatures, the LSCF-GDC composite cathode has demonstrated some encouraging results (Baharuddin et al., 2013). The composite cathode has the potential to improve the electrochemical performance by enhancing the kinetics of the oxygen reduction reaction (ORR) and lowering the polarization resistance.

Another study investigated the usage of GDC as a barrier layer between the cathode and the electrolyte in a fuel cell in order to reduce unfavorable reactions and improve the fuel cell's overall performance (Sumi et al., 2021). Before putting the material that makes up the cathode, you should first deposit a thin layer of GDC on the surface of the electrolyte. This will allow the GDC layer to help minimize the interfacial resistance and increase the adhesion between the cathode and the electrolyte.

In addition, researchers have investigated the possibility of using GDC-based composite cathodes in conjunction with other materials, including silver (Ag) and samarium-doped ceria (SDC) (Liu & Duan, 2021). When compared to more conventional cathode materials, the Ag-SDC-GDC composite cathode displayed superior electrochemical performance as well as greater stability at lower temperatures.

In a nutshell, the goal of the earlier research on composite cathodes made from GDC-based materials was to improve the performance of LTSOFCs while maintaining their stability. Researchers have been able to increase the electrochemical efficiency of these fuel cells at lower operating temperatures by mixing GDC with other materials or utilizing it as a barrier layer. This has enabled them to operate at lower temperatures.

3.0 CONCLUSION

Composite cathodes for low-temperature solid oxide fuel cells (LT-SOFCs) employing gadolinium-doped ceria (GDC) as an electrolyte are significant because they have the potential to improve the overall performance and efficiency of fuel cells. This is the relevance of composite cathodes. GDC is a viable electrolyte material for LT-SOFCs because to its high ionic conductivity, which is 4 to 5 times higher than that of the commonly used yttria-stabilized zirconia (YSZ) electrolyte in the temperature range of 600 to 800 degrees Celsius [1]. This makes GDC an attractive option for the electrolyte material in LT-SOFCs. In addition, GDC is chemically compatible with cobalt-containing perovskite oxide cathodes and possesses thermodynamic stability in the presence of water and vapors of hydrocarbons.

Composite cathodes have the potential to improve the electrochemical performance of LT-SOFCs by lowering the resistance of the electrode reaction and the ohmic resistance of the electrolyte [2]. These resistances are the primary obstacles that need to be overcome to improve cell performance. The use of composite cathodes can also promote greater interfacial contact between the cathode and the electrolyte, which can ultimately result in improved electrochemical processes and less polarization resistance.

In recent years, researchers have focused their attention on developing alternative co-doped electrolyte composites, such as samarium-doped ceria (SDC) and lanthanum strontium gallium magnesium oxide (LSGM), along with geometrical modifications of the cell structures by minimizing the electrolyte thickness and fabricating anode-supported SOFCs. In addition, these researchers have made modifications to the cell structures to increase the efficiency of the cells. These efforts are geared towards bringing the working temperature of SOFCs down to a more manageable level while simultaneously improving their performance, durability, and cost-effectiveness.

In conclusion, composite cathodes for low-temperature solid oxide fuel cells (SOFCs) that use gadolinium-doped ceria as an electrolyte are significant because they have the potential to improve the electrochemical performance, efficiency, and durability of the fuel cells. The creation of these composite cathodes, along with alternate electrolyte materials and sophisticated cell designs, has the potential to contribute to the development of long-term solid oxide fuel cell (LT-SOFC) technology and its widespread use in a variety of energy applications.

Acknowledgments: The authors would like to express their gratitude to Dr. Rafidah and parents.

References

Adams, T. A., Nease, J., Tucker, D., & Barton, P. I. (2013). Energy conversion with solid oxide fuel cell systems: A review of concepts and outlooks for the short- and long-term. *Industrial and Engineering Chemistry Research*, *52*(9), 3089–3111. https://doi.org/10.1021/ie300996r

Appetecchi, G. B. (2020). Composite electrolyte & electrode membranes for electrochemical energy storage & conversion devices. *Membranes*, *10*(11), 1–4. https://doi.org/10.3390/membranes10110359

Baharuddin, N. A., Rahman, H. A., Muchtar, A., Sulong, A. B., & Abdullah, H. (2013). Development of lanthanum strontium cobalt ferrite composite cathodes for intermediate- to low-temperature solid oxide fuel cells. *Journal of Zhejiang University: Science A*, *14*(1), 11–24. https://doi.org/10.1631/jzus.A1200134

Choolaei, M., Cai, Q., Slade, R. C. T., & Amini Horri, B. (2018). Nanocrystalline gadolinium-doped ceria (GDC) for SOFCs by an environmentally-friendly single step method. *Ceramics International*, *44*(11), 13286–13292.

https://doi.org/10.1016/j.ceramint.2018.04.159

Costa, P., Pinto, F., André, R. N., & Marques, P. (2021). Integration of gasification and solid oxide fuel cells (SOFCs) for combined heat and power (CHP). *Processes*, *9*(2), 1–26. https://doi.org/10.3390/pr9020254

Fan, L., Wang, Y., Jia, Z., Xiong, Y., & Brito, M. E. (2015). Nanofiber-structured SSC-GDC composite cathodes for a LSGM electrolyte based IT-SOFCs. *Ceramics International*, *41*(5), 6583–6588. https://doi.org/10.1016/j.ceramint.2015.01.104

Hussain, S., & Yangping, L. (2020). Review of solid oxide fuel cell materials: cathode, anode, and electrolyte. *Energy Transitions*, *4*(2), 113–126. https://doi.org/10.1007/s41825-020-00029-8

Leng, Y. J., Chan, S. H., Jiang, S. P., & Khor, K. A. (2004). Low-temperature SOFC with thin film GDC electrolyte prepared in situ by solid-state reaction. *Solid State Ionics*, *170*(1–2), 9–15. https://doi.org/10.1016/j.ssi.2004.02.026

Li, Y., Wang, S., & Su, P. C. (2016). Proton-conducting Micro-solid Oxide Fuel Cells with Improved Cathode Reactions by a Nanoscale Thin Film Gadolinium-doped Ceria Interlayer. *Scientific Reports*, *6*(February), 1–9. https://doi.org/10.1038/srep22369

Liu, F., & Duan, C. (2021). *Direct-Hydrocarbon Proton-Conducting Solid Oxide Fuel Cells*.

Sumi, H., Takahashi, S., Yamaguchi, Y., & Shimada, H. (2021). Lanthanum-doped ceria interlayer between electrolyte and cathode for solid oxide fuel cells. *Journal of Asian Ceramic Societies*, *9*(2), 609–616. https://doi.org/10.1080/21870764.2021.1905254

Tsipis, E. V., & Kharton, V. V. (2008). Electrode materials and reaction mechanisms in solid oxide fuel cells: A brief review : I Electrochemical behavior vs. materials science aspects. *Journal of Solid State Electrochemistry*, *12*(11), 1367–1391. https://doi.org/10.1007/s10008-008-0611-6

Tsoga, A., Gupta, A., Naoumidis, A., & Nikolopoulos, P. (2000). *1-s2.0-S1359645400002615-main.pdf*. *48*, 4709–4714.

Vostakola, M. F., & Horri, B. A. (2021). Progress in material development for low-temperature solid oxide fuel cells: A review. *Energies*, *14*(5). https://doi.org/10.3390/en14051280

Wachsman, E. D., & Lee, K. T. (2011). Lowering the temperature of solid oxide fuel cells. *Science*, *334*(6058), 935–939. https://doi.org/10.1126/science.1204090

Wachsman, E., Ishihara, T., & Kilner, J. (2014). Low-temperature solid-oxide fuel cells. *MRS Bulletin*, *39*(9), 773–779. https://doi.org/10.1557/mrs.2014.192

Wang, F., Lyu, Y., Chu, D., Jin, Z., Zhang, G., & Wang, D. (2019). The electrolyte materials for SOFCs of low-intermediate temperature: review. *Materials Science and Technology (United Kingdom)*, *35*(13), 1551–1562. https://doi.org/10.1080/02670836.2019.1639008

Xia, C., & Liu, M. (2001). Low-temperature SOFCs based on Gd0.1Ce0.9O1.95 fabricated by dry pressing. *Solid State Ionics*, *144*(3–4), 249–255. https://doi.org/10.1016/S0167-2738(01)00980-8

Yamamoto, O. (2000). Solid oxide fuel cells: Fundamental aspects and prospects. *Electrochimica Acta*, *45*(15–16), 2423–2435. https://doi.org/10.1016/S0013-4686(00)00330-3

Zha, S., Moore, A., Abernathy, H., & Liu, M. (2004). GDC-Based Low-Temperature SOFCs Powered by Hydrocarbon Fuels. *Journal of The Electrochemical Society*, *151*(8), A1128. https://doi.org/10.1149/1.1764566