



Investigation on cobalt-free anodes and cathodes for solid oxide fuel cell

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Accepted 29 July 2019

Abstract

Generally, global warming raised by greenhouse gas emissions is a great threat. New technologies are evolving that can reduce carbon emissions significantly, one of them is fuel cell. Fuel cell combines hydrogen and oxygen to produce electricity through an electrochemical reaction. Because the by products are only water and heat, there are no carbon emissions and as generation continues to shift away from coal and towards natural gas, fuel cells will not only dramatically reduce CO₂ emissions but also combine with power plants burning a less carbon-intensive fuel. Cathodes that have Cobalt are known for their ability to act under high-temperature conditions in solid oxide fuel cells (SOFCs). In this paper, the investigation of results and effects are presented for various studies on the cobalt-free anode and cobalt-free nanofiber cathode development. The polarization resistance of SOFC cathodes, which is one of the important characters in determining the cathodic performance, revealed the importance of nanofiber for this process in this investigation.

Keywords: cobalt-free, nanofiber, fuel cells, cathodes.

1. Introduction

Fuel cell's prime advantage is that it converts the chemical energy of fuels directly into electrical energy. As a result, fuel cells exhibit much higher efficiency unlike other energy conversion devices going through multiple conversion steps. The direct energy conversion in fuel cells occurs at triple-phase boundaries, so-called TPBs where fuels, electrodes, and electrolytes meet simultaneously [1]. Therefore, augmenting domains of TPBs leads to an enlargement of the reaction zone, which is directly linked to the decrease in activation loss. As one device for reducing carbon emissions and use energy efficiently, solid oxide fuel cells (SOFCs) have absorbed wide attention [2].

SOFC is one of the most promising energy conversion devices because of being high efficiency, environmental friendliness, easy scale up and economic competitiveness for fuel cell. However, the required high operating temperature (800–1000 °C) to attain the reasonable ionic conductivity of electrolyte materials induces many practical difficulties such as long-term stability, sealing, material selection, and slow start-stop cycle, limiting their expeditious commercialization [3]. Fabrication of a high-performance cathode has been critical for development of SOFCs operating at reduced temperatures [4].

Recently, nanofibers have attracted significant attention as an alternative electrode structure because of their high specific surface area, facile gas diffusion, and continuous charge transport path with high aspect ratio. Generally, the low-temperature solid oxide fuel cells cause to increase reducing of the cell performance because of losses in the SOFCs. Despite their superior structural properties, nanofiber-based SOFCs have been rarely reported with few exceptions: Lee et al. reported that Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}-Gd_{0.1}Ce_{0.9}O_{1.95} based low-temperature solid oxide fuel cells with nanocomposite anode functional layers showed high current density at 2 W/cm² at 550 °C conditions [5]. Chen et al. reported performance of the fabrication of hollow nanofibers as cathodes for high-performance and durable intermediate-temperature fuel cells (ITFCs) and found the single cells with intact hollow fiber cathodes showed high performance, peak power density of 1.11 W cm⁻², and excellent stability, 0.95 W cm⁻² at 0.6 V for 260 h, at 550 °C when using humidified H₂ as fuel and ambient air as oxidant [4]. Zhi et al. reported performance of the fuel cell with the monolithic lanthanum strontium cobalt ferrite (LSCF) nanofiber cathode exhibits a power density of 0.90 W cm⁻² at 1.9 A cm⁻² at 750 °C. They showed that when improved infiltration of 20 wt% of gadolinia-doped ceria (GDC) into the LSCF

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nanofiber, the fuel cell with the LSCF–20% GDC composite cathode showed a power density of 1.07 W cm^{-2} at 1.9 A cm^{-2} at $750 \text{ }^\circ\text{C}$ [3].

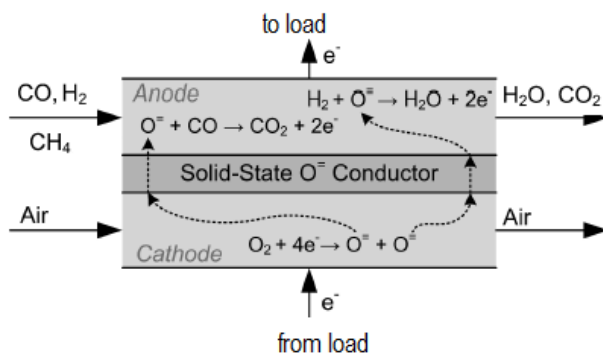


Figure 1. Schematic of reactions on a solid oxide fuel cell.

Among the various fuel cells, ceramic fuel cells have various attractive advantages, including the potential to directly use hydrocarbon fuels, such as fuel flexibility, and do not require high efficiency and precious metal catalysts [6-9]. However, the yttria stabilized zirconia based solid oxide fuel cell (SOFCs) which is first generation results in high costs and material compatibility difficulties at high operating temperatures, 700°C – $1000 \text{ }^\circ\text{C}$ [10]. Second generation of SOFCs based on newer oxygen ion conductive electrolytes (such as samarium doped ceria) (SDC) reduced operating temperatures to about $600 \text{ }^\circ\text{C}$ [11-12]. Third generation which is nanostructured SOFCs rare earths such as Eu or Ru

and ultra-fine multilayer electrolytes or core shell nanofiber composite electrodes from $450\text{--}600 \text{ }^\circ\text{C}$, but performance drops rapidly and falls temperature because of high activation energy with oxygen ion conduction [13-14]. The performance of SOFC generations is shown in Figure 2 as the power density versus temperature. Performance of power density, also means current, on first-generation (YSZ-based), second-generation (SDC, GDC, and LSGM-based) and third generation (PCFCs vs.) compare with each other on figure 2. PCFC shows good promise in the intermediate and low-temperature regime (350°C to 600°C) [6].

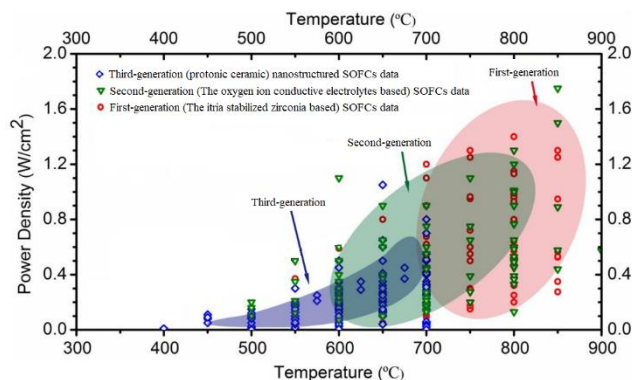


Figure 2. SOFCs performance of generations types.

2. 2. Cobalt-free anode materials of SOFCs

Solid oxide fuel cell (SOFC) anode materials has been changed rapidly reduction of the operating temperature and improvement of the performance. SOFCs are mostly constructed by using ceramic materials due to it is function optimally at high temperatures and operating temperature range of the electrolyte. High temperatures causes significant thermal stresses and effect of SOFC efficient with

some metallic. fuel cell performance can be calculated by using the Nernst equation added losses of actual cell by from various electrochemical processes in shown as following equation.

$$V = E_0 - IR - \eta_{\text{cathodes}} - \eta_{\text{anodes}} \quad (1)$$

where E_0 is the Nernst potential of the reactants, R is

the ohmic resistance, I is the current through the cell, and η_{cathode} and η_{anode} are polarization losses of the cathodic and anodic respectively.

Anode materials are to function efficiently some important criteria should be met:

- ✓ Thermal stability
- ✓ High electronic and ionic conductivity
- ✓ Catalytic activity for fuel oxidation and combustion
- ✓ Stability on successive reducing and oxidizing cycles
- ✓ Chemical stability to contacting components
- ✓ Matched thermal expansion coefficient to contacting components

The electrolyte and operating temperature are

important design of anode materials. must with which the material will operate as the thermal expansion coefficient (TEC) and chemical reactivity are electrolyte dependent. Different anode materials can be used for SOFCs. Comparison of the ionic conductivities of various oxide ion conducting electrolytes are showed Figure 3 by Kharton et al in 2004 [16].

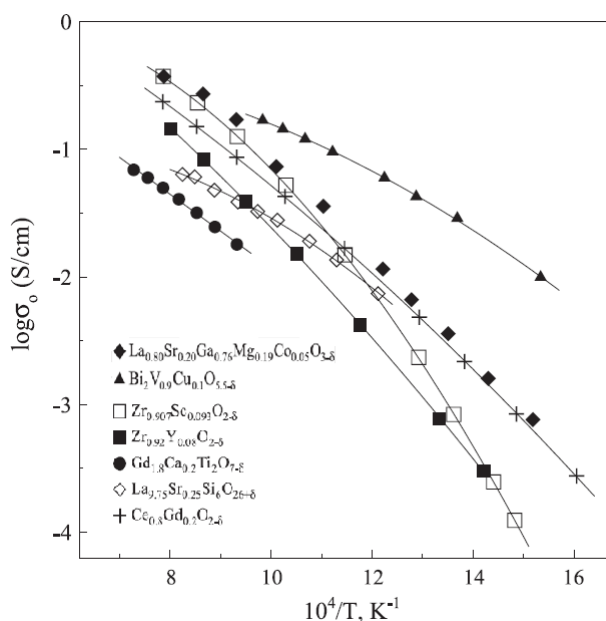


Figure 2. Oxygen ionic conductivity of various solid–electrolyte materials [16].

When designing an SOFC, there are excess of different factors to take into consideration anode material. Main considerations are electronic conduction, production of highly conducting and redox stable materials under SOFC operating conditions. There are three main categories of SOFCs anode materials which are metal-fluorite cermets, Perovskites-based and other anode materials.

Fluorite structured materials were used as both anode and cathode. These materials are optimized with usually added to a metal oxide. A metal oxide can be used to enhance the anode and increase the triple phase boundary for escape from many problems of related pure metal anodes. fluorite structured materials have focused on the based cermets, transition metal and ceria/zirconia anode materials. A cermet consisting of Ni/Yttrium stabilized zirconia,

Ni-CeO₂ / Yttrium stabilized zirconia has many of the properties required for an efficient anode material. But they have multiple problems to effective implementation such as prone to carbon deposition or coking when using hydrocarbon fuels, Sulphur poisoning, nickel agglomeration upon prolonged usage and is not redox stable [17]. Samarium doped ceria with a volume percent of 50 to 60% of nickel was required for the cermet to meet requirements for anode materials based on electrical conductivity data and thermal expansion coefficient [18].

Perovskite materials have been alternative SOFC anode research. much of the research has focused on the development of the properties materials which are the lanthanum doped strontium titanate, Yttrium doped strontium titanate and Perovskite

anode ($\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$).

The tungsten bronze, the pyrochlore structured

3.3. Cobalt-free cathodes

Generally, the traditional SOFCs using oxygen-ion electrolyte which is work at high temperatures, leading to many technical problems. So, many studies efforts have been made to develop new architectures and materials for SOFC cathodes operated at low or intermediate temperature. Cobalt-containing cathodes have some problem that are high thermal expansion coefficient, cobalt evaporation and high price show although they relatively good performance at hydrogen fueled SOFCs [19-20]. So, cobalt-free cathodes can be used to develop high-performance.

The construction of nanofiber cathode has been proposed by some researchers. Li et al. are investigated surface exchange kinetics of Ruddlesden-Popper (R-P) phase lanthanum nickelates upon Mn doping (LNO) as an intermediate temperature solid oxide fuel cells cathode. They found that Mn-doped lanthanum nickel is excellent cobalt-free cathode material for intermediate temperature solid oxide fuel cells also they showed that the apparent activation energy for the porous $\text{Sr}_{20}\text{Mn}_{10}$ electrode is calculated as 1.57 eV as above in the literature [21]. The nickel LNF and LNO cathode materials coupled with the nanofiber structure is a promising cathode system for H-SOFCs. When compared to the prevalent Co-based perovskite cathodes, lanthanum nickelates possess mild thermal expansion coefficients which matches better with current electrolytes such as $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ and cause no concerns associated with Co volatility, thus promising advantages in the dimensional and chemical stability during long-term operation [22]. Research on cobalt-free cathodes have been conducted over the past five years, with strontium ferrite oxide, $\text{SrFeO}_{3-\delta}$, as the preferred subject [23]. It should be note Strontium is a

4. Results and discussion

Cobalt-based cathodes have showed higher electro-catalytic performance than that of the conventional the Strontium-doped lanthanum manganite cathodes. These cobalt-based cathodes often come upon some problems such as high thermal expansion coefficient, poor stability and high cost of cobalt element. So, the cobalt-free cathodes with good electro-catalytic

materials and some metal vanadates, have been investigated as alternative anode materials without much success.

gray/silvery metal that is softer than Ca. It is even more reactive in water, and reacts on contact to produce $\text{Sr}(\text{OH})_2$ and hydrogen gas [24].

Tang et al. [15] reported that nanofiber-structured $\text{La}_2\text{NiO}_{4+\delta}$ (LNO) and $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (LNF) cathodes which are produced by an electrospinning technique for proton-conducting solid oxide fuel cells (H-SOFCs) to develop high-performance cobalt-free cathodes for H-SOFCs. they found that the structure of fuel cell performance was power density of 508 mWcm^{-2} and 551 mWcm^{-2} for LNO and LNF cathode cell at 700°C , respectively.

Zhou et al. presented results of the cubic perovskite oxide, $\text{SrFe}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (SFN) as cobalt-free cathode for intermediate-temperature solid oxide fuel cells. They found a maximum power density of 407 mWcm^{-2} with the electrolyte $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) at 800°C [25]. Jiang et al. prepared cobalt-free cathodes from $\text{SrNb}_{0.1}\text{Fe}_{0.9}\text{O}_{3-\delta}$ (SNF) and evaluated its effect on the electrochemical performance of the fuel cell. They obtained the peak power density of the cell has 1403, 1074, and 841 mWcm^{-2} at 800, 750, and 700°C , respectively [26].

After getting result from processing methods, powder cathode can be prepared different from by the conventional combustion method. Nanofiber cathode has the rod-like structure and three-dimensional network structure so it can be providing efficient diffusion pathways for gas transportation. Also, well electro-catalytic activity and much three-phase reaction sites can be obtained in nanofiber structured cathode. for cobalt-free materials, the performance enhancement of H-SOFCs can be obtained by using nanofabrication techniques.

activity for SOFCs have being improved by a lot of researcher. The cubic perovskite oxide, $\text{SrFe}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (SFN) with pure H_2 as cobalt-free cathode for intermediate-temperature solid oxide fuel cells is highest power density, 1403 mW/cm^2 in Table1. This designates that the SFN oxide has a high electro-catalytic activity and it shows a

promising candidate as a cathode material for SOFCs.

Table 1. Fuel cell performance of cobalt-free anode and cathodes.

	Anode composition	Electrolyte/ Cathode	Temperature (°C)	Fuel	Maximum Power Density (mW/cm ²)	Reference
metal- fluorite cermet based	Ni-Sc _{0.1} Ce _{0.01} Zr _{0.89} O _{1.95}	YSZ/LSM-YSZ	800	H ₂ O saturated H ₂	980	27
	Fe _{0.1} Ni _{0.9} /YSZ	YSZ/LSM-YSZ	800	3% H ₂ O-H ₂	960	28
	Cu-CeO ₂ -YSZ/Ni-ScSZ	ScSZ/PCM	800	H ₂ /O ₂ 50%, H ₂ O-C ₂ H ₅ OH/O ₂	604, 438	9
	2 wt% Gd _{0.2} Ce _{0.8} O ₂ -Ni-ScSZ	ScSZ/PCM	800	3% H ₂ O-H ₂ /O ₂	602	30
	10% Cu- 90% Ce _{0.8} Zr _{0.2} O ₂ /Ni-CeO ₂ /Ni-YSZ	ScSZ/PCM	800	H ₂ /O ₂ 50%, H ₂ O-C ₂ H ₅ OH/O ₂	601, 519	31
	25 wt% Ni- 10wt% CeO ₂ – 65 wt% YSZ	YSZ/Pt	800	3% H ₂ O-H ₂	530	32
	Ni-YSZ	8YSZ/LSM-8YSZ	850	3% H ₂ O-NH ₃ , 3% H ₂ O-H ₂	526, 530	33
	10% Cu- 90% CeO ₂ /Ni-YSZ	ScSZ/PCM	800	H ₂ /O ₂ 50%, H ₂ O-C ₂ H ₅ OH/O ₂	520, 410	34
	NiO-YSZ	8YSZ/LSM-8YSZ	800	3% H ₂ O-H ₂	500	35
	Ni-Gd _{0.1} Ce _{0.9} O _{1.95}	GDC/Bi2V0.9Cu0.1O5.35-Ag	800	H ₂ (3% H ₂ O)	443	36
	CuO-SDC-CeO ₂	YSZ/LSM-YSZ	800	H ₂ , C ₃ H ₇ OH	350, 220	37
	25% Cu- 75% CeO ₂ /Ni-YSZ	ScSZ/PCM	800	H ₂ /O ₂ 50%, H ₂ O-C ₂ H ₅ OH/O ₂	450, 380	38
	Ni-ScSZ	ScSZ/PCM	800	3% H ₂ O-H ₂ /O ₂	466	40
	NiO-BaZr _{0.1} Ce _{0.7} Y _{0.2} O _{3-δ}	LNO / LNF	700		508, 551	15
Sr -based	5% CeO ₂ –0.5% Pd–45% La _{0.3} Sr _{0.7} TiO ₃ –65% Y _{0.08} Zr _{0.92} O ₂	YSZ/LSF-YSZ	800	Humidified H ₂	780	41
	YSZ–Ni	SrNb _{0.1} Fe _{0.9} O _{3-δ} (SNF)	800, 750, 700	Pure H ₂	1403, 1074, 841	26
	NiO-SDC	SrFe _{0.9} Nb _{0.1} O _{3-δ} (SFN)	800	dry H ₂	407	25
La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃ -based	2wt% Ag–6wt% Ni–32% La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃ – 60% Y _{0.08} Zr _{0.92} O ₂	YSZ/LSM	850	Dry H ₂ , Dry CH ₄	1302, 769	42
	37wt% (NiO-La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃)– 63wt% Y _{0.08} Zr _{0.92} O ₂	YSZ/LSM	800	Dry H ₂ , Dry CH ₄	1151, 704	43
	Ni -Sm _{0.2} Ce _{0.8} O ₂ – La _{0.75} Sr _{0.25} Cr _{0.5} Fe _{0.5} O ₃ –Y _{0.08} Zr _{0.92} O ₂	YSZ/LSM-SDC	800	Dry H ₂ , Dry CH ₄ Dry C ₂ H ₅ OH	960, 744, 406	44
	8.9wt% Ni–5.8wt CeO ₂ – La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃	YSZ/LSM	800	Dry H ₂ , Dry CH ₄	948 197	45
	35% La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃ – 65% Y _{0.08} Zr _{0.92} O ₂ YSZ/LSM	YSZ/LSM	850	Dry H ₂ , Dry CH ₄	567 561	46
	La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃ – Gd _{0.2} Ce _{0.8} O ₂	YSZ/LSM-YSZ	800	Humidified H ₂ Humidified CH ₄	419 158	43
	0.5% Pd–5% CeO ₂ –45% La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃ – Y _{0.08} Zr _{0.92} O ₂	YSZ/LSF-YSZ	700	Humidified H ₂	520	47
	Cu–La _{0.7} Sr _{0.3} Cr _{0.5} Mn _{0.5} O ₃ – Y _{0.08} Zr _{0.92} O	Ni-YSZ/Ni-ScSZ/ScSZ/PCM	800	H ₂ 2:1 mixture CH ₃ CH ₂ OH-H ₂ O	534 384	48

Abbreviations: YSZ: Yttrium stabilised zirconia, LSM: Strontium-doped lanthanum manganite, ScSZ: Scandia-stabilized zirconia PCM: Proton-conducting membrane, SDC: Samarium-doped ceria, LSF: Strontium-doped lanthanum metal.

Cobalt-free perovskites are suggested for use as cathode material, seeing their excellent long-term stability and compatibility. Nickel, molybdenum, and iron are the more promising nominees for replacing cobalt. Between these elements, the cost of iron is the

lowest, and iron-containing perovskites yield favorable electro-catalytic activity on the oxygen reduction reaction. Furthermore, the cell performance would be more enhanced through optimizing cathode microstructures.

5. Conclusions

The development of cobalt-free cathodes for intermediate temperature SOFCs has good potential. Besides the reduction in thermal expansion coefficient difference between cathode and electrolyte, cobalt-free cathodes also show acceptable polarization resistance in electrochemical impedance spectroscopy (EIS) analysis. This paper

investigations various studies on cobalt-free anodes and cathodes with/without nanofiber development including the important characters in determining performance of SOFCs as shown in Table 1. The polarization resistance of SOFC cathodes also importance of cobalt-free anodes and cathodes for this process.

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