Research on Alternative Pt-based or Non-Pt catalysts for Solid Oxide Fuel Cells

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Abstract. Nowadays, heavy environmental and economic pressure from energy consumption is increasingly evident, and the research and application of new batteries is an effective strategy to solve above problems. Fuel cell is a chemical device that produces electricity directly from chemical energy. It has attracted much attention due to its lightweight device, simple mechanism, and clean energy. In the operation of fuel cells, the efficiency and stability of cells are determined by the ability of catalyst in redox reactions. However, pure platinum or platinum-based catalysts commonly applicated in solid oxide fuel cells are normally expensive and not renewable. Therefore, it is particularly important to develop alternative Pt-based catalysts or non-Pt catalysts. In this paper, several alternative low-platinum or non-platinum catalysts are systematically investigated, and novel platinum-based and non-platinum multi-metal composite oxide catalysts are found to have higher catalytic activity and economic feasibility compared with pure platinum catalysts. The popularity of these new catalysts can effectively address the scarcity of resources and energy.

Keywords: SOFC, Cathode, Anode, Catalyst.

1. Introduction

Nowadays, human demand for energy is increasing, and most energy needs are still being fulfilled by burning non-renewable fossil fuels. Therefore, fuel cells can offer a powerful and environmental responsible solution. Fuel cells transform the Gibbs free energy portion of the chemical energy into electrical power through an electrochemical process, without the limitation of the Carnot cycle effect and with high efficiency. Moreover, fuel cell runs on fuel and air, and they are normally free of mechanical drive components, so they emit few harmful gases and have a long service life. So, fuel cells are the most promising power generation technology in saving energy and protecting the ecological environment.

Solid Oxide Fuel Cell (SOFC) normally has the highest theoretical energy density and rarely requires fuel treatment. Internal reforming, heat integration, and manifolds can make the system design simpler, and it is also easy to carry out high efficiency co-generation between SOFC and gas turbines and other equipment. Therefore, it is generally regarded as a type of fuel cell that can be profoundly popularised in the future.

The principle of the SOFC is that the fuel undergoes a redox reaction in the device, and the suitable catalyst can reduce the activated energy of the electrode reaction and improving the reaction rate. The catalyst can dramatically enhance the power density of the fuel cell by reducing the activation polarisation of the fuel cell and it largely affects the performance of the fuel cell and is the key material and operation guarantee of the fuel cell. So, the catalyst activation is very critical. The current commercial catalyst is platinum (Pt), and it normally has good molecular adsorption and dissociation properties. However, platinum is expensive and the storage capacity in China is extremely short. These shortcomings are severe obstacles to the commercialization of SOFC. So, it is especially essential to develop, alternative low-Pt catalysts and Pt-based and non-Pt catalysts.

Therefore, this paper systematically investigates several alternative low-platinum or non-platinum catalysts and finds that compared with pure platinum catalysts, carbon-based catalysts combining platinum and other metals deposited on graphene oxide or nanostructures, and platinum-free multi-metal composite oxides with cubic nanostructures exhibit more advantages. They can significantly reduce the electrode polarisation resistance, increase the peak power density and current density, and show more outstanding mass-specific activity and electrochemical stability. Most importantly, Extensive research and widespread application of these new catalysts can effectively address the enormous environmental and economic pressures and alleviate the current scarcity of resources and energy.

2. Platinum-based Catalysts

Platinum-based catalysts are widely used in the fuel cells due to their high-level catalytic activity, good selectivity, superior thermal stability and corrosion resistance. However, pure platinum is normally more expensive and harder to regenerate. Therefore, it is important to develop new high activity catalysts to enhance the efficiency of the battery.

Mhamad Hamza Hatahet et al. presented a new design (Figure 1. (a)) [1]. In this way, platinum and iron oxide were deposited on each side of the graphene oxide substrate. Then, platinum was applied to the graphene oxide substrate using atomic layer deposition to decorate the surface as the iron oxide at the bottom precipitates from the etching solution (Figure 1. (b)). A significant increase in the impedance value of the (platinum|graphene) electrode with the addition of iron ions. Electrochemical impedance measurements of (Fe_2O_3|graphene|platinum) electrodes in humidified hydrogen at 240 ℃ showed that the electrodes had excellent mass standardized activity (Figure 1. (c)). In addition, the presence of Fe_2O_3 nanoparticles improves the availability and electrochemical stability of the (Pt|Graphene) cathode. The relative current density of Fe_2O_3 nanoparticles on $Pt_{ALD-200}$@5L-$OGr_{8/100}$ cathode was increased from 0.66 to 0.92 after 60 h of process at 0.35 V constant voltage (Figure 1. (d)). Noha A. Elessawy et al. converted PET bottle waste into N-doped graphene as an electrocatalyst carrier, and this catalyst had a larger specific surface area and greater catalytic activity [2]. The results of CV and LSV measurements showed that the catalysts had a significant effect on BOR The NG/Pt_1 catalysts were more active, with an exchange electron number of about 2.7. Besides, the highest power density of the fuel cell with NG/Pt_1 catalyst increases significantly between 25 ℃ ~ 45 ℃. Daisuke Takimoto et al. synthesised bilayer platinum oxide nanosheets with a thickness of 0.5 nm by topologically reducing 0.9 nm thick monolayer platinum oxide nanosheets (Figure 2. (a)) [3]. The efficiency of this Pt catalyst is higher than that of conventional standard performance Pt nitrides in the 3 nm size. Apart from its high ECSA, Pt NSs exhibited excellent characterisation (Figure. 2 (b)). Furthermore, Pt NSs had a higher durability. After 5000 cycles, the ECSA of Pt NSs was twice that of Pt NPs, decreasing from 124 to 93 m^2 g^{-1} (Figure 2. (c)). Ultra-thin platinum nitrides outperform classical 3 nm platinum nitrides in terms of mass activity, durability and ECSA (Figure 2. (d)). This suggested a major breakthrough in the trade-off between ECSA and electrical activity of Pt NSs.

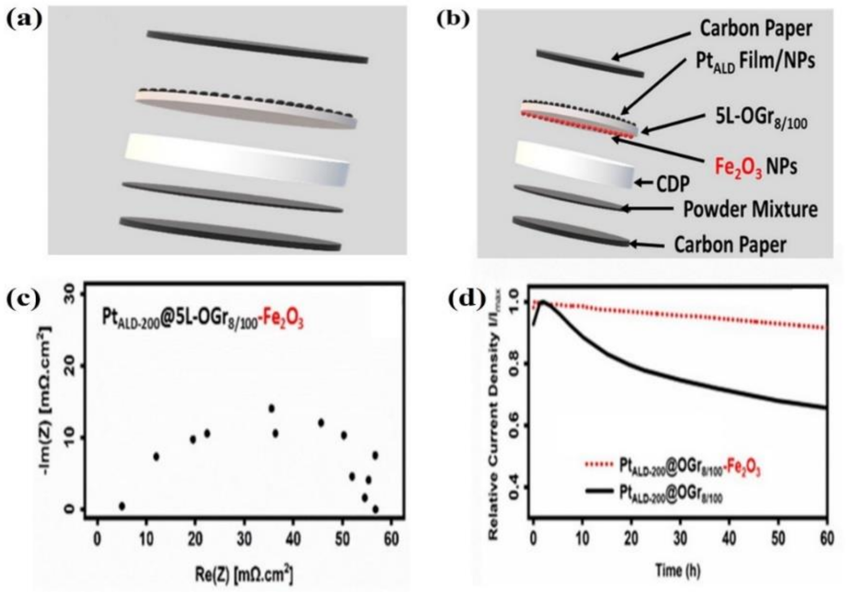

Figure 1. (a) Structure of Pt$_{ALD-200}$@5L-OG$_{r8/100}$; (b) Layered structure of Pt$_{ALD-200}$@5L-OGr$_{8/100}$; (c) Nyquist plot of electrode impedance for Pt$_{ALD-200}$@5L-OGr$_{8/100}$; (d) Electrical density of Pt$_{ALD-200}$@5L-OG$_{r8/100}$·Fe$_2$O$_3$ and Pt$_{ALD-200}$@5L-OGr$_{8/100}$

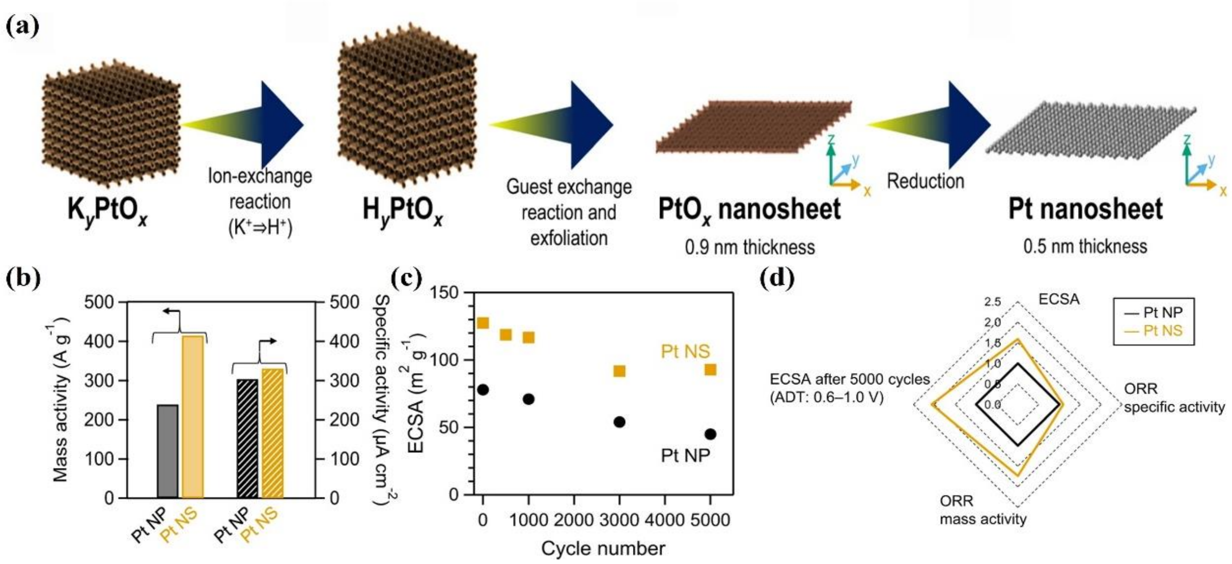

Figure 2. (a) Synthesis method of double-layer Pt nanostructures; (b) The mass and specific activation of samples at 0.9 V; (c) The relationship between ECSA and potential cycle; (d) The photocatalytic performance of Pt NSs and 3 nm size Pt NPs

Amisha Beniwal et al. formed CoPt nano-alloys and nanocatalysts decorated with platinum clusters with various metal-metal oxide interfaces over CSPP-50 catalyst [4]. This structure has several metal-metal oxide interfaces. The mass activity is 4330 mA·mg$_{Pt}^{-1}$ at 0.85 V in the RHE alkaline ORR, 78 times that of the J.M.-Pt/C catalyst phase containing 20 wt.% Pt. Islam M. Al-Akraa et al. modified glassy carbon electrodes sequentially with nanostructures of platinum, gold and cobalt oxide [5]. The triadic n-CoOx/n-Au/n-Pt/GC catalysts exhibited significantly enhanced electrocatalytic effect on FAEO, 53 times higher than that of the Pt/GC catalysts. Compared with the n-Pt/ GC and n-Au/n-Pt/GC catalysts, the n-CoOx/n-Au/n-Pt/GC catalyst showed higher catalytic activity. In addition, it showed higher stability after continuous electrolysis for 3000 seconds. Yellatur Chandra Sekhar et al. used a simple liquid-phase chemical reductive method to fix platinum-ruthenium bimetallic nanoparticles on RGO-TiO$_2$ nanohybrid carriers [6]. This catalyst showed about 1.4- and 3.2-times higher mass specific activity of the nanocomposite for ethanol oxidation reaction compared to commercial catalysts with higher mass ratio, specific surface area current density and high stability. Jae-Hyeok Park et al. synthesized carbon shell-coated Pt and Pt-Fe catalysts in the liquid phase using plasma reaction [7]. Carbon shell-coated Pt-Fe catalysts with 29 % Fe content showed a mass activity of 730 mA·mg_{pt}^{-1} and a specific activity of 1772 µA·cm^{-1}, representing 2.4 and 5 times higher than that of commercial Pt/C catalyzer.

In summary, the development of new Pt matrix catalysts not only significantly reduces the cost, but even has higher catalytic activity and stability. This can significantly help to refine the behaviour of solid oxide fuel cells.

3. Non-Pt catalysts

Non-platinum-based catalysts can effectively alleviate the cost of SOFC. Now, people are committed to the development of efficient and stable non-metallic catalysts that can replace platinum-based catalysts, and the following development results in recent years are briefly introduced.

Peng QIU et al. successfully prepared k-doped (BCFZ442) series materials as cathodic catalysts for SOFC [8]. K00, K05, K10 and K15 powders (x = 0, 0.05, 0.10, 0.15) (Figure 3. (a)) is a sample with a standard simple perovskite structure fabricated by the sol-gel method. The powder exhibits excellent chemical compatibility with the electrolyte (Figure 3. (b)). The four samples have similar thermal expansion behavior (Figure 3. (c)). The K10 sample showed strong structural stability after at 800 ℃ (10 mol% H_2O) in wet air for 10 h (Figure 3. (d)), and K10 exhibits elevated conductivity for electrons (e-), oxygen ions (O2-), and H+, along with efficient proton absorption. The cathode's polarization resistance is remarkably low, measuring only 0.009 Ω·cm-2 at 750 ℃. Furthermore, the maximum power density of a single cell approaches 1 mW·cm-2. Importantly, sustained stability is observed, as evidenced by the lack of apparent decay within 150 h timeframe (Figure 4).

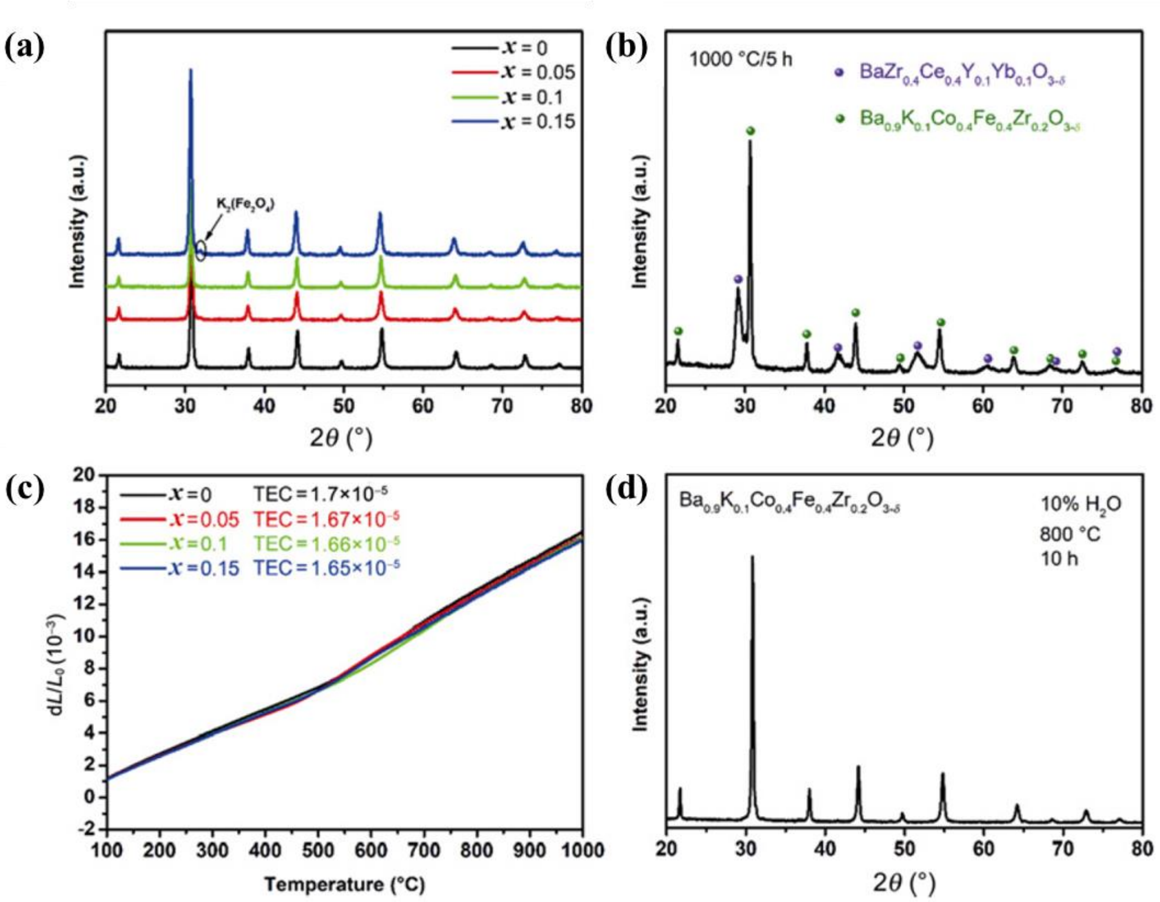

Figure 3. (a) XRD spectra of Kα (α = 00, 05, 10, 15) powders; (b) Chemical compatibility of K10 powder; (c) Thermal expansion coefficients of the Kα (α = 00, 05, 10, 15) specimens; (d) XRD spectrum of K10 powder dissolved in 10 mol% H2O after heat treatment at 800 °C

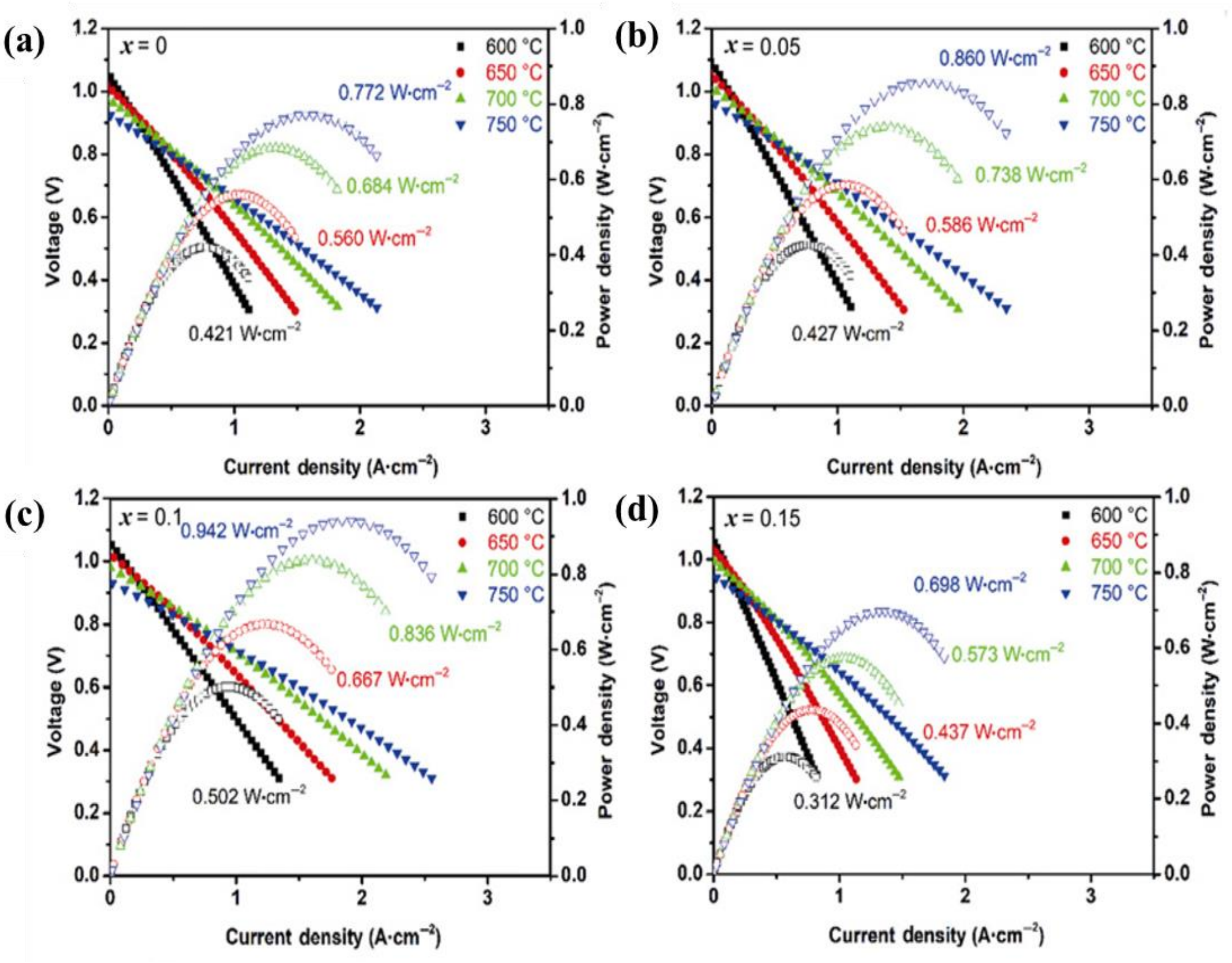

Figure 4. Corresponding I-P profiles and I-V curves of Kα (α = 00, 05, 10, 15) cathode single cells at 600 ℃, 650 ℃, 700 ℃ and 750 ℃

New cathodic catalysts depositing nanostructures (LSM) on $BaZrO_3$ (BZY) were presented by Eman Husni Da′as et.al [9] (Figure 5. (a)). $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20) electrolyte film was fabricated on BZY20-nio composite anode by co-pressure co-firing process. Preparation of NiO-BZY20 composite powder by one-step combustion method. La0.8Sr0.2MnO3-δ (LSM20) nanoparticle precursors were impregnated on a BZY20 skeleton using inkjet printing technique. The diameter of LSM20 nanoparticles is about 25 nm, and every LSM20 nanoparticle linkage to the BZY20 backbone can be viewed as a TPB site. Maximum power densities of 2, 6, and 14 mW·cm^{-2} were achieved at 500, 550, and 600 ℃, respectively. The polarization resistance (Rp) of the inkjet-impregnated LSM20 cell was 3.32 Ω·cm^{2} at 500 ℃, and that of the mechanically mixed cathode cell was greater than 90 Ω·cm^{2}. Increasing the amount of LSM20 in the composite cathode to the 1:1 ratio at 600 ℃ The power density reaches 16 mW·cm^{-2}, as shown in Figure 5 (b-c).

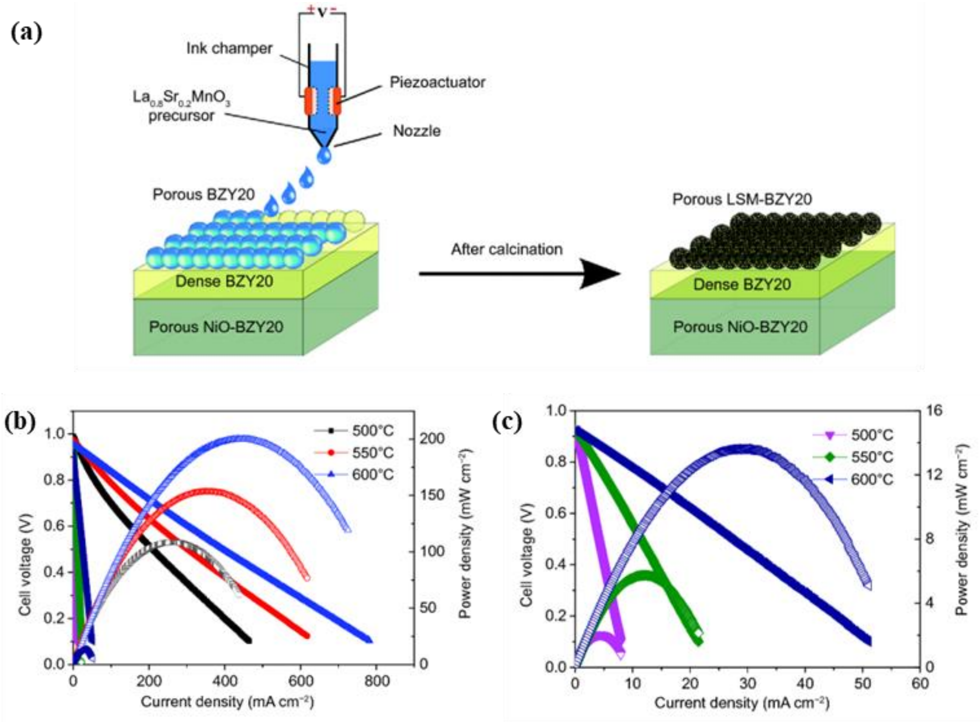

Figure 5. (a) Principle of LSM nanoparticles impregnation on BZY skeleton; (b) Comparison of performance of impregnated cathodes of LSM and of mechanical mixing LSM BZY fuel cell at 500℃, 550℃ and 600℃; (c) Mechanical Hybrid LSM Positive BZY Battery Performance Details

Liling Zhang et al. successfully prepared Sc-doped $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFMSc) cathode catalysts [10]. SFM and SFMSc powders were synthesized using a standard combustion process. In this process, most Mo was replaced by Sc to produce more empty oxygen sites for improved performance (Figure 6. (a)). The catalyst exhibits a low barrier for proton migration and demonstrates excellent chemical stability, as shown of Figure 6 (b-c). The peak power densities of SFMSc at 600, 650, and 700 ℃ are recorded as 545, 966, and 1258 mW·cm^{-2} respectively (Figure 7).

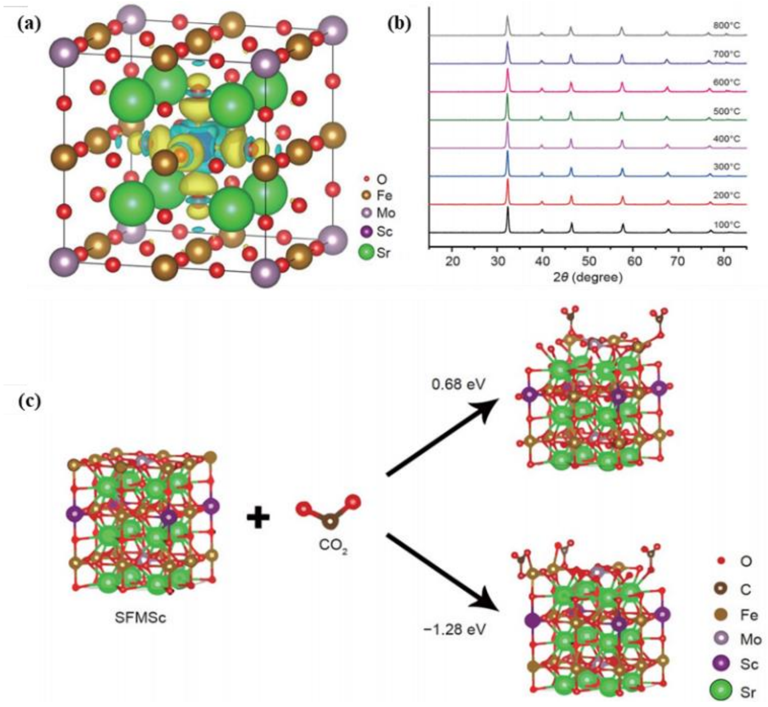

Figure 6. (a) Charge density crystalline cell plot of Sc-doped SFMs; (b) In-situ XRD spectra of SFMSc powders at 100-800 °C; (c) Surface CO2 adsorption calculation and structure diagram of SFMSc

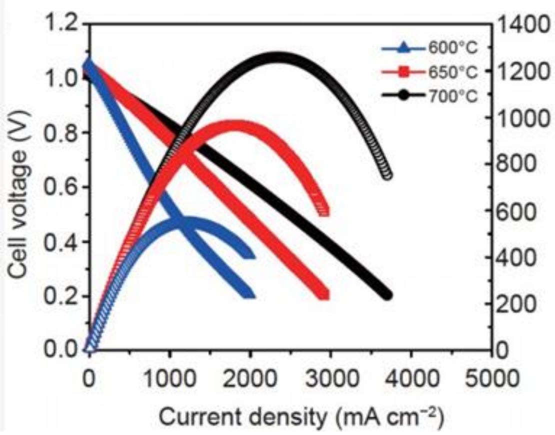

Figure 7. I-V and power density profiles for SFMSc

Z. Zhongliang et al. used lanthanum-replaced $La_xSr_{2-3x/2}Fe_{1.5}Ni_{0.1}Mo_{0.4}O_{6-\delta}$ (La_xSFNM, x= 0, 0.1, 0.2, 0.3, 0.4) as the anode catalyst [11]. La_xSFNM powder was prepared by standard solid phase method, and the synthesized powder had good cubic symmetric single perovskite structure. The anode catalyst produced the highest catalytic activity at x = 0.3 and the lower battery polarization resistance of 0.16 Ω at 750 °C (Figure 8. (a)). In Figure 8. (b-c), for the impedance data, the Bode plot reveals that the response discrepancy primarily manifests within the frequency range of 10-1000 Hz. The peak power densities at 750, 650 and 550 °C were 1.26, 0.90 and 0.52 W·cm^{-2} respectively. (Figure 9. (a-b)).

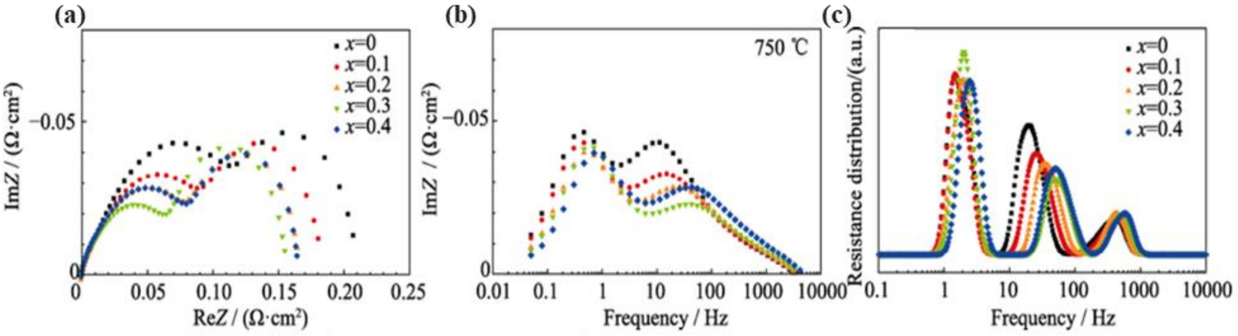

Figure 8. Impedance results (a) Nyquist and (b) Bode plots for a symmetric anode fuel cell operated at 750 ℃ in hydrogenated H_2 (3 vol% H_2O, 100 mL·min^{-1}); (c) The results shown in (a) and (b) are distributed in relation to time graphs

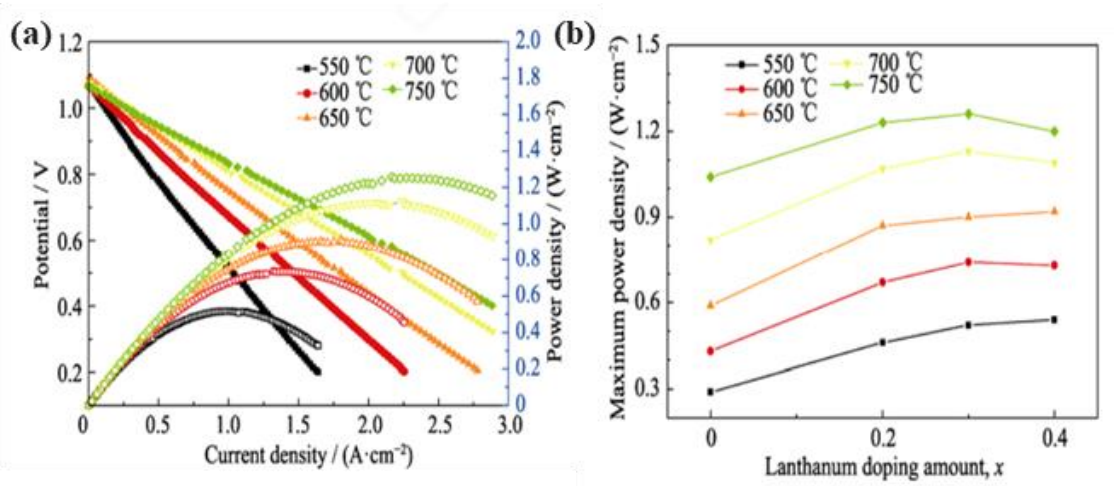

Figure 9. (a) Voltage and power density with the maximum power density at 750, 700, 650, 600, and 550 ℃; (b) Peak power density of fuel cells with La_xSFNM catalyst at 750, 700, 650, 600, and 550 ℃

In summary, the development of novel non-platinum catalysts not only significantly reduces costs but also exhibits excellent catalytic activity and stability. This is conducive to enhancing the efficiency and durability of SOFCs, thereby extending their service life.

4. Conclusions

Nowadays, energy consumption brings about great environmental and economic pressure. Solid oxide fuel cells are widely researched for their superiorities of high generation efficiency and adaptability of fuels. The catalytic ability of the electrode catalyst determines the performance of this cell. In this paper, several alternative low-platinum or non-platinum catalysts are systematically investigated, and new platinum matrix composite catalysts and non-platinum multi-metal composite oxide catalysts are found to perform more prominently. They can show higher catalytic activity and economic feasibility compared with pure platinum catalysts. The popularity of these new catalysts can effectively address the scarcity of resources and energy.

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