

# *Research on electrode catalysts for solid oxide fuel cells*

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**Abstract:** The consumption of energy brings great environmental and economic pressure, and fuel cells, especially solid oxide fuel cells, have gain significant attention in the research, due to their eco-friendliness and remarkable efficiency. The electrode catalyst is crucial for enhancing the electrochemical reaction rate and advancing the progress of the fuel cell. Pure platinum catalysts are frequently employed in solid oxide fuel cells. However, platinum is expensive and non-renewable, and the resolution of this issue is crucial for the advancement of solid oxide fuel cells. This paper reviews current work on several cutting-edge platinum-based catalysts alternative materials. The performance of the cathode and anode catalysts is being analyzed and compared. Based on this analysis, some issues regarding the current catalysts are being raised. This is conducive for the following researchers to develop new electrode catalysts for solid oxide fuel cells.

## 1. Introduction

As society continues to develop, traditional fossil fuels are gradually being phased out, due to their low conversion efficiency, waste gases, solids and other combustion emissions. These can seriously cause environmental pollution. As a kind of new energy resource, fuel cell is a better method to solve the above problems. It is an efficient and environmentally friendly energy conversion equipment. Unlike heat engines, fuel cells do not have the same limitations as the Carnot Cycle. This results in their remarkable energy efficiency and minimal environmental impact. So, they are widely favored by enterprises and scientists. However, it also sprouts a lot of problems.

Fuel cell is a device that consumes chemical energy and electrical energy. It employs oxygen and fuel (such as hydrogen, methane, etc.) in the electrochemical reactions at the cathode and anode. Through the electrolyte conductive ions, the solid oxide fuel cell produces the potential difference between the positive and negative poles and the flow of electrons output the electric energy. Now, common fuel cells on the market include Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC). Compared with the other two cells, solid oxide fuel cell fuel has greater ingredient selectivity and can achieve better energy efficiency. However, SOFCs continue to face numerous challenges. For instances, the cathode and anode materials must be stable for a long time and the electrolyte material can deactivate.

In solid oxide fuel cells, catalysts are quite important. It can be employed as an electrode material for the cell constructing and promote the electrochemical reaction to improve the efficiency of the battery. Pure platinum metal is widely recognized for their better electrochemical reaction rates. And it is used as the catalysts in SOFCs. However, the significant expense and limited availability of pure

platinum have hindered the widespread implementation of SOFCs in markets. Therefore, I offer two solutions and reviews the researches and development of SOFC electrode catalysts in recent years. Improve the Pt-based electrode catalysts and develop the non-Pt metal electrode catalysts to replace pure Pt catalysts. We will talk about it in the second part. This could enable more people to systematically understand the progress of the research in this field, and provide references to the relevant research.

## 2. SOFC Catalyst

### 2.1 Cathode Catalyst

The cathode catalyst holds great significance in SOFC technology. The role of it is shown in Equation (1) (ethylene as a fuel gas).



The cathode catalyst can provide active sites for the reaction of the solid oxide fuel cell. In cathode catalyst, metal active centers or oxygen vacancies can adsorb oxygen molecules to provide catalytic activity for this reaction. This could improve the speed of the electrochemical reaction.

#### 2.1.1 Platinum-based Catalysts for Cathodes

Pt-based cathode alloy catalysts have shown great structural and practical properties. The Pt/Ti alloy cathode catalysts prepared by Jaehyeong Lee and his team using room-temperature co-sputtering had low activation resistance degradation rates [1]. Compared with the pure Pt, the maximum power density of Pt/Ti alloy is increased by 33% after two hours of cell operation. This greatly enhances the energy conversion efficiency of the SOFC, and its electrochemical performance evaluation is illustrated in Figure 1. Another kind of catalysts was successfully developed by Wonyeop Jeong's team. This is an ultrathin platinum-molybdenum-cerium-cerium metal-ceramic valence layer cathode catalyst by ultrathin sputtering with gadolinium-cerium doping on a platinum substrate [2]. The utilization of the catalyst resulted in a 42.7% boost in the peak power density, compare it with the reference cell synthesized by the team. One of the ultrathin platinum gadolinium cerium metal-ceramic valence layer cathode catalysts (Pt-GDC) has an ultrathin structure with a thickness of less than 50 nm. Jeong Woo Shin's team improved the pure Pt-based cathode catalyst by using ALD technology to obtain CeO<sub>2</sub>-coated Pt cathode on the basis of Pt-based. After 10 h of operation, its activation resistance was reduced by 50%. Its thermal stability was doubled in comparison to the pure Pt catalyst [3]. And in 2021, the team prepared doped ceria (YDC) shell layer catalysts on Pt substrates again by ALD technique [4]. They achieved further improvements to pure platinum-based cathode catalysts. Compared with the original Pt cathode catalyst, its exchange current density was increased by five times. And its activation resistance was reduced by 80% under the condition of doping a certain proportion of YDC. It has a very big effect, and its electrochemical performance test is shown in Figure 2. Meanwhile, Han Gil Seo et al. applied the ALD technique to coat alumina on a platinum base to achieve improvement of the cathode platinum-based catalyst. The electrode activity was seen an increase of over twice the amount compared to the uncoated electrode catalysts. [5].

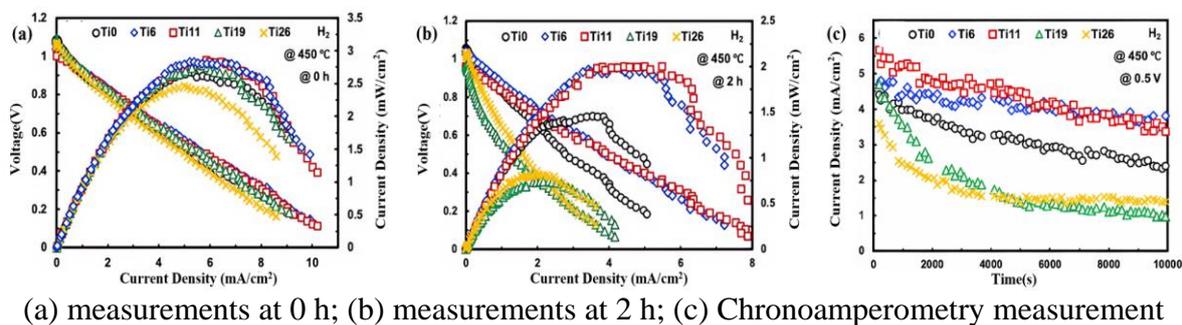


Figure 1: Electronic performance of Pt/Ti alloy.

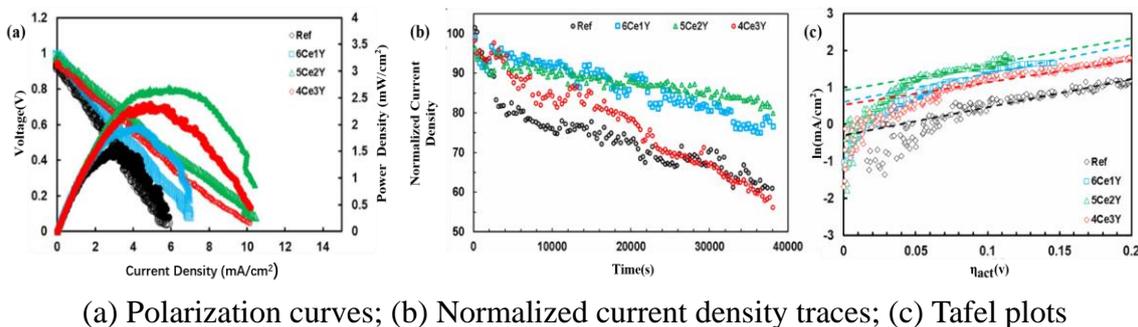


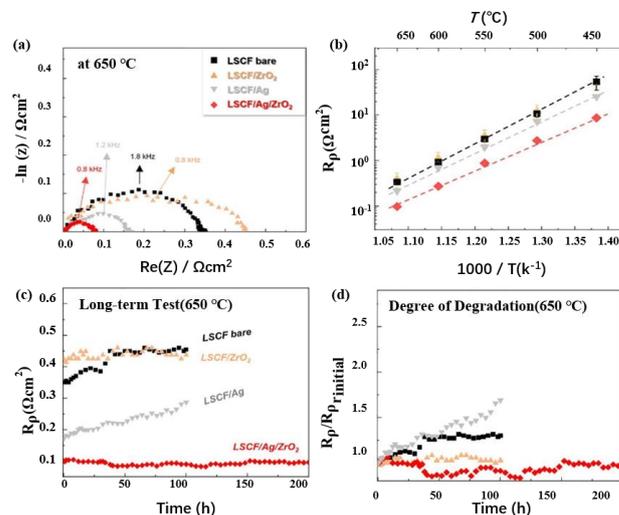
Figure 2: Electrochemical performance of CeO<sub>2</sub>&Yi Over Pt.

The advent of catalysts has partially addressed the existing issues regarding the expensive nature and limited efficacy of SOFCs. However, the non-renewable and expensive nature of platinum, electrode poisoning, catalyst material degradation and other issues, have led scientists to never stop researching non-platinum catalysts. Most common non-platinum cathode catalysts use elements such as La, Yi, Ni, Ca, etc. However, many scientists are continuously developing various non-platinum catalysts. It also has a wide range of applications today. Its performance is comparable to, or some even superior to, that of platinum-based catalysts.

### 2.1.2 Cathodic non-platinum catalysts

Element La, considered the initial cathode material for SOFCs, has witnessed ongoing enhancements. Shuai Wu's team synthesized Sr and Zn co-doped LaMnO<sub>3</sub> cathode catalysts (LSMZ) by the wet chemical method. They also analyzed the source of the superior performance of this catalyst using the first principle [6]. The performance reaches the maximum value of similar cathodes in H-SOFC. Nanostructured cathode material catalysts consisting of La<sub>0.10</sub>Sr<sub>0.90</sub>Co<sub>0.20</sub>Zn<sub>0.80</sub>O<sub>5-δ</sub> (LSCZO) were synthesized by Ghazanfar Abbas et al. via a wet chemical route. The electrochemical tests indicate a low conductivity and a power density of 850 mW/cm<sup>2</sup> at 550 °C [7]. This also confirms the promising improvement of LSM (Sr-doped LaMnO<sub>3</sub>) as a cathode catalyst for solid oxide fuel cells. Meanwhile, as mentioned above, ALD technology is now evolving. And SungHyun Jeon's team applied ALD technology to improve La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCF). It had been dispersed with silver nanocatalysts, by the ALD technique, constituting a LSCF cathode catalyst deposited with Ag/ZrO<sub>2</sub> nanocomposites [8]. Electrochemical tests showed that the electrode resistance was low at 0.085 Ωcm<sup>2</sup> after 200 h of operation. The results are shown in Figure 3. In addition, the introduction of Ag-Ceria into the LSCF [9], and the introduction of Ba into LSCF [10] or introduce a GDC middle layer [11] to improve the original cathode catalyst, can also enable the original solid oxide fuel cell to show better electrochemical performance. Several research studies have been undertaken to investigate the application of Pt-Lanthanide element pairings as catalysts in order to augment the characteristics of

the original catalysts. Arunkumar Pandiyan et al. improved the electrochemical performance of the original  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$  electrode by introducing 18 nm Pt particles into it using ALD technique [12]. As a result, the original solid oxide fuel cell experienced a significant increase in output power, with an 84% boost.



(a) Nyquist plot; (b) Corresponding Arrhenius plot; (c) Stability test at 650 °C; (d) Normalized resistance

Figure 3: Electronic performance of LSCF symmetrical cells.

Cathodic catalysts with non-La elements, such as the K-doped  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$  cathodic catalyst, was synthesized by Peng QIU's team [13] and  $\text{Nd}_{0.9}\text{Sr}_{0.10}\text{Co}_{0.9}\text{Fe}_{0.10}\text{O}_{3-\delta}$  (NSCFO) cathode catalyst developed by the team of Srinivasan Dharani Priya [14] and  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  cathode catalyst developed by Ahmed Sheraz's team [15]. All of them show good electrochemical properties. Although non-La cathode catalysts can exhibit electrochemical properties not inferior to those of La cathode catalysts. However, studies about non-La cathode catalysts are less than studies about La, according to our collection and analysis of the literature. To better compare the performance of different catalysts, we made a table. The performance of some cathode catalysts is shown in Table 1. And in the table, the percentage increasing or decreasing are compared to pure Pt electrode catalysts.

Table 1: Performance of Cathode Catalyst

Materials	Power Density (mW/cm <sup>2</sup> )	Resistance (Ωcm <sup>2</sup> )	References
Pt/Ti Alloy	Increased 33%	Reduced 50%	[1]
Pt-GDC	334 mW/cm <sup>2</sup>	-	[2]
CeO <sub>2</sub> -coated Pt	800	Reduced 50%	[3]
CeO <sub>2</sub> -coated Pt	Increased 5 times	Reduced 80%	[4]
$\text{La}_{0.10}\text{Sr}_{0.90}\text{Co}_{0.20}\text{Zn}_{0.80}\text{O}_{5-\delta}$	850	-	[7]
LSCF Deposited with Ag/Zro	-	0.085	[8]

Although cathodic non-platinum catalysts can replace cathodic platinum-based catalysts to a certain extent and its price, catalytic performance also shows some advantages. But an ability gap still be found compared with platinum-based catalysts and cathodic non-platinum catalysts. The durability of non-platinum is not as good as the platinum-based. Besides, platinum metal shows a lot of stability. This is much better than non-platinum metal. So, improving the stability of non-platinum metals remains to be an important issue.

## 2.2 Anode Catalysts

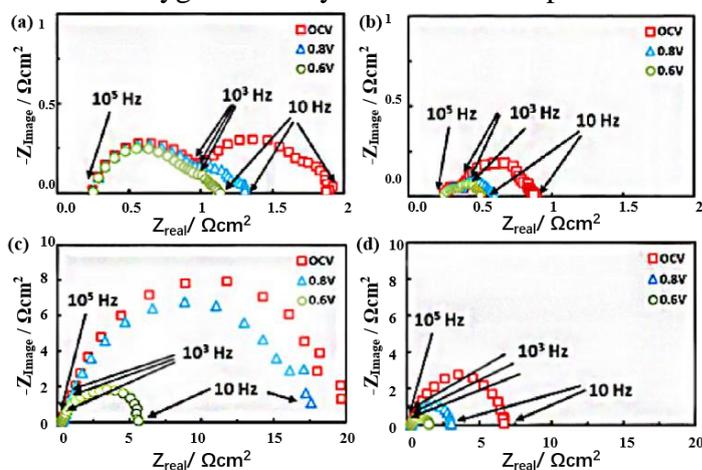
Similarly, a corresponding catalyst exists at the anode in the SOFC, and the anode catalyst acts as shown in Equation (2) (ethylene as a fuel gas).



In the SOFC, the fuel gas reacts with solid oxygen ions on the solid oxide electrode to generate current and water vapor, and the anode catalyst provides active sites for adsorption and dissociation of oxygen ions to reduce the activation energy of electrochemical reaction. Meanwhile, the high-performance anode catalyst could also provide the electrode with a certain degree of anti-carbon accumulation ability and anti-electrode poisoning ability.

### 2.2.1 Anode platinum-based catalysts

Now, pure platinum or Pt-based alloys are the more widely used materials for anode catalysts. These catalysts exhibit high structural and electrochemical properties. Byung Chan Yang et al. developed Pt-Samaria doped ceria (SDC) alloy anode electrode catalysts by DC co-sputtering method [16]. With a particle size smaller than that of pure Pt anode catalysts, it exhibits better structural properties. Meanwhile, the anode catalysts have improved poisoning resistance and activation capacity. Their thermal stability is higher than that of pure Pt. Jeong Woo Shin et al. successfully prepared CeO<sub>2</sub> coated porous Pt anode catalysts by using ALD and DC magnetron sputtering techniques [17]. Its maximum power density significantly increased by two times, compared with the pure Pt. Its electrochemical performance is shown in Figure 4. They successfully modified the Pt electrode catalyst. Meanwhile, Wonjong Yu et al. improved the cell activity by depositing Pt plasma on the surface of anode electrode by ALD technique. The obtained power density was increased by 60% compared to the bare electrode, and the ohmic was reduced by 25%. Additionally, the plan resistance was reduced by 50% [18]. This reflects better electrochemical performance. Besides, this improved performance can be explained by the expansion of the contact area and the increase of the reaction sites. In addition to the improved electrochemical and structural properties, the LaCo<sub>0.94</sub>Pt<sub>0.06</sub>O<sub>3</sub> anode electrode catalyst was successfully prepared by WenYu Li et al. using the sol-gel method [19]. The electron transferring properties of the catalysts were improved. This is mainly manifested in the increase of oxygen vacancy ratio and the improvement of charge transferring.



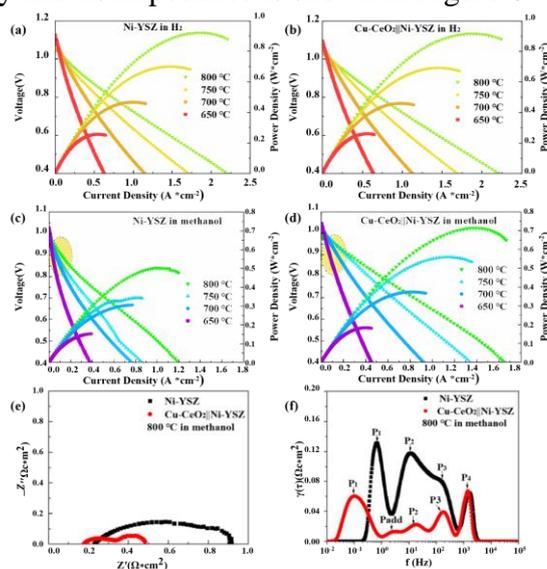
(a) 0 h without ALD-CeO<sub>2</sub>; (b) 0 h with ALD-CeO<sub>2</sub>; (c) 2 h without ALD-CeO<sub>2</sub>; (d) 2 h with ALD-CeO<sub>2</sub>

Figure 4: EIS results of AAO-supported SOFC.

The improvement of anode platinum-based catalysts can solve the current problem of low electrode performance to a certain extent. However, it still cannot solve the problem of high-cost and non-renewable platinum-based catalysts. Meanwhile, the platinum-based catalysts in the high temperature and redox environment are prone to oxygen migration and surface detachment and so on. So, the necessity of the development of anode non-platinum-based catalysts is increasingly rising.

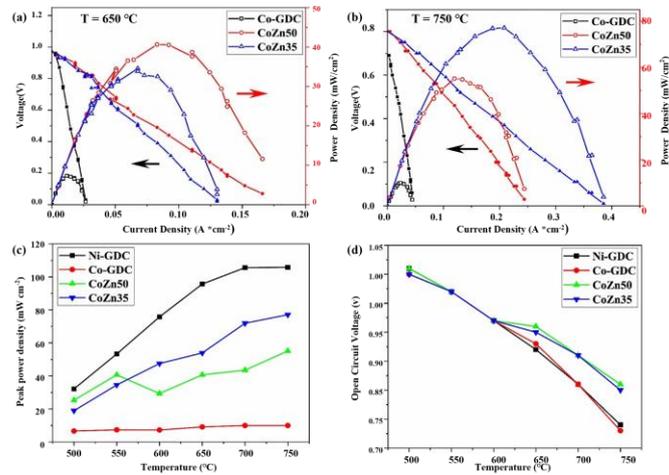
### 2.2.2 Anodic non-platinum catalysts

The traditional anode electrode catalysts are Cu-based and Ni-based electrode catalysts. Cu-based anode catalysts are a new type of anode catalysts. They can effectively improve the carbon buildup of Ni-based anode catalysts, and increase the service life of solid oxide fuel cells [20]. Planar Cu-doped Cerium-containing anode catalysts developed by Vincenzo De Marco [21], enhanced electronic conductivity achieving a peak power density of 200 mW/cm<sup>2</sup>. Meanwhile, in Panpan Zhang's study, independent Cu-CeO<sub>2</sub> catalyst layers were prepared by wet co-impregnation method [22]. Compared with the cell without this catalyst layer, the power density has increased by 42.32%. This showed better electrochemical performance, and its electrochemical performance was shown in Figure 5. Studies have also been conducted for the improvement of Ni-based anode electrode catalysts. Zhixiang Liu's team prepared Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95-δ</sub> nanoparticles through in-situ solvothermal method and modified the surface of the original Ni-Y<sub>0.16</sub>Zr<sub>0.84</sub>O<sub>1.92</sub> anode catalysts [23]. Such surface modification improves carbon accumulation problem of anode and also enables better stability of the anode inside the SOFC. In addition, Jie Hou and his team synthesized NBZCY65-35-20SS (NiO-BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2</sub>O<sub>3-δ</sub>(BZCY)) anode electrode catalysts through one-step gel combustion method of citrate-nitrate. This nicely improved the reactivity of the anode. In addition, Yao Yao et al. prepared a kind of catalysts, Ni<sub>0.7</sub>Co<sub>0.3</sub>/Al<sub>2</sub>O<sub>3</sub>+(10% La<sub>2</sub>O<sub>3</sub>), through wet impregnation method [24]. The power density was increased by 384 mW/cm<sup>2</sup> compared with the cell without catalyst. The Ba (Ce<sub>0.9</sub>Y<sub>0.1</sub>)<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>3-δ</sub> (BCYN) anode catalyst developed through the solution impregnation method employed by Yangya Liu et al. showed a very good resistance to carbon buildup in a long-term polarization test. Under the atmosphere of methane and at 750 °C, its polarization resistance is 0.12 Ωcm<sup>2</sup>. And under hydrogen atmosphere, its polarization resistance reached only 0.085 Ωcm<sup>2</sup> [25]. This shows the great stability and its impedance is shown in Figure 6.



(a) I-V(P) curves(H<sub>2</sub>); (b) I-V(P) performance, using Cu-Ceria(H<sub>2</sub>);(c) I-V(P) curves (MeOH); (d) I-V(P) curves, using Cu-Ceria(MeOH); (e) EIS plots; (f) DRT plots

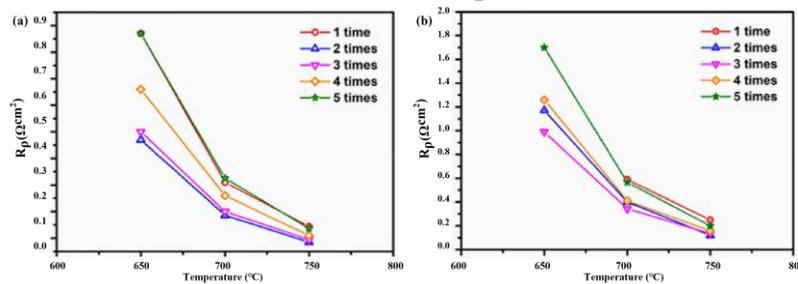
Figure 5: Performance of cells.



(a) H<sub>2</sub>; (b) CH<sub>4</sub>

Figure 6: Polarization impedances with different impregnation times and atmosphere.

Ce has also been used as a great new catalyst substrate in SOFC anode electrode materials, besides element Ni and Cu. A number of researchers have also improved and used it in SOFC anode catalysts due to its abundant oxygen vacancies, strong interactions with metals and other advantages. And it shows great electrochemical properties [26]. B. Bochentyn et al. prepared Pr and Sm co-doped CeO<sub>2</sub> anode electrode catalysts through the reverse phase microemulsion method and explored the stability of the catalyst materials under different compositions [27]. Two catalysts, Ce<sub>0.9</sub>Sm<sub>0.1</sub>O<sub>2-δ</sub> and Ce<sub>0.8</sub>Pr<sub>0.15</sub>O<sub>2-δ</sub>, have showed great stability over a longer period of time and were the most attractive catalytic materials among similar lanthanide-doped CeO<sub>2</sub> catalysts. In addition, B. Bochentyn et al. also developed Cu- and Co-doped CeO<sub>2</sub> anode electrode catalysts through the reversed-phase microemulsion method. This enhancement improved the performance of the electrode and increased the long-time stability of the SOFC. [28]. Meanwhile, the Co<sub>1-x</sub>Zn<sub>x</sub>Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> anode electrode catalyst developed by Mehdi Choolaei et al. showed excellent performance. Compared with the original Co-based catalyst, the Zn and Ce-doped electrode catalyst can increase the power density of the original cell by about five times [29]. Its electronic performance is shown in Figure 7.



(a) at 650 °C; (b) at 750 °C; (c) Peak power densities; (d) Recorded open circuit voltages

Figure 7: Electronic performance of different cells.

So, the improvement of anode Pt-based catalysts can well improve its reaction activity in solid oxide fuel cells. This well solves part of the current problems in fuel cells. However, Pt is still a scarce precious metal resource. Meanwhile, the development of alternative anode catalysts that are not based on platinum improves the potential for their application. We also summarize the performance of cathode catalysts accordingly. Table 2 presents a performance comparison of various catalysts. In the table, the percentage increase or decrease in performance is indicated for comparison with the type of electrode.

Table 2: Performance of Anode Catalyst

Materials	Power Density (mW/cm <sup>2</sup> )	Resistance ( $\Omega$ cm <sup>2</sup> )	References
CeO <sub>2</sub> Coated Porous Pt	478	Reduced 86% (Pure Pt)	[18]
Deposited Pt plasma	Increased 60% (Pure Pt)	Reduced 25% in ohmic and 50% in polarization (Pure Pt)	[19]
Planar Cu-doped Cerium-containing	200	-	[22]
Cu-CeO <sub>2</sub> Layer	Increased 42.32% (Ni-YSZ)	Reduced 55.2% (Ni-YSZ)	[23]
NiO <sub>0.7</sub> Co <sub>0.3</sub> /Al <sub>2</sub> O <sub>3</sub> +(10% La <sub>2</sub> O <sub>3</sub> )	651	-	[25]
Co <sub>1-x</sub> Zn <sub>x</sub> Gd <sub>0.1</sub> Ce <sub>0.9</sub> O <sub>1.95</sub>	Increased 5 times (Co- based)	-	[33]

### 3. Conclusions

Nowadays, traditional catalysts in fuel cells normally have high cost, and it is increasingly important to explore new catalyst materials. Therefore, this paper reviews several new developed fuel cell catalysts. Platinum is still being improved as the most commonly used anode catalyst. And the electronic performance of non-Pt catalysts, represented by the element La, is being improved. However, the stability and chemical activity of cathode catalysts still need to be improved. As for the anode, its properties such as carbon resistance and sulfur resistance still need to be improved. But the appearance of non-platinum catalysts, such as Cu and Ni, and the improvement of platinum catalysts can solve the problem to a certain extent. These catalysts can significantly mitigate environmental pollution and operational expenses of solid oxide fuel cells. Hence, this study can serve as a valuable resource for future investigations into electrode catalysts for SOFCs.

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