A Short Review on Selection of Electrodes Materials for Symmetrical Solid Oxide Fuel Cell

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Abstract. Symmetrical solid oxide fuel cells (SOFCs) operate at high temperatures and consist of a dense electrolyte which is sandwiched between two electrodes. An anode acts as a fuel electrode where fuel is oxidised, while a cathode serves as an air electrode in which oxygen is reduced. However, the use of two different materials as electrodes poses several significant issues concerning durability, reliability and fabrication costs of SOFCs. Furthermore, at least two thermal steps are required for the sintering of both electrodes, thereby increasing energy usage. In overcoming these challenges posed by conventional SOFCs, the concept of symmetrical solid oxide fuel cells (S-SOFCs) has been introduced. S-SOFCs comprise of two identical materials for the anode and cathode. The use of two similar materials decreases the interfacial regions among the electrolyte and electrodes and consequently improves the compatibility among the components. Sulphur poisoning and carbon deposition at the fuel electrode can be solved by merely reversing the flow of oxidant and fuel to oxidise all the species that degrade the performance of SOFCs. Although, the electrode material for S-SOFCs requires some unique properties, such as high electrocatalytic activity for fuel oxidation and oxygen reduction, high electrical conductivity in oxygen and hydrogen/hydrocarbon environments, promising the capability to resist sulphur poisoning and carbon deposition in hydrocarbon fuels and good structural and chemical stability under actual fuel cell conditions. As the works related to S-SOFCs are limited in this respect, this paper reviews the available reports in this field to allow a better understanding of the operational mechanism and the potential of S-SOFCs.

1.0 Introduction

The application of solid oxide fuel cells (SOFC) is one of the most practicable and viable alternatives to alleviate future energy source demands. Offering many advantages with respect to high energy conversion, and with fewer harmful emissions plus greater flexibility on the consumption of fuel makes SOFCs a prominent proposition [1-2]. The configuration of a common single-cell is mostly made of two porous electrodes (anode and cathode) and a densified electrolyte material. The electrode components typically comprise of different material which is able to undertake the specific electrochemical reaction for the SOFC application to operate effectively. The use of two different materials as electrodes has fewer serious issues regarding durability, reliability and the fabrication cost of SOFCs. For example, using two different materials as electrodes leads to the formation of at least two interfacial regions within a single SOFC. Although, these interfaces can cause various thermo mechanical stresses at high operating temperatures primarily due to the difference in their thermal expansion coefficients, less compatibility among components and different compositions. Furthermore, at least two thermal steps are required for the sintering of both electrodes, thereby increasing the fabrication cost of SOFCs [3-4]. Moreover, traditional Ni-based anode materials have a weak ability to resist sulphur poisoning and carbon deposition in hydrocarbon fuels [5]. Therefore, in overcoming and addressing the challenges posed by conventional three-component SOFCs, Badding et al. introduced the concept of symmetrical solid oxide fuel cells (S-SOFCs) in 2001 [6].

The basic configuration of the S-SOFC alongside SOFC is illustrated is compared as shown in Fig. 1 below. The S-SOFC configuration exhibits several advantages over the conventional SOFC such as aiding in the fabrication process while enhancing the interaction between the electrodes and the electrolyte component. Secondly, the S-SOFC fabrication process can minimise production costs, reducing the coking phenomenon in addition to sulphur poisoning [7]. Though,

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the exhibition of a unique configuration by the S-SOFC requires both the anode and cathode to have excellent stability (structural and chemical) and good electrical and electrochemical performance. Good electrochemical performance includes the active reaction for an oxidising and reducing condition which is an important characteristic for the electrodes. However, the material that suits the characteristic as the electrodes for the S-SOFC remains limited given the material itself needs to satisfy both the requirement from the anode and cathode while reducing the existence problem that continues to hinder this application to perform at its optimum. By acknowledging the solution to these limitations, it is therefore important to examine the basic properties and characteristic of the recommended material to be utilised, which suits both the anode and cathode components. Thus, a review involving the base material, dopants, material’s limitations are among the crucial parts that require detailed understanding for the electrodes to function well during operation.

Fig. 1. Basic working mechanism for (a) SOFC and (b) S-SOFC

2.0 Anode

Commonly used anode material in SOFC application, such as Ni-YSZ cermet, is where the utilisation of nickel (Ni) helps in conducting the electron actively while YSZ is charged for ionic conduction [8]. Most Ni-based anodes perform well, especially when the operating system is coupled with hydrogen as a fuel. However, unfortunately, this type of anode experiences unavoidable carbon coking whenever the system is operated using hydrocarbon as fuel. For example methane, is an active catalyst for the reaction involving hydrocarbon cracking [9]. As such, this situation may lead to the deterioration of overall performance since the deposition may be enclosed and reduce the active site for the reaction to occur. Moreover, given the low tolerance towards coking which may limit the development of direct hydrocarbon SOFC, this is one of the significant drawbacks of Ni cermet for anodes [10].

A further reason that has suppressed SOFC advancement to operate using natural gas as the fuel is the susceptibility to sulphur poisoning where this material is present in natural gas due to the formation from the NiSx compound. Secondly, this problem possibly occurred due to the aggregate fluctuation during the redox reaction and nickel particle agglomeration in the Ni cermet anode [11]. However, despite the drawback presented by Ni cermet, this type of material remains the best option when researchers are working towards developing strategies to enhance coke resistance throughout the modification process. One of the favourable strategies for modification of the anode structure surface is to use other active oxides and to introduce other metals into nickel cermet [10].

3.0 Cathode

The primary function of the cathode is to cause a reaction between the reactant (oxygen or air) and the electrolyte, without itself being consumed or corroded. A cathode plays the role as a catalyst in the oxygen reduction and works in the air or oxygen atmosphere. As such, the problem of non-stability is practically eliminated for the cathodes, which are typically oxide materials [12]. The perovskite-type oxide crystal structure with the general formula of ABO₃ (A is usually a rare earth element and B is usually a transition element) is commonly used as cathode materials. This is due to their stability in geometrical and electrostatic configurations, and many oxides of this type are stable even when a considerable number of defects are introduced [13]. The reality of SOFC operation has mostly evolved around the activation of the oxygen reduction reactions (ORR) occurring on the cathodes [14].

Oxygen activation is normally more laborious as compared to hydrogen activation thereby raising the issue on the effort in reducing the operating temperature which may degrade the cell’s performance due to insufficient electrochemical activity driven by the operating temperature [15]. A detailed material design composition, in addition to the microstructure of the cathode material, has a significant consequence on the performance of SOFC operations. For example, controlling the oxygen nonstoichiometric can enhance the ionic and electronic conduction including catalytic activity, which is associated with ORR in the cathode component [16]. Thus, one of the affirmative strategies that can be adopted in
idealising the SOFC system is by using new oxides with mixed ionic and electronic conductivity (MIEC). This type of cathode material may elevate the active site for a reaction ahead of the triple-phase boundary (TPB) including the adaptation of nanostructured materials which may increase the electrode specific surface [17].

4.0 Electrode Candidate for S-SOFC

S-SOFCs comprise of two identical compositions/materials for both the anode and cathode. The use of two similar materials decreases the interfacial regions among the electrolyte and electrodes and improves the compatibility among the components. Only one single sintering step is required to fabricate the cells, consequently reducing the fabrication cost. Sulphur poisoning and carbon deposition at the fuel electrode can be solved by merely reversing the flow of oxidant and fuel to oxidise all the species that degrade the performance of the SOFCs [18]. The electrode material for S-SOFCs requires some unique properties, such as having high electrocatalytic activity for fuel oxidation and oxygen reduction, high electrical conductivity in oxygen and hydrogen/hydrocarbon environments, promising the capability to resist sulphur poisoning and carbon deposition in hydrocarbon fuels and good structural and chemical stability under actual fuel cell conditions [19].

Extensive studies have been conducted to develop materials that satisfy the abovementioned requirements. However, all studied materials such as La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$–δ (LSCM) [20], Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_{6}$–δ (SFMO) [21], PrBaFe$_{2}$O$_{5}$+δ (PBFO) [22], Sm$_{0.5}$Sr$_{0.5}$Fe$_{0.5}$Ru$_{0.5}$O$_{4.5}$ (SSFR) [23], and La$_{0.5}$Sr$_{0.5}$Co$_{0.5}$Ti$_{0.5}$O$_{3}$–δ (LSCT) [24] have limitations. LSCM cannot resist sulphur poisoning, PBFO is structurally unstable, and SFMO is chemically unstable [5]. Therefore, innovative materials and novel structures that encounter all the requirements for cathodes and anodes should be developed for the practical application of S-SOFCs under actual fuel cell conditions [18-25].

From this perspective, lithiated nickel oxide has the potential to be used as an electrode for S-SOFCs since this material demonstrates good chemical, physical and thermal stability in oxidation and reduction environments [26]. Although despite the stability of lithiated nickel oxide, its electrical and electrochemical behaviour under actual fuel cell conditions remains a significant challenge. Comprehensive studies have been performed to enhance its electrical and electrocatalytic performance by adding transition metals, such as Zn, Fe, Co, and Al [25–28]. Tan et al. [26] studied lithiated nickel oxide electrodes by adding Cu, Fe and Co and obtaining a power density of 0.38 mW/cm$^2$ at 560 °C when Co is used as a dopant. Chen et al. [27] co-doped Al and Co into a lithiated nickel oxide electrode and reported a power density of 159.7 mW/cm$^2$ at 550 °C. However, despite this positive improvement, the values recorded are profoundly different from those of traditional SOFCs that have a power density above 500 mW/cm$^2$ [29].

Table 1. Summary of previously researched electrode for S-SOFC

| Electrode | Electrolyte | Sm$m^{-1}$ | ASR | Ref |
|-----------|-------------|-------------|-----|-----|
| BaFe$_{1-x}$Zr$_{x}$O$_{3}$-δ | La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3}$-δ | - | 0.005 (800 °C) | [7] |
| - | La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3}$-δ | - | 0.02 (700 °C) | |
| La$_{0.5}$Sr$_{0.5}$Fe$_{0.5}$Mo$_{0.5}$O$_{3}$-δ | Sm$_{0.5}$Co$_{0.5}$O$_{1.95}$ | - | 0.46 (750 °C) | [30] |
| La$_{1-x}$Sr$_{x}$Fe$_{0.5}$Cu$_{0.5}$O$_{3}$-δ | La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3}$-δ | - | 0.454 (800 °C) | [31] |
| La$_{1-x}$Ba$_{x}$Cu$_{0.5}$Mn$_{0.5}$O$_{1.95}$ | YSZ | 178 (air) | 33.3 (Hydrogen) | - | [32] |
| Nd$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$O$_{1.95}$ | YSZ | 33.4 (air) | 0.9 (hydrogen) | - | [33] |

Therefore, the structural, electrical and electrochemical properties of doped lithiated nickel oxide should be systematically improved. Table 1 summarises the potential materials reported for S-SOFC. Detailed selection of the based material is not only the primary consideration in determining the overall performance of the S-SOFC application. The strategy to involve modifications onto the based materials itself plays a vital role to improve the performance. The utilisation of potential dopants possesses suitable characteristics and the ability to reduce drawbacks or to enhance the conductivity. In this context, some reports have shown that ceramics and using metals as dopant, is useful especially when aiming for higher catalytic properties of the electrode, for example, Ni, Ru, Pt and Mo [34].
5.0 Conclusion

Questions about the most suitable material to be used for both electrodes for the S-SOFC remain. However, answering this question depends on several factors, including the selection of materials, the fabrication process, mechanical factors and operating conditions. This study suggests a feasible idea by highlighting the crucial characteristics as well as the drawbacks of electrodes which could help in progressing future studies in this field. However, the practicability surrounding newly developed materials must be first verified for lab-scale before progressing in verification for a prototype.

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