Review of anodic reactions in hydrocarbon fueled solid oxide fuel cells and strategies to improve anode performance and stability

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Abstract
Direct utilization of hydrocarbon fuels in solid oxide fuel cells (SOFCs) has drawn special attention for high energy conversion efficiency, low cost, and simple devices. However, when fueled with hydrocarbons, SOFCs encountered great difficulty in both performance and stability, which should be attributed to the sluggish hydrocarbon oxidizing reactions, the severe carbon deposition reactions, and the possible sulfur poisoning reactions in the anode. This review summarizes potential anode reactions in hydrocarbon-fueled SOFCs and discusses the possible anode deactivation mechanisms. Further, various strategies to improve the anode performance and stability are reviewed, including substituting alloys or increasing oxide basicity for nickel-based anodes, adopting oxide anodes, and adding catalyst layers. The advantages and challenges of each strategy are discussed. Special attention is paid on properties and models of novel oxide anodes, of which nano-metal catalysts are in-situ exsolved. The publications concerning SOFC anodes, mainly in recent 5 years, are listed and compared in this article.

Keywords Solid oxide fuel cell · Anode · Hydrocarbon fuel · Carbon deposition

Introduction
Fossil fuels have largely contributed to the development of mankind by providing a power source for various technologies. However, the excessive usage of fossil fuels, such as oil and coal, have triggered many problems such as air pollution, green-house effects and animal extinction. Moreover, the efficiency of the direct use fossil fuels by combustion still needs to be improved, because the efficiency of burning fuels is limited by the temperature gap between two media, which is referred to as the Carnot cycle. Solid oxide fuel cells (SOFCs) are devices that, in principle, have high conversion efficiency, low pollution, and no noise. These can also transform chemical fuels to electricity beyond the limitation of the Carnot cycle. The unique properties of SOFCs, such as high operating temperatures and high catalytic activity toward fuel oxidizing reactions, make them capable for operating with hydrocarbon fuels, such as methane and propane, and oxygen-containing fuels, such as methanol and ethanol. Hydrocarbon-fueled SOFCs are expected to be more applicable in commercial markets because of the narrow explosive limits, low price, and easy storage of hydrocarbon fuels. Among the hydrocarbon fuels, methane may be the most attractive fuel because of their abundant storage in natural gas, combustible ice and relatively easy conversion from biomass and/or CO₂. However, methane has the highest C–H bond energy among all alkanes with the first bond dissociation energy (BDE) of 439.3 kJ/mol (in standard condition) [1]. The high dissociation energy of methane indicates it the least active alkane and requires efficient catalysts to ensure its conversion. Thermodynamic calculations indicate...
methane is unstable above 773 K, however, the conversion of methane is negligible below 1200 K at 1 bar without the presence of catalysts due to slow kinetic rates [2, 3]. And, therefore, efficient catalysts are very important to improve the conversion rate of methane. In recent years, increased interests have been attracted on the biofuels, especially the bioethanol [4–8], which can be easily obtained from the fermentation of crops, sugar-cane, wheat and low-grade biomass such as woodchips, and bagasse [9]. Compared with methane, bioethanol has the advantage in easy storage and transportation [4]. Moreover, ethanol can be easily mixed with water, which increases the O/C and H/C ratio, and brings it out of the carbon deposition region in O–H–C ternary phase diagram.

The main problems for hydrocarbon fueled SOFCs are relatively lower performance and much faster performance decay than that use hydrogen fuel. The low electrochemical performance of hydrocarbon-fueled SOFCs should be ascribed to the difficulty in direct oxidation of hydrocarbon fuels and/or in the thermal dissociation and internal reforming reactions of hydrocarbons. Emir Dogdibegovic et al. used hydrogen, ethanol, ethanol-water blend, simulated reformate gases and hydrogen–nitrogen mixtures to evaluate the type of fuels on the cell performance, and suggested that the decrease of electrochemical performance when switching from simulated reforming gases to ethanol-water blend should result from the competition between reforming reactions and electrochemical reactions on Ni catalysts, or the slow kinetics of electrochemical oxidation of hydrocarbons [4]. The fast performance attenuation in hydrocarbon-fueled SOFCs may result from carbon deposition, which is the consequence of fast C–C bond cracks, carbon diffusions, or aromatic reactions during hydrocarbon conversions, then result in blocking reaction sites on the catalyst, rupturing the button cell, and threatening the button cell operation. Another key problem is sulfur poisoning because most hydrocarbon fuels are obtained from natural gas or mineral oil, which usually contain sulfur compounds such as thioether, disulfide, and hydrogen sulfide. The strong adsorption of sulfur-containing species may hinder the adsorptions of fuels and impede their subsequent reactions over the catalyst. Driven by these issues, many studies have focused on discussing the hydrocarbon reaction mechanisms in the anode and on developing novel stable anode catalysts. Up to now, many high-level reviews have been published concerning SOFC anodes [10–14]. In the past two decades, the number of publications about SOFCs had increased and reached its highest level in 2006. Thereafter, the “SOFC anode” remained a popular subject for research until the present, as shown in Fig. 1a. The country-wise distribution for publications concerning SOFC anodes is shown in Fig. 1b, in which China, USA, and Japan published half of the total publications.

In this review, we will discuss the basic reaction mechanisms in SOFC anode and the deactivation mechanisms for anodes, which mainly consist of carbon deposition and sulfur poisoning. We will then present some strategies for improving anode activity and stability, including adopting alloy anodes, improving the basicity of catalysts, using oxide anodes, and adding a catalyst layer. The latest reports about SOFC anodes, mainly from 2015 to 2019, are listed for each strategy. Finally, we will provide a summary of SOFC anodes.

Hydrocarbon reactions in SOFC anodes

To simplify the reactions in anode, hydrocarbons reactions can be divided into two parts: catalytic thermal reactions and electrochemical oxidation reactions. Take methane as an example. When methane molecules encounter active
catalysts, methane decomposes to hydrogen and carbon atoms or other CH_x species. When water is injected into the reaction system, a water reforming reaction may occur simultaneously, forming CO and H_2. After that, CO, CH_x, and H_2 are further oxidized by the oxygen ions that come from the electrolyte and react at the electrolyte-catalyst-gas three-phase boundaries (TPBs), as shown in Table 1. The unreacted methane along with the generated H_2 and CO can also be directly oxidized by the oxygen ions at the TPBs, which is referred to as the direct oxidation, as shown in Fig. 2b. By testing the out-gas compositions with and without discharge current densities, the fraction of the described reactions can be determined. Previous researches have been conducted on the determination of the direct oxidation of hydrocarbons in SOFCs [15, 16]. Olga A. Marina, et al. have tested the outlet gases of a button cell when fueled with methane. Apart from the conversion improvements of methane with the increase of current density, the selectivity to CO_2 is also increased with the sacrifice of CO in discharging conditions, as shown in Fig. 2c, d.

It should be greatly noted that the reactions that occur in anode are very complex, and interact with each other. The degree of catalytic reactions and reforming reactions impacts

| Number | Reactions               | Reaction type                     |
|--------|-------------------------|-----------------------------------|
| 1      | CH_4 + H_2O = CO + 3H_2 | Catalytic thermal reactions       |
| 2      | CH_4 + CO_2 = 2CO + 2H_2|                                    |
| 3      | CH_4 = C + 2H_2         |                                    |
| 4      | C + H_2O = CO + H_2     |                                    |
| 5      | 2CO = CO_2 + C          |                                    |
| 6      | CH_4 + O_2^- = CO + 2H_2| Electrochemical oxidation reactions|
| 7      | CO + O_2^- = CO_2       |                                    |
| 8      | H_2 + O_2^- = H_2O      |                                    |

Fig. 2  
(a) Working principle of hydrocarbon fueled SOFCs.  
(b) Schematic illustration of thermal and electrochemical oxidation of methane.  
(c) Current-overpotential curve of the Ce_0.6Gd_0.4O_1.8 electrode vs. air and the production rates of H_2, CO, CO_2, C_2+ hydrocarbons as well as the consumption rate of methane.  
(d) The selectivities to the CO, CO_2 and C_2+ as a function of overpotential. P_(CH_4) = 9 kPa, P_(H_2O) = 3 kPa, T = 1000 °C, F = 100cm^3/min. Reproduced with permission [15]. Copyright 1999, Elsevier
the type and the concentration of fuels involved in the direct reaction. Moreover, the rates of these reactions differ with the specific operating conditions. For example, catalytic reaction mechanisms are highly related to the type of catalysts and the hydrocarbons, the morphology of catalysts and the operating temperatures. Compared with Ni catalyst, large thermodynamic and kinetic barriers to methane dissociation are observed on Cu catalysts, indicating the importance of the type of catalysts on the hydrocarbon thermal catalytic reactions [17]. Moreover, different crystal planes of catalysts may also play a different role in accelerating the decomposition of hydrocarbon. Natasha M. Galea et al. investigated the methane dissociation pathway on the (111) and (211) terminal surfaces of Ni catalyst via Density Functional Theory (DFT) and found that the dissociation of methane to carbon is endothermic on Ni (111) surface while exothermic on Ni (211) surface, indicating the Ni (211) terminal surface has higher catalytic activity toward methane dissociation and lower resistance to carbon formations than Ni (111).

As for the direct oxidation of hydrocarbons, it is also impacted by the conducting behavior and the electrocatalytic activity of catalysts, the length of TPBs, the concentration of hydrocarbons, the concentration of pre-conversion species (e.g. H2 and CO), the operating current densities and also the operating temperatures. Notably, the heterogeneous catalysts in anodes may have synergistic effects on oxidation reactions. M. Shishkin applied DFT to study direct methane oxidation at TPBs and concluded that the oxidation of methane in anodes should result from the oxygen spillover form YSZ electrolyte to Ni, while the proton spillover from Ni to YSZ accounts for the water formation [18].

Although lots of studies have been focused on investigating the mechanisms and the functional ratio of these anodic reactions, there are still too many parameters to be

Table 2  Carbon species formed in the steam reforming of hydrocarbons. Reproduced with permission [20]. Copyright 1982, Taylor & Francis

| Formation | Encapsulating film carbon | Whiskerlike carbon | Pyrolytic carbon |
|-----------|--------------------------|--------------------|------------------|
| Slow polymerization of CnHm radicals on Ni surface into encapsulating film | Diffusion of C through Ni crystal, nucleation and whisker growth with Ni crystal at top | Thermal cracking of hydrocarbon, Deposition of C precursors on catalyst |
| Critical parameters | Low temperature. Low CnHm. Low H2/CnHm. Aromatic feed | High temperature. Low H2O/CnHm. No enhanced H2O adsorption. Low activity. Aromatic feed | High temperature. Low H2O/CnHm. High void fraction. High pressure. Acidity of catalyst |
| Temperature range, °C | < 500 | > 450 | > 600 |
| Effects | Progressive deactivation | No deactivation of Ni surface. Breakdown of catalyst and increasing ΔP | Encapsulation of catalyst particle. Deactivation and increasing ΔP |

Fig. 3  a ternary phase diagram of O–H–C and the carbon deposition region are marked at various temperatures. Reproduced with permission [21]. Copyright 2003, The Electrochemical Society. b Equilibrium partial pressure of H2S vs. reciprocal temperature for the nickel-sulfur system (values of ΔHf based on 1 mol H2S); open symbols for coverage from 0.5 to 0.6 and solid symbols for coverage from 0.8 to 0.9. Reproduced with permission [24]. Copyright 1982, Elsevier
modulated to make them clear. Yet strategies that can be utilized to improve the electrochemical performance of anode can be proposed. In general, based on the above discussions, improving the anode performance should be made from two aspects: developing anodes with high catalytic activity to facilitate catalytic reactions and adopting anodes with higher charge carrier properties, which can improve electrochemical performance.

Table 3  Comparison of electrochemical performance of button cells with alloy anodes

| Anode | Button cell configuration | Fuel | Button cell peak power density (mW/cm²) | Stability tests | Year | References |
|-------|---------------------------|------|----------------------------------------|----------------|------|------------|
| Sn0.01–Ni0.99 | Sn–NiYSZ|YSZ–LSM | CH₃CH₂OH | 250@740 °C | > 20 h | 2016 | [8] |
| 0.5wt.%Sn–Ni | Sn–NiGDC|GDC–LSCF | CH₄ | 930@650 °C | > 250 h | 2015 | [30] |
| Ni0.5Co0.5 | Ni0.8Co0.2|Y–YSZ|YSZ–YDC|LSCF | CH₃CH₂OH | 550@800 °C | 8 h | 2015 | [32] |
| Ni0.5Co0.5 | Ni0.8Co0.2|SDC|LSCF | CH₄ | 379@600 °C | 72 h | 2017 | [33] |
| Ni0.7Cu0.2Co0.1 | Ni0.8Cu0.2|SDC|SSC–SDC | CH₄ | 150@700 °C | 72 h | 2017 | [34] |
| Ni-Cu/Ni–Fe | Ni–Cu/Ni–FeNi–YSZ|YSZ|LSCF | CH₄,H₂O = 2:1 | 1638@800 °C | 48 h | 2016 | [35] |
| Ni0.8Cu0.2 | Ni0.8Cu0.2|SDC|LSCF | CH₄ | 550@800 °C | 8 h | 2015 | [31] |
| Ni0.9Cu0.1 | Ni0.9Cu0.1|SDC|SSC–SDC | CH₄ | 379@600 °C | 72 h | 2017 | [33] |
| Ni0.7Cu0.2Co0.1 | Ni0.7Cu0.2Co0.1–SDC|SDC|LSCF | CH₄ | 150@700 °C | 72 h | 2017 | [34] |
| Ni-Cu/Ni–Fe | Ni–Cu/Ni–FeNi–YSZ|YSZ|LSCF | CH₄,H₂O = 2:1 | 1638@800 °C | 48 h | 2016 | [35] |
| Ni0.8Cu0.2 | Ni0.8Cu0.2–GDC|GDC–LSCF | CH₄ | 42@600 °C | – | 2018 | [36] |
| Sn0.05Ni0.95 | Sn0.05Ni0.95–SDC|SDC|BSCF | CH₄ | 600@700 °C | 70 h | 2019 | [37] |
| Ni0.5Fe0.5 | Ni0.5Fe0.5–GDC|YSZ|YDC|LSCF | CH₄ | 250@800 °C | > 15 h | 2016 | [38] |
| Co0.75Mo0.25 | Co0.75Mo0.25–PBM|YSZ|NBCaCF–GDC | CH₄ | 1100@800 °C | 50 h | 2018 | [39] |

YSZ: Y₀.₀₈Zr₀.₉₂O₂, LSM: La₀.₈Sr₀.₂Mn₀.₈O₆, GDC: Gd₀.₃Ce₀.₇O₂, SDC: Sm₀.₂Ce₀.₈O₂, LSCF: La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃, YDC: Y₀.₁Ce₀.₉O₂, SSC Sm₀.₅Sr₀.₅CoO₃, BSCF: Ba₀.₈Sr₀.₂Co₀.₈Fe₀.₂O₃, PBM: PrBaMn₂O₅, NBCaCF: NdBa₀.₇₅Ca₀.₂₅Co₀.₈₅Fe₀.₁₅O₃

Fig. 4  a Proposed mechanism for water-mediated carbon removal on the anode with BaO/Ni interfaces. b DFT predication for the removal of chemisorbed carbon species energies. c Raman spectra collected from BaO/Ni samples in dry and wet H₂ (with ~3%H₂O) atmospheres at room temperature. d I–V plots of button cell with the configuration of BaO/Ni–YSZ|YSZ|SDC|LSCF operated at 750 °C when fueled with dry propane and ambient air as oxidant. e Terminal voltages measured at 750 °C as a function of time with the constant current density of 500 mA/cm² with dry propane as fuel. Reproduced with permission [40]. Copyright 2011, Springer Nature
Carbon deposition and sulfur poisoning

Many factors may lead to button cell degradation, such as the oxidation of anodes, materials decomposition, carbon deposition, and sulfur poisoning. Among these problems, carbon deposition and sulfur poisoning are frequently encountered when using hydrocarbons as fuel. Carbon deposition occurs when the formation rate of carbon is much higher than the removal rate. On Ni catalysts, the accepted carbon growth mechanism from hydrocarbons is the dissolution–precipitation mechanism, in which the carbon dissociated from hydrocarbon dissolves into nickel particles, diffuses through the nickel and precipitates as a deposited carbon in the end [10, 19]. The deposited carbon can be classified as whisker carbon, pyrolytic carbon and encapsulating film carbon according to their morphology. Calvin H. Bartholomew [20] summarized the carbon morphology and formation conditions during hydrocarbon reforming reactions, as shown in Table 2. The morphology of deposited carbon is strongly related to the reaction temperatures, the type of fuels, the catalysts, and H2 or H2O content. With nickel as the catalyst and feed with low H2O/CnHm fuel, the dissolved carbon in nickel should nucleate and grow to whisker carbon at the top of nickel. This is fatal to SOFC operations, for the growth of whisker carbon may rupture the anode and damage the button cell integrity, leading to the fast performance drop of button cell.

Carbon deposition can be controlled from two aspects: the thermodynamic aspect and catalytic aspect. According to thermodynamic laws, carbon deposition is controlled by the O–H–C ternary phase diagram and temperature, as shown in Fig. 3a [21]. Hydrocarbons or mixtures with high C/H or C/O ratio easily form solid carbons. Higher temperatures favor fuel decomposition then carbon formation at a set C/H ratio. Based on this, the addition of water or oxygen to the fuel can depress the carbon formation. However, it should be noted the addition of oxygen-containing species may reduce the open circuit voltages and the fuel efficiency of SOFCs. Besides, thermodynamic laws merely show the possibility of carbon deposition. With catalysts in a real operation system, the carbon deposition region may greatly differ from the ternary phase diagram because of the dynamics effects root- ing in the catalytic activity of catalysts toward cracking and reforming reactions of hydrocarbons. For metal-based catalysts, the catalytic activity is related to their electron states, which may be modulated by alloying with other metals. For example, the enrichment of Cu on Ni surface in Ni–Cu alloy can block active sites for methane dissociation and thus improve coke resistance [17]. While for oxide catalysts, the catalytic activity of a catalyst towards hydrocarbons is strongly related to its acidity. Catalysts with Bronsted acid sites are prone to react with hydrocarbons such as alkane to form a carboxcation, which then decomposes according to the β crack and forms C2 products. Thereafter, the carbocation rearranges and further decomposes to form more C2 hydrocarbons [10]. Based on this mechanism, it is safe to conclude that employing catalysts with high acidity should lead to fast hydrocarbon decomposition and carbon deposition, consequently [22].

Sulfur is usually present in the hydrocarbon fuels, and sulfur poisoning also impedes the stable operation of a fuel cell. Poisoning, however, has an operational meaning. This indicates that the sulfur species may act as a poison depending on their adsorption strength relative to the other species competing for the catalytic sites [23]. Nickel is the most studied catalyst with respect to sulfur poisoning because the adsorbed sulfur species are stable and have low reversibility on nickel. Figure 3b shows the equilibrium partial pressure of H2S vs. reciprocal temperature for the nickel-sulfur system. The solid line corresponds to the equilibrium rate for the bulk Ni3S2 species. Using the equation

\[
\text{BaO @ Ni–SDC} \quad \text{BaO@NiO–SDCISDCIBSCF} \quad \text{CH}_4 \quad 563@700 \, ^\circ\text{C} \quad – \quad 2016 \quad [44]
\]

Stability tests Year References

Table 4 Comparison of electrochemical performance of button cells decorated with alkaline oxides

| Anode        | Button cell configuration   | Fuel            | Button cell peak power density (mW/cm²) | Stability tests | Year | References |
|--------------|-----------------------------|-----------------|----------------------------------------|-----------------|------|------------|
| BaO@Ni–SDC   | BaO@NiO–SDCISDCIBSCF        | CH₄             | 563@700 °C                             | –               | 2016 | [44]       |
| CaO@Ni–SDC   | CaO@NiO–SDCISDCIBSCF        | CH₄             | 1051@700 °C                           | 70 h            | 2016 | [44]       |
| MgO@Ni–SDC   | MgO@NiO–SDCICLSCGMISCOGDC  | CH₄             | 714@800 °C                           | 330 h           | 2016 | [42]       |
| BCY@Ni–GDC   | BCY@Ni–GDCYSZILSCF–GDC      | CH₄             | 246@800 °C                            | 48 h            | 2015 | [45]       |
| BCYb@Ni–GDC  | BCYb@Ni–GDCYSZILSCF–GDC     | CH₄             | 274@800 °C                            | 48 h            | 2015 | [45]       |
| BCYb@Ni–GDC  | BCY@Ni–GDCICDGCINBCA–GDC   | 500 ppm H₂S–H₂  | 166@650 °C                            | 20 h            | 2016 | [46]       |
| BaO@Ni–YSZ   | BaO@Ni–YSZILSCF–YSZ         | CH₄             | 21@800 °C                             | 8 h             | 2014 | [47]       |
| BaO@Ni–YSZ   | BaO@Ni–YSZILSCF–YSZ         | C₃H₈           | 900@750 °C                             | 100 h           | 2011 | [40]       |

SDC: Sm₀.₂Ce₀.₈O₃ BSCF: Ba₀.₉Sr₀.₀Co₀.₈Fe₀.₂O₃ LDC: La₀.₉Co₀.₁O₂ LSGM: La₀.₉V₀.₀₅Ga₀.₉₅Mg₀.₀₅O₃ SCCO: Sr₀.₉₅Ce₀.₅CoO₃ GDC: Gd₀.₅Ce₀.₅O₂ LSCF: La₀.₉Sr₀.₀Co₀.₈Fe₀.₂O₃ YSZ: Y₁₀₀Zr₀₉₂O₂ BCY: BaCe₀.₉Y₀.₁O₃ BCYb: BaCe₀.₉Yb₀.₁O₃ NBCaC: NdBa₀.₇₅Ca₀.₂₅O₂ O₃ LSM: La₀.₉Sr₀.₀₂Mn₀.₉₈O₃
\[ \Delta G^\circ = RT \ln \left( \frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}} \right) = \Delta H - T \Delta S \]

\( \Delta H \) was found to be \(-75\) kJ/mol for the bulk \( \text{Ni}_3\text{S}_2 \) species. Most dashed lines are within the range of \(-125\) to \(-165\) kJ/mol for the sulfur coverage from 0.5 to 0.9, which indicates that sulfur is more prone to adsorb on the nickel surface and the adsorbed sulfur species are more stable than the bulk sulfide \([24]\).

### Strategies and progress for improving cell performance and stability

Based on the deactivation mechanism of catalysts, especially carbon deposition and sulfur poisoning as mentioned above, plenty of researches have been done to improve cell performance and stability. From the aspect of thermodynamics, adding more oxygen or hydrogen to shift the reactions away from the carbon deposition region is a feasible way to control it. However, the addition of water or oxygen in the reaction system will inevitably decrease the cell efficiency, leading to lower cell performance. In addition, oxygen must be added to the reaction system with caution because of the possibility of explosion and ignition during cell operation. Aside from this, modifying the properties of the anode catalyst and adopting novel catalysts are other possible directions for research. This may be achieved using alloy anodes, increasing anode basicity, adopting oxide anodes, and adding a catalyst layer.

### Using alloy anodes to replace nickel anodes

Nickel anodes are mostly used in SOFCs because of their low price, high catalytic activity toward \( \text{H}_2 \) oxidation reactions, high conductivity, and high sintering activity. However, nickel easily reacts with hydrocarbons and forms carbon deposition on the anode surface. The catalytic activity of transition metal catalysts is strongly dependent on the filled states of their d-orbit. The partially occupied d-orbit of nickel makes it extremely reactive in C–C crack reactions, steam-reforming reactions, and dehydrogenation reactions. Controlling the filled states of Ni d-orbit by alloying can reduce its reactivity, thus consequently reduces carbon deposition. Plenty of alloy anodes, such as Ni–Cu, Ni–Fe, Ni–Sn, and ternary alloys, such as Ni–Fe–Cu, have been studied in the past years. Besides the catalytic activity toward cracking reactions, it is generally believed that fast carbon diffusion over catalysts and the accumulation of such carbon atoms also contribute to solid carbon deposition. Hence, the stability of catalysts should also be governed by the competing of the oxidation of such carbon species and the C–C formations. Eranda Nikolla et al. studied the mechanism of carbon tolerance of a Sn–Ni alloy during methane-reforming reactions \([25]\). They found that carbon atoms are mobile over Ni (111) surfaces with a low activation energy barrier for carbon attachment on the nucleation center. This results in a fast carbon deposition on the nickel surface. However, higher carbon mobile energy barriers were observed over the Ni–Sn surface, which leads to faster carbon oxidation rates than C–C bond formation. This suggests that the growth of carbons can be suppressed by alloying Sn with Ni. In addition, Sn displaces Ni from the step-edge sites and repels carbon from the low-coordinated step sites, which is the site for carbon nucleation and growth, further reducing carbon formation. Thereafter, they impregnated \( \sim 3 \) wt\% of Sn–Ni in the Ni–YSZ anode and used it for isoctane reforming reactions. They found that carbon filaments are formed when only Ni was present in the anode, while no carbon depositions occurred after impregnating with Sn.

![Fig. 5](image-url) **Fig. 5**  a Schematic of possible carbon fiber growth mechanism, b reforming test on a \( \text{La}_{0.65}\text{Ca}_{0.28}\text{Ni}_{0.06}\text{Ti}_{0.94}\text{O}_3 \) perovskite powder with exsolved Ni particles. Reproduced with permission [53]. Copyright 2015, Springer Nature
Bin Hua et al. studied the NiSn/Al₂O₃ deposited on Ni foam and functioned as a catalyst layer, which proved with high catalytic activity as well as great stability toward biogas reforming reactions [27]. In the button cell with the configuration NiSn/Al₂O₃|NiSn–Y₀.₀₈Zr₀.₉₂O₂|Y₀.₀₈Zr₀.₉₂O₂
|Y₀.₀₈Zr₀.₉₂O₂–(La₀.₈Sr₀.₂)₀.₉₉MnO₃, the peak power density of 0.946 W/cm² was achieved at 850 °C with the inlet gas of CH₄–CO₂–200 ppm H₂S, and conversion rate to methane reached around 95% with the discharge current density of 1.25 A/cm².

Apart from Sn–Ni alloys, Ni–Cu has also been considered for alloy anode applications. Copper has low catalytic activity toward methane-reforming reactions and only functions as an electricity-conducting phase. A. Sin et al. studied the NiCu–Ce₀.₉Gd₀.₁O₁.₉ anode and fabricated an electrolyte (Ce₀.₉Gd₀.₁O₁.₉) supported button cell. They found a performance increase during the first 120 h of operation and proposed that this improvement should be ascribed to the decrease in anodic porosity. Notably, the button cell performance can be regained by the oxidation of solid carbons, a stable operation for over 1300 h was achieved with this button cell with methane as fuel [28].

It should be mentioned that the preparation method has a significant effect on the final performance of the button cell. Wei Wang et al. investigated the nitrate process (GNP), physical mixing (PM), and impregnation method (IMP) on the coke resistance and button cell performance. The button cell showed similar electrochemical performance with these three methods. Nevertheless, they found that NiFe–ZrO₂/Cu prepared using the IMP exhibited superior coking resistance both in high and low temperatures when compared with the other two methods. They believed that this rooted in the low catalytic activity of copper, which covers the nickel surface and reduces the contact of nickel to methane, thereby decreasing the coke formation rate [29].

Table 3 lists the publications concerning alloy anodes from 2015 to 2019, some of which partially substituted Ni with Cu, Sn, Co, Fe. In general, the lifetime of the button cell still requires further improvements, because carbon deposition reactions cannot be completely controlled over these catalysts. It should be also mentioned that the effectiveness and the carbon tolerance of catalysts cannot be simply evaluated from the electrochemical performance of cells due to the large variety of cell configurations (e.g. porosity and thickness of electrodes, particle size and distribution of catalysts) and the working conditions (e.g. the composition and injection rate of hydrocarbons, operating temperatures and current densities).

Increase catalyst basicity

The hydrocarbon decomposition rate is strongly correlated to the acidity of the catalysts as mentioned above. The increase in the surface basicity of the catalysts can reduce dehydrogenations and C–C cracking reactions, thereby depressing carbon deposition on the catalyst surface. Adding alkaline oxides such as MgO, BaO, and CaO are frequently studied for hydrocarbon oxidation reactions. Lei Yang et al. investigated the addition of BaO on the Ni–YSZ surface using the evaporation deposition method. The existence of BaO on the surface was found to promote the adsorption of water, which facilitated carbon removal during the propane conversion process. As shown in Fig. 4a–c, with BaO in anode, the button cell shows high performance (Fig. 4d) and operates stable for 100 h in propane fuel (Fig. 4e); while in contrast, the bare Ni–YSZ anode shows a fast attenuation in the first 1 h operation (Fig. 4e) [40]. MgO has also
Fig. 7 The self-regeneration mechanism for LSCrFeCo10 with respect to processing time and temperature. Reproduced with permission [56]. Copyright 2018, ACS Publications

Fig. 8 Current-overpotential curve ($I_{dc}$ vs $\eta$) of LSF in a humid reducing atmosphere (0.25 mbar H$_2$ + 0.25 mbar H$_2$O). The symbols represent measured values; the line is not a fit but a guide for the eye. The reaction proceeding on the surface of the LSF working electrode is given top right. For selected points of the curve (indicated by arrows), Fe 2p XPS spectra are shown as insets. The sketches indicate the situation for the LSF surface and the resulting reactivity, respectively. Reproduced with permission [58]. Copyright 2015, Wiley
Table 5  Comparison of electrochemical performance of button cells with oxide anodes

| Anode | Conductivity (S/cm) | Button cell configuration | fuel | Button cell peak power density (mW/cm²) | Stability tests | Year | References |
|-------|---------------------|---------------------------|------|----------------------------------------|-----------------|------|------------|
| La0.4Sr0.6TiO3 – La0.4Sr0.6TiO3-LDC| YSZ|GDC-LSCF | 0.5%H2S-CH4 | 158@900 °C | 20 h | 2015 | [63] |
| La0.3Sr0.7Co0.07Ti0.93O3 – La0.3Sr0.7Co0.07Ti0.93O3-YSZ|YSZ|LSM | 0.5%H2S-H2 | 300@900 °C | 48 h | 2013 | [64] |
| Sr1.92Y0.08/2Ti0.98/Rh0.02|Pt|YSZ|CH4 | 150@800 °C | 40 h | 2019 | [62] |
| La0.8Sr0.2Ti0.9Ni0.1O3 – La0.8Sr0.2Ti0.9Ni0.1O3|ScSZ|GDC|GDC-LSCF | CH4 | 130@800 °C | 100 h | 2015 | [65] |
| Y0.05Sr0.95/2Ti0.98/Sr0.02|Pt|YSZ|YSZ-YSZ-LSM | 0.5%H2S-CH4 | 500@900 °C | 20 h | 2018 | [66] |
| Fe1.3Mo1.5O6|LSGM| | H2 | 240@900 °C | > 5 h@C8H18 | 2010 | [69] |
| Fe1.3Co1.2Mo1.5O6|LSGM|LSCF | CH4 | 290@850 °C | 300 h | 2019 | [70] |
| Sr1.8La0.2FeMoO6 – Sr1.8La0.2FeMoO6|GDC|YSZ|GDC-LSCF | CH4 | 790@800 °C | - | 2019 | [71] |
| La0.75Sr0.25Cr0.5Mn0.5O3 – La0.75Sr0.25Cr0.5Mn0.5O3|YSZ|LSM | CH4 | 300@900 °C | - | 2003 | [73] |
| La0.6Sr0.4Co0.2Fe0.7Mo0.1O3 – La0.6Sr0.4Co0.2Fe0.7Mo0.1O3|SDC|LSCF-SDC | C3H8 | 350@750 °C | 130 h | 2018 | [72] |
| (PrBa)0.95Fe1.6Ni0.3Mo0.1O6 – (PrBa)0.95Fe1.6Ni0.3Mo0.1O6|SDC|LSCF-SDC | C3H8 | 332@750 °C | 50 h | 2019 | [76] |
| PrBaMn1.7Ni0.3O5 – PrBaMn1.7Ni0.3O5|SDC|NBSCF-GDC | C3H8 | 322@800 °C | 200 h | 2017 | [79] |

LDC: La0.4Ca0.6O3, YSZ: Y0.05Zr0.95O2, ZSC: Zr1.5Sn0.4Ce0.01O3, ScSZ: Sc0.1Zr0.9O2, GDC: Gd0.2Ce0.8O1.9, LSM: (La0.8Sr0.2)0.95MnO3, LSGM: La0.8Sr0.2Ga0.8Mg0.2O3, LSCF: La0.8Sr0.2Co0.2Fe0.8O3, SDC: Sm0.2Ce0.8O2, BZCY: BaZr0.1Ce0.7Y0.2O3
been studied in the past years and proved to have high coke resistance and to accelerate electrochemical reactions when fueled with hydrocarbons [41]. Qi Yang impregnated a Ni–Sm0.2Ce0.8O1.9 anode with MgO and found that the peak power density of the prepared button cell decreased with the increase of the amount of MgO when operated in H2 fuel, which may be ascribed to the low conductivity of MgO. Yet, a remarkable improvement in performance was observed when the cell fueled with humidified methane with an anode impregnated with 2.5% MgO, and the operation was stable for over 300 h. DFT calculations indicated that the existence of MgO could promote the adsorption of H2O, and release the energy of about 0.14 eV. The decomposition of H2O results in more hydroxyl species on the interface between MgO and Ni. Thereafter, OH∗ reacts with the carbon atoms to form HCO∗ intermediates and then further decomposes to CO and H with a small energy barrier of 0.23 eV. Then, CO and H react with O2− to form CO2 and H2O, which are released to the gas phase [42].

Apart from the catalysts, the basicity of catalyst supports also influence the conversions and carbon formation. Hasan Özdemir et al. [43] studied the basicity of catalyst supports for methane conversions and carbon deposition. They found that with the increasing amount of MgO in the supports, the H2/CO ratio and carbon deposition decreases in the order of Ni/Al2O3 > Ni/MgO/Al2O3 > Ni/MgAl2O4 > Ni/Sorbacid (Mg2.5AlO) > Ni/MgO. The reduction of carbon formation indicates that Mg could improve the interaction of surface-adsorbed carbon with gaseous oxygen, leading to the formation of CO precursor species. Jifa Qu et al. systemically studied basic oxide additives to the SOFC anodes, such as CaO, SrO, MgO, and La2O3 [44]. They found that the addition of SrO caused Ni particle agglomeration in the anode, while MgO contributed to the uniform distribution of Ni and SDC (Sm0.2Ce0.8O2) [44]. Table 4 list some alkaline oxides decorated anode, among which the proton-conducting materials such as BaCe0.9Y0.1O3 and BaCe0.9Yb0.1O3 were also selected to prevent carbon deposition because such proton conducting materials usually have high basicity to adsorb

### Table 6 Comparison of electrochemical performance of button cells with a catalyst layer

| Catalyst layer | Button cell configuration | Fuel | Button cell peak power density (mW/cm²) | Stability tests | Year | References |
|----------------|--------------------------|------|----------------------------------------|----------------|------|------------|
| Ru–CeO2        | Ru–CeO2|PSZ|YSZ|LSCF–GDC | CH4 | 10.7%C3H8–18.7%O2–70.6%Ar | 480@825 °C| – | 2005 [86]|
| La0.6Sr0.4Co0.7Fe0.2O3–Al2O3 | La0.6Sr0.4Co0.7Fe0.2O3–Al2O3|Ni–YSZ|YSZ|LSM | CH4 | 380@800 °C| 116h | 2016 [95]|
| LaNi0.6Co0.4O3 | LaNi0.6Co0.4O3|Ni–BZY|BZY|BZY|LSCF–LSCF | CH4 | 980@650 °C| 200h | 2016 [96]|
| Mn1.5Co1.0O4 | Mn1.5Co1.0O4|Ni–SDC|SDC|BSCF | CH4 | 849@700 °C| 6h | 2017 [97]|
| 15 wt.%Ni–La2.0Ce0.7O3 | 15wt.%Ni–La2.0Ce0.7O3|Ni–SDC|SDC|BSCF | CH4 | 699@650 °C| 26h | 2017 [98]|
| Ni–GDC | Ni@GDC|GDC–Ni|Ni–YSZ|YSZ|YSZ–BSCF–SDC | CH4 | 1420@610 °C| 1000h | 2016 [99]|
| La0.6Sr0.4Co0.7Fe0.2O3–NiO–Gd0.1Ce0.9O1.95 | La0.6Sr0.4Co0.7Fe0.2O3–NiO–Gd0.1Ce0.9O1.95|Ni–YSZ|YSZ|LSM | 10%CO2–90%CH4 | 455@850 °C| 10h | 2015 [100]|
| Ce0.25Co0.75O1.95 | Ce0.25Co0.75O1.95|Ce0.25Co0.75O1.95|Ce0.25Co0.75O1.95|Ce0.25Co0.75O1.95 | CH4 | 207@800 °C| – | 2019 [101]|
| Ni–BaO–Ce0.2SiO2 | Ni–BaO–Ce0.2SiO2|Ni–YSZ|YSZ|YSZ–BSCF–SDC | CH4 | 938@800 °C| 163h | 2020 [102]|
| Nano Ni | Nano Ni|Ni–SDC|Ni–SDC|Ni–SDC | CH4 | 870@700 °C| 100h | 2020 [4]|
| Ir–CGO | Ir–CGO|Ni–YSZ|YSZ|YSZ–LSCF | CH4 | 10%CH4–90%Ar | 420@850 °C| 600h | 2016 [5]|
| Ir–CGO | Ir–CGO|Ni–YSZ|YSZ|YSZ–LSCF | CH4 | 10%CH4–90%Ar | 90@850 °C| 400h | 2014 [6]|
| Cu–CeO2 | Cu–CeO2|Ni–YSZ|YSZ|YSZ–LSCF | CH4 | 7.3%C2H5OH–92.7%H2 | 400@800 °C| 2.5h | 2012 [7]|

YSZ: Y0.08Zr0.92O2; GDC: Gd0.2Ce0.8O1.9; LSM: (La0.8Sr0.2)0.95MnO3; LSGM: La0.9Sr0.1Ga0.8Mg0.2O3; LSCF: La0.6Sr0.4Co0.2Fe0.8O3; BZY: BaZr0.1Ce0.7Y0.1Yb0.1O3; BZY: BaZr0.1Ce0.7Y0.1Yb0.1O3; SDC: Sm0.2Ce0.8O2; SDC: Sm0.2Ce0.8O2; BSCF: Ba0.8Sr0.2Ce0.8O2; BSCF: Ba0.8Sr0.2Ce0.8O2; LSCF: La0.6Sr0.4Ce0.8Co0.2Fe0.8O3; LSCF: La0.6Sr0.4Ce0.8Co0.2Fe0.8O3; BZY: BaZr0.1Ce0.7Y0.1Yb0.1O3; BZY: BaZr0.1Ce0.7Y0.1Yb0.1O3; CGO: Gd0.1Ce0.9O1.95; CGO: Gd0.1Ce0.9O1.95; ScCSZ: Sc0.1Ce0.01Zr0.89O2; CGO: Gd0.1Ce0.9O1.95; CGO: Gd0.1Ce0.9O1.95;
waters, and with an ability of oxygen storage, which is helpful during carbon removal process [45, 46].

**Adopting oxide anode**

Oxide anodes have been frequently studied in recent decades because of their high stability and great coke resistance during hydrocarbon conversions. Among the oxide anodes, perovskite structure catalysts are most widely investigated. Perovskite catalysts toward hydrocarbon oxidations and CO oxidizations were initially studied for automotive three-way catalytic conversions (TWC). Perovskite materials have the formula ABO3, where A site is a rare earth (La, Sm, Pr), alkaline earth (Sr, Ba, Ca), or alkali metals (Na, K), and B site is a transition metal (such as Ni, Co, Fe, Ti, Cr, V) [48].

The stability of perovskite materials is strongly dependent on the geometric structure and reduction-resist ability of the elements in the B site. Geometric stability is represented by the Goldschmidt tolerance factor t [49], which can be shown as

\[
t = \frac{r_A + r_B}{\sqrt{2}(r_A + r_O)}
\]

where \(r_A\), \(r_B\), and \(r_O\) are the ion radii of ions in the A site, B site, and oxygen ions, respectively. When \(t\) is close to 1, the perovskite structure is stable. Perovskite anodes should be stable in reducing atmospheres, which is related to the reduction-resist ability of elements in the B site. Nakamura summarized the stability of LaBO3 perovskites in reducing atmospheres, and the stability is with the order of LaCrO3 > LaVO3 > LaFeO3 > LaMnO3 > LaCoO3 > LaNiO3, in which LaCrO3 is the most stable and can be exist in pO2 = 10–21 atm, while LaNiO3 remains stable only below pO2 = 10–0.6 atm [50].

Conductivity is important for fuel cell anodes. It is strongly correlated to the electronic structure and delocalized electrons of the material [51]. For example, an undoped SrTiO3 is an insulator with a measured band gap of approximately 3 eV in air. However, because the cations in the B site are valance-state changeable elements, the reduction of B site elements and lattice oxygen may introduce electrons, and SrTiO3 would thereby exhibit n-type conductivity in reducing atmospheres.

Besides conductivity, catalytic activity is also dependent on the oxygen vacancy and cations in the B site. Changing the cations in the A site may not have a strong influence on catalytic activities. Taihei Nitadori et al. substituted the A site with La, Ce, Pr, Nd, Sm, Eu, and Gd, in LnCoO3, LnMnO3, and LnFeO3. They found similar reaction rates toward propane oxidation and methanol oxidation for different substitutions, and the catalytic activity was always in the order of LnCoO3 > LnMnO3 > LnFeO3. However, a significant change in the catalytic activity was observed when B site elements in LaBO3, SmBO3, and GdBO3 were substituted. Mn and Co-doped catalysts had high catalytic activity toward propane oxidation compared with Cr, Fe, and Ni. However, the doping of low valance state elements to the A site may introduce oxygen vacancy or increase the valance state of B site elements because of electric neutrality. The vacancy could facilitate the mobility of oxygen ions in the catalysts and increase the catalytic activity. According to Nitadori’s work, by doping 20 mol% Sr in LaCoO3, the reaction rates increased by 5–10 times for propane oxidation [52].

To increase the catalytic activity toward hydrocarbon fuels, exsolving metallic nanoparticles from the B-site have been mostly studied in recent years. The exsolved nanoparticles proved to have good carbon tolerance in hydrocarbon fuels. In Dragos Neagu’s work [53], coke resistance of methane reforming reactions was compared between nickel exsolved catalysts and deposited nickel on the substrates. They found that the carbon fibers are short and fewer in nickel exsolved catalysts. Carbon growth over the metallic particles follows the “tip-growth” mechanism, in which carbon initially dissolves in the nickel lattice, and then grows from the metal particle–oxide support interface. The deactivation of catalysts results from the uplifting of metal particles. For the metal nanoparticles exsolved catalysts, there exists a strong interaction between the socketed particles and oxide support, thus reducing carbon formation and prolonging the lifetime of the catalysts, as shown in Fig. 5a. The author also pointed out that such particle uplifting occurs at the particle size of over 80 nm, which indicates that the interaction between the metal particle and the oxide support may diminish with the increase of particle size. Besides, such catalysts do not work toward H2S poisoning compared with that of the deposited metal particles on the substrates, because catalytic performance dropped after adding H2S to the reaction system, as shown in Fig. 5b.

The exsolution progress and model were investigated by Tae-Sik Oh et al. [54]. Through atomic force microscope (AFM) tests, a trench was observed during the initial stage of the exsolution of the nanoparticles. The morphology was different from that fabricated through the physical vapor deposition method. However, the trench disappeared after reducing and increasing the temperature. They proposed that the interplay between surface free energy and strain energy is the driving force for the exsolution. Yang Gao [55] systematically studied the exsolution of metallic particles from catalysts and proposed four processes that should be considered during the exsolution process, including diffusion, reduction, nucleation, and growth, as shown in Fig. 6a. And nucleation can be expressed as
\[ \dot{N} = \frac{C}{\tau} \exp \left( \frac{-\Delta G^* + E_a}{RT} \right) \]

where \( \dot{N} \) is the formation rate of nuclei per unit or volume, \( C \) is the density of nucleation sites, \( \tau \) is the characteristic timescale, \( \Delta G^* \) is the critical free energy, and \( E_a \) is the free energy. \( \Delta G^* + E_a \) can be further expanded as

\[ \Delta G^* + E_a = \Delta G_{\text{bulk}}^* + \Delta G_{\text{interface}}^* + \Delta G_{\text{surface}}^* + E_{\text{strain}} + E_{\text{diffusion}} \]

\( \Delta G_{\text{interface}}^* \) and \( \Delta G_{\text{surface}}^* \) are related to the surface morphology, and should be expressed as

\[ \Delta G_{\text{interface}}^* = \gamma_{\text{interface}} S_{\text{interface}}^* \]

and

\[ \Delta G_{\text{surface}}^* = \gamma_{\text{surface}} S_{\text{surface}}^* \]

where \( \gamma \) is the surface tension, \( S_{\text{interface}}^* \) is the solid–solid interface area expressed as \( 4\tau^{4*} (\pi - \theta) \), \( \theta \) is particle wetting angle, and \( S_{\text{surface}}^* \) is the solid–gas surface area given by \( 2\tau^{4*} S^p \). The growth of nanoparticles may be limited by the strain, reactant, and diffusion. In Yang’s work, the fitting results revealed that both the size-related strain and limited Ni amount are possible factors that determine the particle size growth.

In addition to the exsolution mechanism, exsolution conditions as well as morphology were investigated by Ke-Yu Lai et al. on La0.3Sr0.7Cr0.3Fe0.6Co0.1O3 (LSCrFeCo10) [56]. They found that the Co–Fe alloy could be exsolved from the oxide material in air and self-regenerated after re-reducing in 5% H2–Ar. However, the exsolved nanoparticles could not be fully reincorporated to the perovskite lattice after treating in air at lower temperatures (700 °C). The particles grew into flat particles in oxidizing atmospheres and then disintegrated into dispersed nanoparticles after a longer re-reducing, as shown in Fig. 7. At low temperatures, the exsolved nanoparticles maintained in a small size, which led to a higher number of exsolved nanoparticles, thus ensuring higher catalytic activities for fuel oxidation and higher electrochemical performance for SOFCs. The authors also pointed out that the growth was likely the result of Ostwald ripening, in which large particles grow by consuming smaller particles without direct connections. The final nanoparticle shape was determined by balancing two driving forces: (1) maintaining metal-oxide interaction and (2) reducing the total metallic surface energy by minimizing the surface area.

Interestingly, some studies found that the exsolution of nanoparticles can be controlled by applying a voltage to certain catalysts. Jae-ha Myung et al. [57] studied the exsolution of Ni particles in La0.43Ca0.37Ni0.06Ti0.94O3. They found anchored metal nanoparticles finely dispersed on the oxide electrode by electrochemical poling of the SOC at 2 V for a few seconds. When applying the electrolysis voltage, the partial pressure of oxygen in the anode was decreased from 10−19 to 10−35 atm (estimated from the Nernst equation), thus greatly decreasing the reduction time of the anode. In addition, such deep reduction also increased the electronic and ionic conductivity, thereby improving the button cell performance. Alexander K. Opitz et al. [58, 59] studied the Fe valance state change in La0.6Sr0.4FeO3 in a button cell with different voltages using near-pressure X-ray photoelectron spectroscopy (XPS) technique. In the SOEC mode, with an overpotential of over 20 mV, a sharp increase in the electrolysis current density was observed. This does not follow the Butler–Volmer equation, indicating that the physical change of the electrode materials occurred during the process. XPS results indicated that Fe ions in La0.6Sr0.4FeO3 can be reduced to a metallic state and that the Fe0 promotes water electrolysis in such conditions, as shown in Fig. 8. It should be noted that when the amount of the exsolution metals in the B-site is high, the oxide base may be transformed from perovskite to a K2NiF4-type structure. Chenghao Yang et al. reported that the perovskite structure of Pr0.8Sr0.2CO0.2Fe0.7Nb0.1O3 can be transformed into Pr0.8Sr0.2(Fe0.5Co0.5)0.8Nb0.2O3 with a K2NiF4-type structure after treating with H2 at 900 °C. The anode showed a similar performance to nickel, and the button cell maintained stably in CH4/C3H8 for over 150 h [60, 61]. However, the thermal compatibility between the anode and the electrolyte should be considered with such phase transformation.

Even though a high catalytic activity is exhibited by such exsolved nano-catalysts, it does not mean that substituting the B-site with more amounts of reducible elements is better. Ghus Sik Kim et al. [62] studied the amount of Rh doping in the B-site of Sr0.92Y0.08TiO3 and this catalyst was used for methane oxidation reactions. They found that with the increase of Rh doping amount, the metal dispersion percent is decreased, and the metallic surface area also decreased from 26.74 to 10.70 m2/g after increasing the amount of Rh doping from 2 to 15 mol%, respectively. The increase of Rh doping led to a decrease in turnover frequency towards methane oxidation reactions. Substituting 2 mol% of Rh to the perovskite is sufficient to exsolve Rh into surface and consequently improve catalytic activity and carbon tolerance.

Table 5 lists publications concerning oxide anodes, mainly from 2015 to 2019, the stability of button cells with oxide anodes were significantly improved when compared with alloy anodes, while the button cell performance remained relatively low, indicating that further studies are needed in the future.
Adding catalyst layer

Adding a catalyst layer is a method to pre-react the hydrocarbons to CO and H₂ before such hydrocarbons encounter the anode. The generated gases such as CO and H₂ can reduce carbon formation and increase cell stability during fuel cell operations [80–83]. The catalyst layer should have a high catalytic activity toward hydrocarbons and should have excellent stability in harsh conditions. Publications that studied the catalyst layers on the SOFC anode in recent years are listed in Table 6. From here, we found that a CeO₂ based catalyst layer is frequently investigated and proved to have high performance and stability.

Zhongliang Zhan et al. firstly reported a Ru–CeO₂ catalyst layer. They prepared a poriferous partially stabilized zirconia (PSZ) substrate, and the catalyst consisting of 10%RuO₂–90%CeO₂ was screen printed on the substrate. Since the thick insulating catalyst layer prevents current collection through the anode, the current was collected at the side of the anode. With such a catalyst layer, the button cell was able to operate with C₈H₁₈–CO₂ for over 50 h [80]. Zhiquan Wang used a similar cell configuration and applied NiTiO₃ as the catalyst layer, which can be totally reduced into Ni and TiO₂ in working conditions, and the button cell also showed high electrochemical performance and stability in propane fuels with such unique structure [84]. It should be mentioned that decrease the catalyst size could improve catalytic activity toward hydrocarbons, Yu Chen et al. studied the Ni, Ru co-doped CeO₂ catalysts which were prepared by hydrothermal treatment. The exsolved Ni and Ru were deemed with the size of a single cation. Better performance was achieved by doping Ni or Ru into the CeO₂ compared to that of CeO₂ alone. The DFT calculation results indicated that the energy barrier for breaking the first C–H bond of CH₄ is lower in the Ni site. And Ni site is favorable for activating CH₄ to form CO, while Ru contributes to the coupling of surface oxygen vacancies and mainly participates in the activation of H₂O. With this catalyst on the anode surface, a high electrochemical performance was achieved for a cell fueled with near-dry methane at low temperatures, and the button cell stably operated for 300 h at 500 °C [85].

However, a disadvantage of such catalytic layers is their low conductivity [80], which may lead to the poor current collection. Aside from this, two problems should also be addressed when using catalyst layers. One is sluggish gas diffusion, and another is the poor compatibility of the catalyst layer with the button cell after cyclic tests. After adding a catalyst layer, gas diffusion may cause the concentration polarization of the button cell. In Zhongliang Zhan’s later work, they investigated the concentration polarization of a button cell with a Ru–CeO₂ layer and found that the gas diffusion limits the button cell at high temperatures and high discharge current densities (0.5 W/cm² at 750 °C). Fortunately, even with the gas diffusion limitations, the cell performance was better than that without a catalyst layer. The calculation results indicated the poor performance of the non-catalyst layer SOFCs is not only due to the slow diffusion of the propane-air mixture gases but also from the localized heating at the anode-electrolyte interface because of the direct oxidation of hydrocarbon fuels. The addition of a catalyst layer can decrease such heating effect because of the heat-insulating property of the catalyst layer, which then improves cell performance [86].

To prevent concentration polarization in the anode, unique anode microstructures should be developed [87]. Plenty of studies have been done for gas diffusion accelerations, such as fabricating straight open pores, decreasing the thickness of the function layer, and infiltrating with nanocatalysts. Zongying Han et al. [88, 89] fabricated a tubular SOFC using the phase inversion method. Ni, Fe were added to the Ni–YSZ anode to improve its catalytic performance. The results of electrochemical impedance spectroscopy indicated that low-frequency resistance, which corresponds to gas diffusion, decreased slightly after adding Ni to the anode, indicating such anode configuration should accelerate electrochemical performance. Detailed studies were conducted by the group of Chusheng Chen, which proved that the gas penetration performance was higher for the electrode with straight open pores [90–92]. Nano-catalysts used as a catalyst layer for anodes also proved helpful with increasing the anode performance. Zhangbo Liu systematically studied the infiltration of CeO₂, Sm₂O₃, SDC, and Al₂O₃ in nickel-based anodes and their performance was compared. Anodes infiltrated with CeO₂, Sm₂O₃, and SDC showed enhanced performance. SDC increased the TPBs for anodes, while CeO₂ and Sm₂O₃ had much lower ionic conductivities compared with that of SDC. Such oxides were expected to increase the catalytic activity for anodes [93]. Later, Zhebiang Liu et al. systematically reviewed the SOFC anodes prepared using the infiltrating method and concluded two motivations for infiltration. One is to increase the conductivity for the oxide anode, and another is to increase the anode catalyst activity with the nano-sized catalysts [14].

Another issue when applying a catalyst layer is its poor compatibility with the anodes. A desquamation was observed for the Ru–CeO₂ catalyst layer after 20 rounds of H₂–O₂ cyclic tests at 850 °C in Wei Wang’s work [94]. This roots in the mismatch of the thermal expansion coefficients of the catalyst layer and the anode or the strain during the reduction process. In a later work, Hong Chang et al. co-expressed La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃–Al₂O₃ and fabricated with a mesoporous structure, which was used as an independent catalyst layer for a Ni–YSZ button cell. With such a separated catalyst layer, the button cell free the poor conductivity...
and incompatibility during operations. The low-frequency resistance, which corresponds to mass limitation, was lower for the button cell with a catalyst layer compared to that without a catalyst layer, suggesting that there is a smaller mass transfer resistance in such button cell [95].

Conclusion

In this review, the reaction mechanisms and catalyst deactivation mechanisms were briefly discussed, and the strategies for improving cell performance as well as stability were classified. Moreover, the developing progress, as well as performance comparisons were summarized. Carbon deposition is a fatal problem when using hydrocarbon fuels and can be solved using alloy anodes, modifying the basicity of catalysts, adopting oxide anodes, and adding a catalyst layer. When alternative anodes are used to replace nickel-based anodes, conductivity, catalytic activity, and thermal compatibility should be carefully considered. (1) Alloy anodes may replace nickel-based anodes because alloys usually have sufficient conductivity and a similar thermal expansion as nickel-based anodes. However, they still suffer from the incompatibility of high anode performance and great carbon tolerance. (2) Modifying the catalyst basicity is a feasible method, but the preparation process is complex, and adding alkaline oxide may decrease the conductivity of anodes. (3) Adopting oxide anodes were proved effective when dealing with carbon deposition, but they usually have low conductivity and low catalytic activity toward hydrocarbons. Nevertheless, exsolve nanoparticles on an oxide anode surface proved to improve activity toward hydrocarbons. But further studies are needed to reveal the laws between the material physical properties and catalytic activities towards hydrocarbons. (4) Adding a catalyst layer can pre-catalyze hydrocarbons to CO and H2 and free the anode from carbon deposition. However, low conductivity, concentration polarization, and poor thermal compatibility introduce further complexity and impede its application. It should be noted that these strategies used to modulate anode electrochemical performance and carbon tolerance seem still far from perfect, considering the cost, the repeatability, and the coexistence of high electrochemical performance and great carbon tolerance of anodes. In conclusion, one of the unique advantages in SOFCs is fuel flexibility, and developing novel anodes is very important for SOFCs to ensure operating with hydrocarbon fuels. Although each solution has its advantages and limitations so far, remarkable progress has been made in improving catalyst activities and stability.

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