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Review article

Methane reforming in solid oxide fuel cells: Challenges and strategies

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HIGHLIGHTS

- Reforming of hydrocarbons using SOFC systems is promising.
- Sustainable sources for green hydrogen and power production are practical.
- Catalysts with high catalytic activities and stability is highly desired.

ARTICLE INFO

ABSTRACT

Methane, mainly derived from fossil fuels, coal and natural gas, is a widely used industrial resource for hydrogen production via the reforming process. However, due to their unsustainability and the high carbon emission during the reforming process, more effective utilization of precious natural resources is desired. Therefore, sustainable resources such as biogas derived from biomass are attracting more and more attention for hydrogen and power production. A renewed interest in the flexible application of biogas in solid oxide fuel cells has recently attracted attention as a green pathway for hydrogen and power production driven by the fast development of fuel cell technology, especially in material technologies. However, the methane reforming process in solid oxide fuel cells suffers from low long-term operability, such as carbon deposition and sulphur poisoning over the anode materials. Therefore, the operational strategies for safe and stable operations are first discussed. Following that, the development of the anode materials to facilitate the methane reforming reaction while mitigating the subsequent insufficient catalyst stability such as deformation and degradation is conducted. Hopefully, this review can provide a practical perspective for sustainable hydrogen and power production in solid oxide fuel cells using biogas.

1. Introduction

Today, climate change is a major global emerging issue of environmental concern. To commit to the Paris Agreement, all participating countries should substantially increase their emissions reduction target, enhance emissions reduction efforts, achieve the global emissions peak as soon as possible, and vigorously promote global low-carbon energy transformation [1]. For example, many states in the USA have a long-term goal to achieve a 100% clean or renewable electricity-supported grid by 2050. New South Wales (NSW) in Australia

also has a long-term goal to reach the net-zero Greenhouse Gas (GHG) emissions target by the same time [2,3].

Hydrogen (H_2) is considered a promising fuel and can satisfy the requirements of green and clean mobility. Currently, 70% of the annual global H_2 production is from natural gas and CH_4 derived from fossil fuels and coal, the primary sources of large-scale H_2 production [4,5]. However, these unsustainable resources need to be replaced with more sustainable resources, and H_2 can be retained completely sustainably if the resource for its production is supplied from renewable sources [6]. CH_4 can be converted to H_2 via steam (H_2O) reforming [7–9], dry

reforming [7–10], bi-reforming [11], tri-reforming [12], or cracking under the same reaction conditions and with similar catalysts whether originating from biomass or fossil fuels. Due to the high carbon emission during the hydrogen production process from unsustainable sources such as fossil fuels, coal and natural gas, biomass and biogas are promising alternative renewable sources. They have attracted extensive active investigations for the past decades [12–21]. A project funded by the European Fuel Cells and Hydrogen Joint Undertaking (FCH-JU) has suggested that the less expensive and promising way for green H_2 production is by biomass processing and biogas reforming, provided that the electricity used in the process comes from sustainable energy sources [22]. Through pyrolysis [23], gasification [24], or anaerobic digestion [25,26], biomass may be converted to bio-syngas (or biogas), which mainly contains carbon monoxide (CO), H_2, methane (CH_4), H_2O, a trace of ammonia (NH_3), ethane (C_2H_6), and contaminants such as sulphur and chlorides [27,28]. The compositions and concentrations of the contaminants vary on the biomass resources and the specific treatments, and the interested readers can refer to Refs. [13,14,20,22,28]. Various combined processes, such as auto-thermal reforming with H_2O and oxygen (O_2) [29], low-temperature Methane Steam Reforming (MSR), combined H_2O and Dry Reforming of Methane (DRM) [7,30], chemical looping MSR process [31], sorption-enhanced MSR [32], as well as a combined chemical looping sorption-enhanced MSR process [33] can also be applied to generate H_2 from CH_4 as well as minimising the GHG effect of CO_2 and CH_4. Each of the processes, as mentioned above, produces a bio-syngas mixture with different H_2 to CO ratios, and the reaction conditions such as temperature and pressure determine the actual gas composition [13].

Although it has been developed for several decades, CH_4 reforming technology still faces several challenges resulting from the reactant properties and thermodynamics. CH_4 is very stable as the C-H bond in CH_4 is hard to break. CH_4 reforming requires intensive energy supply due to the highly endothermic nature and facilities required to maintain a high reacting temperature, introducing mass and heat transfer issues and low overall efficiency and low process stability [34–39]. Solid Oxide Fuel Cell (SOFC) technology was first studied in 1899 by Nernst when zirconia (ZrO2) was introduced as an oxygen ion conductor and has been rapidly developed for the past few decades [40]. The effects of materials, temperature, current, feed, flowrate, and other experimental parameters on the SOFC and its efficiencies have been investigated vastly [41]. Current SOFCs have demonstrated exemplary performance when fuelled with a wide range of hydrocarbon fuels. The integration of methane reforming with SOFCs has shown its potential in three aspects: (1) The high energy required for the reforming reaction can be provided by the high operating temperature of SOFCs. The low efficiency of methane reforming may be improved by integrating the endothermal reforming process with a source of high-temperature heat and H_2O provided by SOFCs. A variety of light hydrocarbon fuels, such as CH_4, can be internally reformed on the SOFC electrode while making direct use of the heat and H_2O produced internally [34,35,42–46] by converting the chemical energy of the fuel to electricity and H_2 [13,40,47]. In addition, Direct internal reforming (DIR) SOFCs can achieve high electrical efficiencies and even higher efficiencies when applied for combined heat and power (CHP) [48–52], combined cooling, heating and power (CCHP) [53–56] and combined heat, H_2 and power (CHHP) [57,58]. (2) Reforming catalysis plays an essential role in fuel processing technology that converts sustainable hydrocarbons to green H_2. Although noble metal catalysts showed high CH_4 reforming activity with excellent stability, the expense of noble metals limits their application [30,59–64]. The design of catalysts still needs further improvements in increasing activity and reducing the propensity to easy sintering, coke forming and impurity poisoning [65]. Nickel (Ni) is a widely applied catalyst for CH_4 reforming, which is also often used in SOFC anodes to catalyst the electrochemical oxidation reaction. The working condition of SOFCs influences the propensity to coke formation of methane reforming on Ni-base catalysts, and the carbon coking can be reduced by changing the

current drawn from the cell [66]. In addition, the current density was found to impact the methane reforming reaction rate [67,68]. Therefore the reforming reaction rate can be altered by varying the current density. (3) CH_4 reforming co-produces CO_2 (9–14 kg CO_2/kgH_2), which is a GHG and needs to be avoided or removed [45]. CO_2 can be recycled in SOFCs as a reforming agent in the reforming process for electricity and hydrogen production.

However, challenges remain for direct practical applications of methane in SOFCs [4,69]. Several undesirable side reactions may still form solid carbon deposits, blocking and damaging the porous electrodes [40,47,66,70–74]. In addition, it is difficult to optimize the catalyst for the different internal reactions occurring simultaneously, compromising overall performance [40,47,72–74]. Many reviews have described the electrolyte, the anode, and the cathode [4,69,75–78]. An excellent review on the CH_4 conversion in SOFCs via electrochemical-oxidation has been published by Gur [79] on the prospects for efficient electricity generation from natural gas, including the environmental benefits, efficiency, the mechanism of the catalysis of methane, the role of lattice oxygen in methane catalysis and the electrochemical conversion of methane in SOFCs. However, Gur only briefly reviewed the strategies to mitigate the carbon deposition. The authors of this review believe the expansion of the strategies to mitigate the carbon deposition in direct internal reforming SOFCS would benefit the development of the methane (especially biogas) application in SOFCs for hydrogen and electricity generations. Another excellent review on the strategies for carbon and sulphur tolerant SOFC materials, incorporating lessons from the traditional heterogeneous catalysis, has been thoroughly reviewed by Boldrin et al. [80]. The authors do not want to repeat the content but instead focus more on the recent development of the anode materials for the direct hydrocarbon application in SOFCs. The main focus of this review is the challenges of carbon deposition in the internal reforming SOFCs and the operational and fundamental strategies for its mitigation. The challenge of sulphur poisoning and its mitigation has been a secondary focus of the review, therefore not expanded as detailed as carbon deposition. More comprehensive reviews on the sulphur poisoning of SOFCs and the techniques for overcoming sulphur poisoning in hydrocarbon reforming have been reported by Wang et al. [81] and Kumar et al. [82]. This current review aims not to duplicate those pieces of literature but summarize the fundamental operating principles of direct CH_4 reforming in SOFCs with some general aspects, including the catalysts and reported strategies to solve the related issues. Specifically, operational technologies are discussed with new research and development trends to condition CH_4 reforming in SOFCs to best reduce or tolerate any carbon deposition or sulphur poisoning. In addition, a variety of anode materials is reviewed, as they drastically impact the reforming process via differentially catalysing the MSR reaction. Finally, we evaluate the catalyst development associated with the SOFC development to mitigate carbon deposition and sulphur poisoning, including the current status and potential future directions. Overall, this review provides a comprehensive overview of the status and challenges of direct CH_4 reformation in SOFCs and provides the readers with a perspective of applying biogas to produce power and H_2 using SOFCs. Further research is identified to accelerate the direct implementation of hydrocarbon species derived from sustainable sources in SOFCs for green power and H_2 production, which significantly benefits climate change and energy security.

2. Scientific and technical challenges of methane reforming in SOFCs

SOFC is an electrochemical device that converts fuel to electricity, and the electrochemical reactions are briefly introduced first. Then, the readers can refer to a detailed electrochemical reaction mechanism [47]. A schematic illustration of the SOFC's working principle is shown in Fig. 1. The electrochemical reactions are relatively fast if the electrode materials are porous, ionically/electronically conductive and
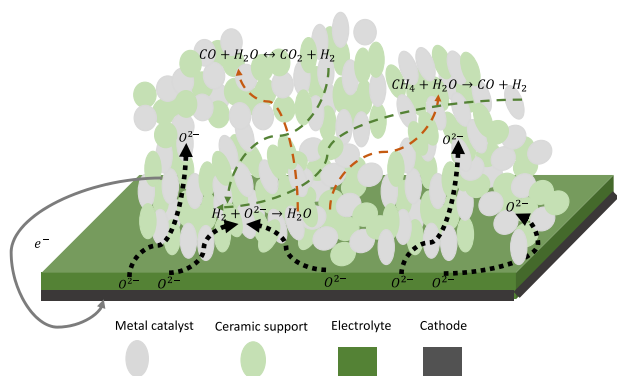
Fig. 1. A schematic illustration of the SOFC's working principle. Light grey dots are the metal catalyst, green dots are the ceramic support, dark green plate is the electrolyte, and dark grey plate is the cathode. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

catalytically active. The cathode reduces O_2 and has sufficient conductivity to provide electrons for this reaction. O^{2-} then travels through the electrolyte to the Triple Phase Boundary (TPB) in the anode, where it oxides the fuel. In case H_2 is used as the fuel, the electrochemical reaction can be written as Reaction 1:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$
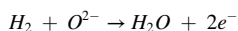
Reaction 1: Oxidation of Hydrogen Gas.

In order to transport gas from the fuel channels to the TPB and electrons to the interconnect, the anode material needs to be chemically and thermally compatible with other SOFC components. The electrolyte must be dense to separate the air and fuel compartments and must be an electronic insulator that possesses high ionic conductivity for easy migration of O^{2-} from the electrolyte to the TPB. In addition, these properties for the electrolyte need to be maintained over a wide range of oxygen partial pressure (p_{O_2}), from ~1 atm at the cathode side to ~10^{-20} atm or lower at the anode side [47,83,84]. Material, temperature, current, fuel composition, and flow rate have been investigated intensively to understand their effects on the SOFC performance [68, 84–92]. The readers can refer to the review reported by Sun et al. [93] for more detailed information on the requirement and development of the cathode and the cathode materials. Ni-based anodes, especially Nickel-Yttria-Stabilized Zirconia (Ni-YSZ) and Nickel-Gadolinium Doped Ceria (Ni-GDC), have been widely used in SOFCs due to their stable activity. Many reviews have summarized the development of various electrode materials [40,75,78,94–97]. Therefore, the discussion in this review focuses on SOFC systems using these anode materials.

An SOFC operates as a catalytic electrochemical facilitator to provide reasonable control and optimization over H_2 and power production at 800–1000 °C, utilizing any fuel containing hydrocarbons and is generally mixed with various reforming agents [45]. CH_4 reforming chemistry is rich and includes various reactions, depending on the available agent, which could be H_2O, O_2, and CO_2 or a mixture of them. Among these reforming techniques, MSR is the most widely and well-developed technology for H_2 production [45]. As shown in Fig. 1, MSR is a catalytic process expressed by the following overall reaction (Reaction 2, $H_{298} = +206 \frac{kJ}{mol}$) [7–9]:

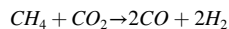$$CH_4 + H_2O \rightarrow CO + 3H_2$$
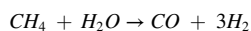
Reaction 2: Methane steam reforming reaction.

CO can be further converted to CO_2 via Water Gas Shift (WGS) reaction (Reaction 3, $\Delta H_{298} = -41 \frac{kJ}{mol}$), thus maximizing the production of H_2 [98–100]:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
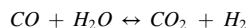
Reaction 3: Water-gas shift reaction.

In DMR, CO_2 is used as the oxidant in place of H_2O ($\Delta H_{298} = +247 \ kJ/mol$) shown as in Reaction 4 [7,10,101]:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

Reaction 4: Methane dry reforming reaction.

Development in this technique is mainly driven by the possibility of capturing and reusing the main components of biogas, CH_4 and CO_2. Besides the high energy duty, another critical issue is the requirement for a nearly pure source of CO_2 as feedstock. Other possible reforming methods are Partial Oxidation of Methane (POM) and autothermal reforming, a hybrid process combining POM with conventional MSR. SOFCs are the most prospective type of fuel cell for direct CH_4 reforming [102], providing new opportunities to develop a sustainable, energy-saving, and cheaper technology for green H_2 and power production. In addition, more direct utilization of various hydrocarbon fuels would considerably reduce the system and operation costs to support the commercialization [4,69,78]. The operation of SOFCs on various sustainable fuels, including biogas and bio-syngas derived from biomass, has been an active research area for many decades [13,17,20,103–106].

CH_4 reforming may occur directly in an SOFC, whose anode catalyzes CH_4 decomposing. Utilizing direct internal reforming of CH_4 in SOFCs (DIR-SOFCs) enables a less complicated system with a high overall thermal efficiency at a lower cost [107]. The main focus of CH_4-fed SOFC operations today is to increase the durability and stability of the SOFCs and optimize the operating conditions to achieve operational flexibility for H_2 and power production [13,28]. Issues such as the fabrication and electrode materials costs [108,109], microstructural changes or degradations of anode materials during operations [110], defect segregation [111–113], insufficient current collection [114,115] and high cost for interconnect materials and fabrication [116–118], and the system design [119–121] are common to all SOFCs, regardless of the fuels. They have been thoroughly discussed in the previously published comprehensive reviews by Faes et al. [110], Badwal et al. [122,123], Tao et al. [4,76,77] and Gorte et al. [78,97,124,125]. However, the direct operation of hydrocarbons in SOFCs can lead to carbon deposition on the anodes [60,66,71,80] and sulphur poisoning of the anodes, which are significant challenges when fuelling hydrocarbon fuels to SOFCs [80, 81,126]. In addition, the influence of operating conditions such as the current density on the SOFC performance fuelled with hydrocarbon fuels is still not clear and needs further investigation [67,68,88,90]. The specific scientific and technical challenges are discussed in the following sub-sections.

2.1. Carbon deposition

Direct CH_4 conversion in SOFCs brings in the issue of carbon formation on the anode catalysts. Solid carbon formation can deteriorate the porous structure of the anode block the gas pathway to the TPB. The principal reactions leading to carbon deposition are [80]:

$$C_mH_n \rightarrow nC(s) + \frac{m}{2}H_2(g)$$
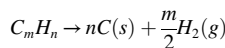
Reaction 5: General carbon generation reaction

$$2CO(g) \rightarrow C(s) + CO_2(g)$$
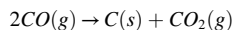
Reaction 6: Boudouard reaction.

The mechanism evolves from carbon deposition on the Ni surface to the dissolution of carbon into the bulk of the Ni and further precipitation of carbon on Ni [66,70,71]. In addition, the formation of carbon deposition can also lead to fuel cell fracture due to the mechanical stresses caused by the growth of carbon, as shown in Fig. 2 [71,127–129]. These issues severely impede the direct application of hydrocarbon fuels in SOFCs. It can also impede the CH_4 reforming reaction due to the
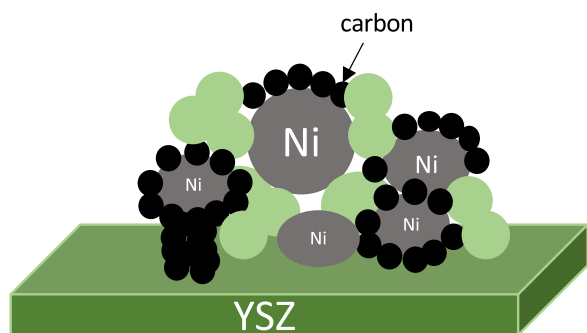
Fig. 2. Carbon deposition mechanism on a typical Ni-YSZ anode. Green dots are the YSZ particles, grey dots are the Ni particles, and black dots are the carbon deposition. Carbon deposition can happen on the surface of the Ni particle, and the dissolution of the carbon into the bulk of the Ni expands the volume of the anode materials. Additionally, the growth of carbon deposition can push the metal particles off the support materials and eventually fail the anode structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 3. Sulphur poisoning mechanism. Green dots are the YSZ particles, grey dots are the Ni particles, and the yellow dots are the sulphur poisoning. The sulphur poisoning happens on the surface of the Ni particle blocking the active sites for the reforming and electrochemical reactions with oxygen involved. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

blockage of the effective TPB by carbon deposition.

The extent of carbon formation in SOFCs depends on the operation conditions such as the temperature, fuel compositions, and the catalytic properties of the anode materials [69,130]. For example, Ni particle size affects carbon whisker formation, with optimal sizes ranging from 2 nm to 3 nm at temperatures from 500 °C to 600 °C [4,131]. Carbon can deposit not only on the catalyst such as Ni in SOFC anode materials but also on the supporting materials such as YSZ in SOFC anode. Under extreme conditions, the carbon deposition can fail the entire cell and operation [4,70,131]. The properties of both the catalyst surface and the type of the oxides, and the operating conditions may influence carbon formation during the reforming process.

The carbon deposition and growth mechanisms have been reviewed comprehensively by Hanna et al. [69] and are thus not further expanded in detail in this current review. Boldrin et al. [80] have also reported an excellent review on the strategies for carbon tolerant materials. The fundamentals of carbon deposition and the material design strategies to mitigate carbon deposition are comprehensively reviewed and discussed. The authors of the current review do not intend to repeat the fundamentals of the carbon deposition mechanism, and readers can refer to these reviews for more detailed discussions [69,80]. However, carbon deposition is determined by both thermodynamic and kinetic contributions [79]. The ternary C-H-O diagram determines the gas-phase thermodynamic chemistry equilibrium, and the elementary composition of CH_4 locates in the thermodynamically favoured carbon coking region [79]. This makes it challenging to use CH_4-containing fuels directly in SOFCs, unless a sufficient amount of reforming agents such as H_2O, CO_2 and O_2 is provided to push the chemical equilibrium composition opposite to carbon deposition. Temperature also impacts the possibility of carbon deposition for most fuel gas compositions [132]. This means the carbon deposition can be mitigated by manipulating the operation condition of the SOFC systems, which is discussed in Section 3.1. Finally, the carbon deposition may also be mitigated by altering the catalytic properties of the anode materials, which is also discussed in Section 3.2.

2.2. Sulphur poisoning

Most available hydrocarbon fuels such as natural gas, syngas derived from coals and biogas contain a certain amount of sulphur which can poison the anode 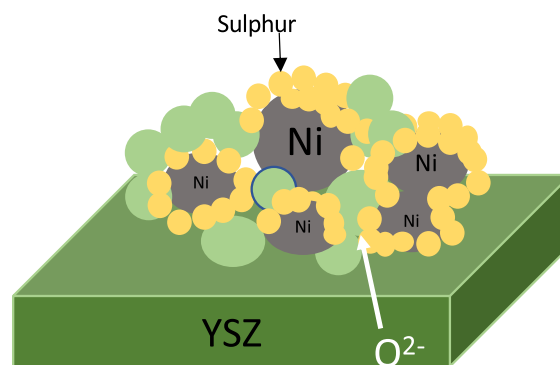catalyst [81]. As shown in Fig. 3, the sulphur species in the fuel block the active reaction sites and deteriorate the catalytic and electrochemical activities of the anode materials. Although sulphur adsorption on Ni is reversible at low concentrations (0.2 ppm), bulk sulfidation can still cause permanent damage to the catalyst at higher concentrations [69]. Therefore, the SOFCs will not be ready for practical utilization of hydrocarbon fuels unless the sulphur poisoning issue is resolved. There are a few possible ways to reduce the sulphur or mitigate the sulphur poisoning issue in CH_4-fed SOFCs: (1) to add a priori de-sulphuration step to remove the sulphurous species in the fuel gas before sending it to the SOFCs. An excellent review on the cleaning options to reduce the sulphur concentration in hydrocarbon fuels has been reported by Aravind et al. [65]. However, this will add cost and complexity to the system [65]. (2) to develop catalytic materials for SOFC anodes with improved sulphur tolerance. This is important for the practical application of various hydrocarbon fuel gases in SOFCs and for reducing the capital and running cost of such systems without the expensive pre-treatment facilities [47,126]. More details, including the development of anode [126,133] and cathode [81] materials, can be found in the previously published reviews. The detailed poisoning mechanism is not within the scope of this current review, and the readers can refer to the review by Nirmal Kumar et al. [82], Wang et al. [81] and Boldrin et al. [80] for the fundamentals of sulphur poisoning and the material development strategies that can improve the sulphur tolerance. In this review, operational strategies to mitigate the impact of sulphurous species on fuel cell performances are briefly reviewed in Section 3.1. The impact of the anode materials on the operation of sulphur-containing CH_4 in SOFCs is also discussed in Section 3.2.

2.3. Methane reforming in an electrochemical device

The CH_4 reforming and electrochemical reactions in an electrochemical device will most likely interact and, thus, not proceed independently [67,68]. However, although great efforts in experimental investigations into methane reforming reaction have been conducted, the influence of the electrochemical reaction on the reforming reaction is rarely reported and often overlooked.

The effect of typical experimental parameters such as fuel compositions, temperature and electrochemical reaction on the catalytic activity was firstly investigated by Nakagawa et al. [70]. A change in the catalytic activity was reported with a current discharge of 0.6 A/cm² while fuelling the SOFC with a gas mixture of CH_4 and H_2O. However, the catalytic activity did not return to the initial value when the circuit reopened, suggesting that the non-reversible catalytic activity

deterioration occurred during a current load as high as 0.6 A/cm^2. Furthermore, higher catalytic activity deterioration was observed during current discharge at a higher steam partial pressure (p_{H_2O}) and a lower hydrogen partial pressure (p_{H_2}). However, the catalytic activity was revived after exposing the anode to a H$_2$ flow for a while which means the accumulated H$_2$O on the anode may have oxidized the Ni at the surface and resulted in the deterioration. The level of the deterioration is determined by p_{H_2O} and p_{H_2}, the anode microstructure, together with the magnitude of the current density. The finding suggests that the anode microstructure for DIR-SOFCs needs to be designed for a higher mass transfer rate to prevent the catalytic activity from deteriorating.

An experimental study on the effect of electrochemical reaction on the MSR reaction in an SOFC was also conducted under both open-circuit (open cell voltage with no current) and closed-circuit (with a discharging current in the circuit) conditions [68]. It was found that the current density has a slightly positive effect on the MSR reaction rate on the Ni-GDC anode. This is perhaps not due to the consumption of H$_2$ since Dicks et al. have reported a positive influence of H$_2$ on the MSR reaction rate [134]. Such effects can be explained by the MSR kinetic model developed by Xu and Froment [99], which shows a positive influence of H$_2$O on the reforming reaction rate at lower H$_2$O concentrations and a negative influence at higher concentrations. This non-monotonic dependency was also confirmed by Elnashaie et al. [135], enabling a more comprehensive understanding of the influence of H$_2$O on the MSR reaction. The kinetic parameters can be directly used in Computational Fluid Dynamics (CFD) models to precisely describe the cell performance. However, a more comprehensive investigation of the effect of current on the MSR reaction requires further studies with higher currents.

The same author further extended the study on Ni-YSZ anodes in complete SOFCs [67]. The electrochemical reaction was confirmed to promote the reforming reaction. The MSR reaction rate increases significantly when a small current is produced; however not change further as current density increases. It is believed that the MSR reaction is promoted by the O^{2-} flux at the TPB [136,137]. However, the adsorption competition between the CH$_4$ molecules and the extra generated H$_2$O molecules from the electrochemical reaction hinder the MSR reaction rate, which explains why the MSR reaction rate does not further increase with a higher current density.

Thallam Thattai et al. [90] also conducted an experimental study on MSR kinetics over a Ni-GDC anode with low steam to carbon (S/C) ratios and moderate current densities. The study emphasizes the need to develop readily applicable MSR kinetic models. They also confirmed the positive effect of electrochemical reactions on CH$_4$ conversion. However, the Power Law (PL) and Langmuir-Hinshelwood (LH) rate expressions were used. Two kinetic models predicted a significant difference in the local MSR reaction rate and species distributions along the normalized reactor length. This reveals the limitations of using previously proposed rate expressions for Ni catalytic beds to study MSR kinetics in SOFCs and a strong need for further experimental verifications.

Internal dry reforming (IDR) of methane for biogas-fed SOFC applications has been experimentally investigated on planar Ni-GDC (cermet anode) electrolyte-supported cells by Saadabadi et al. [138]. This study focuses on CO$_2$ concentration, current density, operating temperature, and residence time on internal methane dry reforming. Different CH$_4$ and CO$_2$ mixture ratios between 0.6 and 1.5. was fed to the SOFC. The I-V characterization curves were recorded under different operating conditions to find the best electrochemical performance and the maximum power production. The methane conversion increases with current density. Steam produced through the electrochemical reaction of hydrogen impacts the methane reforming when CH$_4$ to CO$_2$ ratio $\geq$1. The methane conversions were above 95% for all gas compositions at a current density of 2000 A m^{-2}. However, a high degradation rate has been observed when a 60 mol.% methane was used due to carbon deposition, which led to an anode Ni re-oxidation and cell surface

delamination at the fuel inlet at 850 °C. Furthermore, changing the residence time does not significantly influence methane conversion, which implies the fast kinetics of the internal methane reforming reactions. Long-term experiments have been performed for all gas mixtures at 850 °C under a current density of 2000 A m^{-2}. The results indicate that when the fuel cell is fed with biogas with an equimolar amount of CH$_4$ and CO$_2$, carbon deposition is prevented, and maximum power density is obtained. However, the biogas-fuelled SOFC system's power density is around 19% less than the hydrogen-fuelled one, and this should be considered while designing the biogas-SOFC system.

SOFCs are electrochemical devices that directly convert the chemical energy of fuel into electrical energy via an electrochemical reaction between the gaseous fuel and the oxidant. SOFCs provide a feasible alternative to the conventional energy conversion processes due to their highly efficient and eco-friendly operation. The high operating temperature (800–1000 °C) of SOFCs, oxide-ion conduction through the electrolyte, and the catalytic activity of the anode material for reforming reaction enable them to operate with a wide range of hydrocarbons. In addition, a well-designed anode structure should facilitate the movement of reacting species to the reaction sites from the gas bulk and vice versa for the products. The electrochemical reactions occur at the triple-phase boundaries (TPBs), where the electronic, ionic, and gas-phase interact simultaneously. The number of TPB sites per unit volume, often referred to as TPB density, is a critical geometric parameter of the microporous electrode and directly influences the anode performance. The TPB-based kinetics, developed from the patterned anode experiments, are used in a computational fluid dynamics model to assess the performance of anode-supported Ni-YSZ SOFCs by Tabish et al. [139]. The simulation results suggested that the effective TPB density required to carry out the electrochemical oxidation reactions is several orders of magnitude lower when compared with the physical triple-phase boundary density of similar cermet anodes.

A negative dependence on steam concentration for the MSR reaction rate has been widely reported, mainly with PL expressions. However, the detailed influence of the electrochemical reactions on the reforming reaction, especially on the steam adsorption behaviour over Ni-GDC anodes, remains relatively unknown, which is crucial for a better understanding of CH$_4$-fuelled SOFC systems. However, the complex surface chemistry involved in the MSR reaction was usually ignored, with observations indicative of a possible complex relationship between H$_2$O and the anode via surface adsorption. Besides, the presence of H$_2$O on the anode surface can accelerate H$_2$ electrochemical oxidation. The current density was confirmed to positively influence the overall MSR reaction rate on both Ni-YSZ and Ni-GDC anodes. However, an inconsistent influence of current density on the H$_2$O adsorption constant over the Ni-YSZ anode was also observed. Some of the results mentioned above on the interaction between the electrochemical and reforming reactions in SOFCs contradict, especially the results between Nakagawa et al. [88] and Fan et al. [67,68]. The contradicting observations of the influence of steam on the internal methane reforming reaction in SOFCs require further evaluation, especially the influence of electrochemical reaction on the steam adsorption on the anode surface and its interaction with the reforming reactions. Moreover, the significant difference in the influence of H$_2$O concentration on the CH$_4$ reforming kinetics found in the literature shows that a closer investigation of the influence of the electrochemically generated H$_2$O on the cell performance is needed to fully understand the CH$_4$ conversion process in SOFCs. Further investigations are still needed for a more reliable and precise description of the CH$_4$ reforming reaction in SOFCs with a current discharge.

The physicochemical processes within the anode structure are complex and involve highly coupled (electro) chemical reactions and multiphysics transportation phenomena, including energy, momentum, mass, and charge transfer. The charge-transfer process remains the least understood aspect of the chemistry of the SOFC electrodes. Although CH$_4$ reforming is regarded as a mature technology, the direct application of methane in SOFCs still suffers from several disadvantages caused by the

reactant properties and reaction thermodynamics. Many undesirable side reactions may still form solid carbon deposits, blocking and damaging the porous electrodes. In addition, it is difficult to optimize the catalyst for the different internal reactions occurring simultaneously, compromising overall performance.

Moreover, the direct internal reforming of CH_4 may also prompt high-temperature gradients within the SOFC, resulting in the local thermal stresses, which accelerate cell degradation. Recent work has shown that such thermal stresses severity depends on the CH_4 concentration in the fuel gas and the kinetics of electrochemical and MSR reactions. Therefore, developing an appropriate kinetic expression for the MSR reaction over the Ni-GDC anodes within the SOFC is highly beneficial in predicting accurate temperature and concentration profiles within the fuel cell and, ultimately, the safe operation, design, and development of SOFCs.

3. Mitigation of carbon deposition and sulphur poisoning

3.1. Operational strategies

Reforming CH_4 generates syngas to be directly used as the fuel for SOFCs. Potential issues due to directly fuelling SOFCs with CH_4 have been discussed in Section 2. However, in most cases, attention is required to prevent carbon deposition and sulphur poisoning by manipulating the operation conditions via: (1) adding a reforming agent or diluting agent to prevent carbon deposition and facilitate the CH_4 conversion as well as enhance the performance of the SOFC [4,65,76, 78]; (2) regenerating or recovering the deactivated anode catalysts [140–145].

3.1.1. Conditioning of the inlet fuels

Direct internal CH_4 reforming in SOFCs could potentially lead to several problems, such as carbon deposition, which can be avoided by pre-conditioning the fuel gas. A ternary C-H-O equilibrium diagram is often used to predict the carbon deposition boundary as a function of temperature and gas composition. Piroonlerkgul et al. [104] studied the performance of the CH_4-fuelled SOFC system in a thermodynamic analysis using different reforming agents, including H_2O, air, combined air and H_2O, to determine the most suitable feed. The boundary of carbon formation was calculated using the C-H-O ternary diagram, as shown in Fig. 4, to specify the minimum amount of each reforming agent necessary to avoid carbon depositions. The SOFC performance was
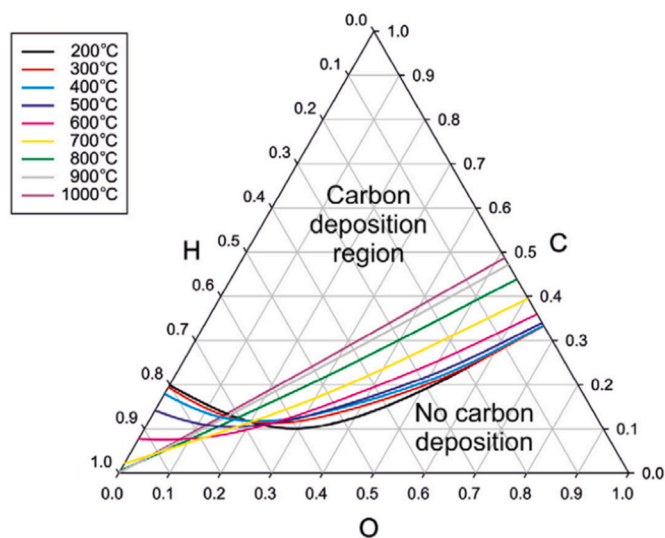
better when the CH_4 content was higher, and MSR was considered the most appropriate process for CH_4-fuelled SOFC, which offers a higher power density. However, the electrical efficiency was slightly lower.

CH_4-fuelled SOFCs have been investigated with variable gas compositions by Staniforth et al. [105,106]. It was demonstrated that carbon deposition was an issue; thus, fuel pre-treatment is needed. However, when the air was used during pre-treatment, CH_4-fuelled SOFCs can provide equivalent power to H_2-fuelled SOFCs, even when CH_4 content was reduced below the lower flammable limit. This suggests that SOFCs could find a niche market in the utilization of CH_4 at a low concentration that cannot be ignited.

Shiratori et al. [20] tested an anode-supported button cell performance fuelled with biogas derived from municipal organic wastes. Stable internal reforming operation with a cell voltage above 0.8 V for over 800 h at a current density of $0.2 A/cm^2$ was achieved at 800 °C. The study also revealed that biogas conditioning with air mitigated carbon deposition and led to a more stable operation. Direct biogas-fulled SOFC has also been investigated by Takahashi et al. [17]. Catalytic activity and thermo-mechanical reliability of Ni–zirconia anode were studied in a DIR- SOFC to develop a carbon-neutral energy system using municipal organic wastes. The authors also claimed that adding air to biogas is one of the most effective ways to solve the substantial temperature gradient issue. Thermal-mechanical reliability, electrochemical performance and reforming efficiency were evaluated while investigating the optimum amount of air addition to biogas.

Ni [147] investigated the necessity of adding H_2O to landfill gas to fuel SOFCs using a numerical model. Although H_2O addition decreases the short SOFC stack performance under typical operating conditions as H_2O dilutes the fuel concentration, H_2O is still necessary at reduced operating temperatures or low operation potential. This study helps identify strategies to convert landfill generated gas into electrical power using SOFC systems.

However, ensuring carbon-free conditions is usually not optimal from an operational perspective. Brus et al. [71] investigated an experimental and theoretical approach to mitigate the carbon deposition using simulated biogas fuelled-SOFC. Efficient and carbon-free working conditions were determined. It was demonstrated that the reaction could proceed safely outside the carbon deposition regime for temperatures from 850 °C to 950 °C, even with only a tiny amount of extra H_2O. The main product is H_2 when H_2O is added. At the same time, adding CO_2 results in the production of mainly H_2 and CO. Both gases can be used as fuels in an SOFC, but a high concentration of CO compared to H_2 can result in a decrease in the overall SOFC efficiency.

Tsai et al. [148] studied the influence of anode off-gas recirculation on the internal CH_4 reforming in an SOFC. MSR and DMR were investigated regarding CH_4 conversion, H_2 yield, and carbon formation. Variable gas compositions, including CH_4, H_2O, and CO_2, were used to simulate the internal reforming conditions, and the crushed materials from a half-cell were used as the catalyst. Thermodynamic equilibrium calculations were implemented to evaluate the concentrations of each constituent at equilibrium. An approximate 20% CH_4 conversion by steam reforming was reported, which was highly affected by the flow rate. An H_2O to CH_4 ratio equal to 1.0 can provide better MSR performance than higher ratios, while a higher CO_2 to CH_4 ratio is generally suggested for DMR. A relatively low H_2O concentration mixed with a relatively high CO_2 concentration was found to promote the CH_4 conversion and reduce the chance of carbon deposition. Detailed investigation of CH_4 reforming was still suggested by full kinetic modelling. The experimental study of the performance of an SOFC short stack fuelled with dry reforming and steam reforming mixtures also revealed in another study that dry reforming compositions could yield better performances with no more significant thermal stresses [8]. Evidence shows that although a high concentration of H_2O in MSR operation strongly reduces performance, substituting H_2O with CO_2 causes less decay as diluent into the gas mixture.

Thermal-neutral operation in DIR-SOFCs was evaluated by

Fig. 4. Ternary equilibrium diagram for the C-H-O system, showing the boundary lines of the carbon deposition possibility as a function of the temperature (600 °C–900 °C) [146].

employing a model combining experimental data and thermodynamic results by Lyu et al. [149]. The influence of CO_2 addition on the electrochemical characteristics and stability of a SOFC was also experimentally studied with a CO_2 to CH_4 ratio ranging from 0 to 3. The maximum power densities were obtained with CO_2 to CH_4 ratios between 1.5 and 1.7, which fall into the carbon-free region based on the thermodynamic calculation. The addition of N_2 as the carrier gas in the fuel could enhance the performance of the fuel cell in the low-current region by increasing the open-circuit voltage and eliminating carbon deposition [127]. The diluting effect of N_2 on the fuel is neglectable when CO_2 to CH_4 ratio is higher than 1. Instead, an enhanced output performance was observed when appropriate N_2 carrier gas was added to the fuel. The SOFC fed with CO_2, CH_4, and N_2 mixture (CO_2 to CH_4 ratios>1.5) exhibited a stable operation with a low current density for 100 h. No carbon deposition was detected during the post-test microstructure observation at the anode. Enhancement of the performance and durability of biogas-fuelled SOFCs could be possibly realised by simply adding the abundantly available N_2 to the fuel. Although the results are helpful for the practical application of methane in SOFCs, experimental verification is still required.

3.1.2. Recovery/regeneration of catalysts

Carbon deposition on the anode materials is inevitable under certain conditions, even on the most resistant catalysts. When the catalytic activity has dropped below the critical level, a choice needs to be made among the following alternatives [145]: (1) catalytic activity recovery; (2) essential and expensive catalyst recycling; or (3) catalyst disposal. Recovery, regeneration and reuse of the catalysts are almost always preferred, while catalyst disposal is always the least desirable option considering the environmental aspect. Nobel metals are almost always recycled, as their regeneration is often impossible. The decision to regenerate, recycle or discard the catalyst can also be made based on the rate of deactivation. Repeated or continuous regeneration is usually implemented for very rapid deactivation, mainly in the cases of Ni-based catalyst deactivation by carbon deposition. Therefore, the recovery and regeneration of the Ni-based anode catalysts in the SOFCs fuelled with CH_4 or other hydrocarbons are crucial to maintaining the sustainability of such systems. Different types of carbon deposition, such as monatomic carbon, polymeric amorphous films, vermicular fibres or whiskers [69, 145], can form under various conditions. Both preparations of the catalysts and reaction conditions can affect the type and amount of the deposited carbon. The corresponding regeneration techniques, therefore, vary accordingly. Anode materials degradation caused by deposited carbon can be recovered with various agents such as O_2, H_2O, CO_2 or H_2 [70,145]. A comprehensive review of the regeneration techniques is not expanded in this review, but interested readers can find more details in the excellent review by Argyle et al. [145].

Biomass fuel contains less sulphur than fossil fuels. H_2S in bio-syngas can vary from 20 ppm to 200 ppm [65]. Similar to carbon deposition, the main existing operational methods to mitigate sulphur poisoning are: (1) processing of the fuel externally to reduce the sulphurous compounds to levels safe SOFC operations by adsorptive desulphurization, for example, using zinc-based sorbents (including zinc oxide, zinc titanate, zinc-ferrite), copper-based sorbents or cerium-based sorbents. The use of mixed sorbents for sulphur compound removal has been suggested by Aravind et al. [65]. Other external desulphurization methods include bio-desulphurization using bacteria to promote the degradation of H_2S, membrane desulphurization using a membrane to selectively separate the contaminants from the fuels and oxidative desulphurization [82]. The cost and the complexity depend on specific desulphurization requirements, which determine the pressure and temperature required to reduce the sulphur level for a safe operation of such a system [80]. (2) Some methods used to regenerate traditional sulphur-poisoned catalysts can be directly applied to regenerate sulphur-poisoned SOFC anode materials. Such methods include thermal treatment in O_2, H_2, H_2O or other reductive or oxidative atmospheres to remove sulphur on the

anodes [141,143,150–152]. Electrochemical re-oxidative methods [142,153] or shifting the electrode potential [140] have also been reported to recover sulphur-poisoned SOFC anodes. The readers can refer to the reviews by Boldrin et al. [80], Argyle et al. [145] and Nirmal Kumar et al. [82] for comprehensive details.

3.2. Anode materials development

SOFC technology has been under development for many decades, and research fields are devoted to it due to its potential societal benefits [85,154]. Different component materials for SOFCs have been comprehensively reviewed in several other reviews from different perspectives [4,7,14,45,75,78,96,97]. As most reactions occur on the anode, its material is perhaps the most important factor for the operational performance of SOFCs. SOFC anode materials should ideally be chemically stable, have sufficient mechanical strength, and possess high conductivity and electro-catalytic activity. In addition to the strategies mentioned above to mitigate the carbon disposition and sulphur poisoning, developing the anode materials based on the requirement is another effective method to facilitate the safe and stable direct internal reforming of CH_4 in SOFCs. A series of MSR catalysts have been designed and fabricated with higher activity and stability, which can be readily used as reforming catalysts in SOFCs, making hydrocarbon fuel-fuelled SOFCs possible and affordable [72,73,96]. Many detailed comprehensive overviews of those anode materials can be found in other reviews [7,75,77,78,95–97,155]. Many constraints are associated with the anode materials due to the high operating temperatures of SOFCs. To determine its suitability for an application, factors such as contaminant resistance, reforming stability, heat stability, and redox stability must be considered. The catalysts applied are essential for the reaction paths, composition and heat distributions, and the tolerance to carbon deposition and sulphur poisoning. The most frequently investigated SOFC anode catalysts are primarily monometallic noble, bimetallic noble and non-noble metal catalysts. Conventional materials for SOFC anode are mostly platinum (Pt), iron (Fe), cobalt (Co) and Ni [40,72,73,156,157].

State-of-the-art CH_4 reforming catalysts to produce H_2 were summarized and reviewed by Sengodan et al. [4]. Some of these catalysts can be readily used in SOFCs. Ni is an excellent catalyst for CH_4 reforming and is one of the most abundantly available inexpensive non-noble elements [72]. Ni also has high catalytic activity for the oxidation of the fuel, excellent chemical stability, and good electronic conductivity. Most other metals perform poorly compared to Ni due to a higher operating temperatures requirement. Another primary reason is the critical nature of the poor interfacial structure between alternative metals and electrolytes when establishing electrodes [158].

Since catalysis of both chemical and electrochemical reactions is required for a successful SOFC operation, the selection and application of anode materials is a crucial factor for cell efficiency and stability. Carbon deposition is a persistent issue in CH_4 reforming at high operating temperatures. Ni-based materials are more prone to carbon deposition and Ni oxidation and hence impact the activity of the cell. Therefore, new thermally stable anode materials development or the current existing catalysts improvement, such as cermet materials, doping the catalyst with promoters or modifiers, or replacing Ni with other more carbon-deposition resistant metals, have attracted significant attention aiming at high resistance to deactivation from sintering or carbon deposition. Therefore, mainly the Ni-based anode materials development from the perspective of carbon coking and sulphur poisoning mitigation raised by CH_4 reforming in SOFCs as mentioned in Section 2 are discussed.

3.2.1. Ni cermet materials

Ni also catalyses the carbon formation in SOFCs when fuelled with hydrocarbons (even CO) at an elevated temperature [127,159]. Therefore, there is a need for alternate materials that can provide a resistant and stable structure while facilitating the required anode reactions. This

led to the use of porous ceramic-metallic (cermet) materials, as shown in Fig. 1, a composite material consisting of ceramic and Ni [160–163]. The cermet is typically prepared via the homogeneous milling of the Ni and ceramic materials, followed by subsequent sintering and reduction of the mixture. This process yields a highly porous solid wherein Ni is supported by a ceramic structure [75,97,164,165]. The ceramic structure also acts as an extension of electrolyte, allowing the O^{2-} flux direct contact to the attached Ni, which acts to adsorb H_2 or CO and catalyse the MSR reaction on the TPB. Charge developed via the electrochemical reaction is then transferred through Ni, which an external conductor can introduce into the fuel cell circuit.

Ni-based cermet has attracted much attention due to specific advantages, including having similar thermal expansion coefficients to metal, chemical compatibility and heat resistance which have shown a good performance as a reforming catalyst. Ni can be loaded on different supports, including Al_2O_3, MgO, CeO_2, La_2O_3, and ZrO_2, to be applied as SOFC anode materials. Among these, ZrO_2 is the most stable one. Substantially more studies have been carried out for Ni-YSZ than other anode materials [4,96,166]. Ceria also shows its high potential as a good candidate for methane reforming with a low risk of carbon deposition due to its outstanding oxygen retention ability [167]. Due to the cost restrictions, mechanical stability and electrochemical efficiency, Ni-YSZ [16,62,87,88,102,128,168–180] and Ni-GDC [181–183] are the most widely applied anode materials. Therefore, they are chosen for the detailed discussion due to their wide adoption and a large expanse of experimental data available for Ni-YSZ and the promising state of Ni-GDC development leading to an extensive number of studies. In the following section, these anode materials are first discussed concerning their state in the industry and notable characteristics. Awareness of the weaknesses involved with applying these materials in the DIR-SOFC is then briefly discussed.

3.2.1.1. Ni-YSZ. The most commonly used SOFC anode materials are cermet composites of Ni-YSZ, in which Ni is the electronic conductivity and catalytic activity provider [86,128]. Zirconium dioxide was theorized to improve the O_2 storage capacity of the cermet, thereby improving its capability to catalyse the reforming reaction and thermal stability. The typical grain size in the cermet is around 1 μm when calcinated at high temperatures. The Brunauer–Emmett–Teller (BET) surface area for this type of material is roughly 1 m^2/g. The impedance of Ni-YSZ can be low for operations with H_2 or synthesis gases [40,72,73, 75].

King et al. [62] reported the effect of Ni microstructure on the MSR activity of a cermet anode catalyst without accounting for electrochemical effects. The Ni-YSZ catalyst materials fabricated for the tests showed high activity initially and then decreased significantly with time on stream before eventually reaching a steady state. Reduction procedure, feed gas composition, the temperature of reforming, and time on stream can all affect the Ni microstructure and thus the reforming activity. The catalytic activities were detected for the large bulk Ni particles derived from the source material and the small Ni crystallites adjacent to the YSZ particles. The activation energy for methane reforming was between 113 kJ/mol and 124 kJ/mol under different reduction and measuring conditions.

Hecht et al. [106] reported experimental and modelling results on CH_4 thermal reforming chemistry using a single porous Ni-YSZ anode with two small co-flowing gas channels on each side. A non-electrochemical heterogeneous reforming chemistry computational model was used to interpret the experimental results obtained on a Ni-YSZ anode. The model was beneficial in predicting the reforming performance and helping optimize the design of anode structures for novel SOFCs. The readers can refer to more experimental investigations [16,46,102,109,175,176,184] and DIR-SOFC modelling studies [160, 161] on Ni-YSZ anodes which many other researchers have widely reported.

Fan et al. [67] investigated the influence of the magnitude of electrochemical reaction and the anode thickness on the MSR reaction using Ni-YSZ anodes. The negative influence of p_{H_2O} on the MSR reaction rate was found. A small current density caused the increase in the reforming reaction rate, which may be due to the O^{2-} flux across the TPB. Further, H_2O molecules and O^{2-} ions accumulated at the TPB may cause Ni oxidation, which could be reflected either as an increase in the activation energy or a decrease in the rate constant. The values for the activation energy fall between 23 kJ/mol to 53 kJ/mol, which is low compared to previously reported values on comparable Ni-YSZ anodes. The results help provide convenient MSR reaction rate expressions to the modelling study of the methane-fed SOFCs using Ni-YSZ anodes. However, more detailed experimental data are needed for a more thorough description of the influence of current density on the reforming activity of the anode.

Although widely applied successfully, other candidate materials are often reported to enable better performance than Ni-YSZ [95] whose major drawbacks are attributed to sulphur poisoning and carbon deposition [13,65]. With a lack of H_2O or low current density, carbon deposition is likely to occur, resulting in deterioration of cell performance. Ni-YSZ anodes allow high carbon deposition rates under an insufficient H_2O supply, coating Ni particle surface and potentially blocking the pathways to TPB, as shown in Fig. 2. The electrical conductivity is affected by YSZ particle size, and pore volume and can be severely reduced if Ni percentages are lower than 30% [78,80]. This has been observed at Ni percentages of 30 vol% or under, referred to as the percolation threshold. Anodes with Ni fractions ranging from 40 to 60 vol% can reduce this phenomenon in the short term, but the agglomeration of Ni particulates will still occur. The thermal expansion coefficient can also be changed by varying the Ni percentages.

Prolonged operation of the SOFC can further reduce the TPB length due to the agglomeration and further increase the resistance, though this issue is not exclusive to YSZ mixed anodes. Ni-YSZ degradation is generally measured via increasing over-potential or decreasing cell potential. Microstructurally, the degradation of anodes is related to a coarsening of the Ni phase or the loss of Ni due to the volatilization of Ni hydroxide species [185]. This decreases electrical conductivity within the cell because the larger Ni particle size causes less Ni particle numbers and less Ni-Ni contact. Unfortunately, a detailed description of microstructural degradation is not discovered in the literature, probably due to the complexity of the structure. However, many studies have attempted to shed some light on specific aspects of it, and the interested readers can refer to them [69,75,90,92,96,162,164,165,186]. Unfortunately, the mechanical properties of these materials are rarely reported and thus mostly inconclusive in literature.

Other major problems with Ni-YSZ anodes are the low stability of electrochemical activity and low tolerance level to sulphur. The redox instability is associated with re-oxidation and subsequent re-expansion of Ni forming nickel-oxide (NiO), leading to cell failure [187,188]. Ni oxidation can occur near the leak and during shut-down procedures, as high H_2O to H_2 ratios and lower temperatures will promote the oxidation process. Ni-YSZ anodes can also experience microstructural changes during re-oxidation cycles with reductions of the electrolyte-Ni-gas area and the electrode activity. Research has been conducted to understand and improve Ni-YSZ [187]. In addition, the replacement of YSZ with Mixed Ionic and Electronic Conductors (MIECs) has increased the reaction efficiency. The readers can refer to Refs. [189–192] for a more detailed discussion of MIECs.

3.2.1.2. Ni-GDC. GDC is an active H_2 oxidation electro-catalyst. Ni-GDC cermet has gained attention as it provides extended reaction sites due to the MIEC property of the GDC phase [182]. The primary benefits for Ni-GDC anodes are commonly noted as a lowered activation energy for the methane reforming reaction, combined with high electro-catalytic activity. While Ni is known to catalyse the formation of

carbon nanofibers and develop coke within pores, Ni-GDC has been observed to be more resistant to carbon deposition than Ni-YSZ anodes. Ni-GDC also shows improved sulphur tolerance due to the GDC phase in the anodes facilitating hydrogen dissociation and diffusion. Another possible reason can be that ceria reacts with H_2S, which prevents the reaction between H_2S and Ni on its surface [133,193]. Furthermore, higher power density can be achieved with ceria-based anodes due to the much higher O_2 adsorption ability of the anode materials [109,181].

As existing literature on MSR kinetics focuses more on Ni-YSZ than on Ni-GDC, there is a notable lack of experimental data [45,75,96]. Timmermann et al. [87,194] conducted a kinetic study over a Ni-GDC anode, investigating the cell performance over various steam to carbon ratios and temperatures. At higher temperatures (950 °C), Ni-GDC and Ni-YSZ anodes performed nearly identical concerning CH_4 conversion. However, higher CH_4 conversion was reported on the Ni-GDC anode at 800 °C. Kinetic analysis revealed an activation energy of 26 kJ/mol for MSR reaction, notably lower than that observed for Ni-YSZ anodes [87]. However, this model did not include pore diffusion, which cannot be neglected in some instances. As such, the apparent activation energy may have been underestimated.

Ramirez-Cabrera et al. [137] studied the MSR catalytic activity of ceria gadolinium oxide (CGO, also known as GDC) powder, which is extremely resistant to carbon deposition under wet conditions. It was found that the reaction rate was controlled by the slow reaction of CH_4 with O_2 in CGO and a facile reaction between H_2O and CGO to replenish the O_2. H_2 was observed to inhibit the reforming reaction significantly.

An experimental study of the performance of tar on the Ni-GDC anode in SOFCs was reported by Liu et al. [66]. Cell performance, such as the polarization behaviour, electrochemical impedance spectroscopy and cell voltage degradation at different operating temperatures (700 °C, 800 °C and 900 °C) under dry and wet conditions, were evaluated. Tar was used as a fuel for SOFCs under carbon risk-free operating conditions. When the moisture content was introduced, the cells with Ni-GDC anodes did not suffer from carbon deposition. CO_2 was also found to be enhancing cell performance. When a dry tar-containing syngas is fed to the SOFC, no carbon formation is found with a small current. However, the possibility of carbon formation under open-circuit conditions still needs investigation.

The relation between current density and MSR kinetics on Ni-GDC anodes was further investigated by different groups [68,88,90,195]. Experiments were conducted on these materials at steam to carbon ratios of 1.5–5.3. The ratios below 1.5 are typically considered at risk for carbon deposition. However, no significantly visible deposition was noted on this anode at ratios ranging between 1 and 1.5, demonstrating Ni-GDC's inherent coking resistance [90]. Additionally, Fan et al. [68] investigated MSR reaction kinetics across an operative SOFC with Ni-GDC anode by varying the discharge current density. An open-circuit design was found to have an activation energy of 88 kJ/mol, and the activation energy was notably lower under closed-circuit conditions. Both tested current densities (600 A/m^2 and 1000 A/m^2) showed similar activation energies at 63 kJ/mol and 68 kJ/mol. They thus concluded that this lowered activation energy resulted from the O^{2-} flux across the electrode, aligning with the conclusions made by Vayenas et al. [195].

A common problem with Ni-GDC is its chemical instability to the adjacent electrolyte, most commonly YSZ. This causes the fusion of GDC and YSZ at high temperatures but can be avoided with a Ni content of more than 40% [78,97,125,196]. Like Ni-YSZ cermet, the presence of Ni inside the anode leaves it vulnerable to carbon deposition, albeit at lower risk [109,182]. This is much less pronounced as the GDC catalytic activity for CH_4 reforming is much lower than Ni [109,182]. However, its degradation mechanism is complicated when both solid phases evolve during operation. Additionally, the morphology of Ni and GDC is also influenced by the humidity of the fuel gases [78,97,172,197].

The two primary issues with oxide-based anodes (YSZ and GDC) are insufficient electronic conductivity and relatively poor catalytic activity for oxidation reactions. The readers can refer to elsewhere for

approaches to deal with low electronic conductivity [77,97]. While Ni-YSZ and Ni-GDC materials are topics of widespread experimentation and discussion, there are also many other tested and theorized anode materials. These range from the use of other supporting materials such as Al_2O_3 and TiO_2, the addition of modifiers or promoters such as ceria and noble metals into a Ni-YSZ/GDC matrix, the use of alternate conductive base metal to replace Ni, and alternative anode materials to improve the long-term operation durability and the resistance to carbon deposition and sulphur poisoning. These materials are reviewed and discussed in the following sub-sections.

3.2.1.3. Other supporting materials. More cermet anode materials [16, 164,198,199], lanthanum derived materials [165], and others [62,95] have been studied as well. Ni-Samarium Doped Ceria (Ni-SDC) investigated by Brus et al. [16] may provide a promising alternative to Ni-GDC and Ni-YSZ. Ni-SDC was shown to have very similar benefits to Ni-GDC catalysts, with ceria lowering the observed and measured activation energy for the MSR reaction and hypothesized to catalyse the WGS reaction [99,200]. However, the Ni-SDC anode has a notable impact on the reaction order of H_2O at −0.25, compared to the −0.09 recorded for a similarly tested Ni-YSZ catalyst. This may imply that this anode material is unsuitable for high steam to carbon ratio environments. However, further study on the catalytic activity in low steam to carbon ratio environments is still needed to confirm this. A numerical model considering methane reforming and WGS reactions was employed to predict the reformer outlet's gas composition [16]. The modelling results were compared with the experimental results, and good agreement was found, implying the successful prediction of the outlet gas composition under different operation conditions [16].

Ni supported on Al_2O_3 is a prominent catalyst due to its low cost and high activity. Catalytic activity increases with Ni content due to the increasing catalytic sites. It was seen that pure Ni with a BET surface area of 0.44 m^2/g exhibited high catalytic activity when the steam to fuel ratio was two at the low-mid temperature range in a seven-cell differential reactor, and the carbon deposition was significantly reduced [201]. However, as a steam reforming catalyst, Al_2O_3 support is typically acidic, not providing enough oxygen ionic conductivity, favouring hydrocarbon cracking and polymerization. This is a crucial reason for the accelerated deactivation of the catalysts [136,202,203].

A study of using alkali metals (such as K) and alkaline earth metals (such as Mg and Ca) as the supporting materials to improve anode catalytic stability has been conducted [204]. MgO [178] and CaO [32,205, 206] supports could prompt the MSR reaction rate and the H_2 selectivity. Following CO_2 absorption by CaO, the reaction equilibrium shifts to the product's side. Absorbed CO_2 can be handled via the decomposition of $CaCO_3$ to recover the catalyst, and it should be noted that CaO regeneration is exothermic. Ni particle size increases to form Ni_4-MgO, which provides sufficient but isolated active Ni sites for CH_4 reforming with CO_2, producing CO, H_2 and H_2O, eliminating carbon deposition [178].

A study of CH_4 reforming on Ni-TiO_2 (110) surface in SOFCs under dry and wet atmospheres was conducted by Yang et al. [207]. H_2O adsorption and dissociation on TiO_2 surface were much easier than those on Ni, YSZ and CeO_2, which could be the critical reason for substantially depressing carbon deposition on Ni-TiO_2 particles compared to conventional Ni-YSZ and Ni-CeO_2 anodes. In addition, the study presented the detailed CO* formation mechanism in the CH_4 reforming process on the Ni-TiO_2 surface, which will benefit future research exploring new carbon-tolerant anode materials.

Material selection is crucial to mitigate fuel cell degradation and system failure whilst maintaining good efficiency and overall performance. Ni composites are widely used because they are catalytic active and stable and relatively easy to manufacture. However, there are arguments for choosing alternatives for pure Ni as anode material. Ni can lead to performance degradation of the fuel cell on repeated use. When

hydrocarbon species are directly used at low temperatures, carbon deposition occurs on the Ni surface, which possesses high catalytic activity. The readers can refer to the previously published articles [60,66, 69,71,127–129,131,208] to better understand the importance of Ni composites' geometric structure on the deposited carbon type and morphology.

3.2.2. Promotors or modifiers

Modification of Ni properties to avoid carbon deposition has also been attempted. Adding catalyst promoters or modifiers can improve the catalyst properties such as H_2 selectivity, thermal stability, chemical stability and carbon deposition tolerance. The catalyst promoters and modifiers are usually combined with Ni to form a bi-metallic Metal-Ni alloy catalyst, as shown in Fig. 5 [7,45,96,174,209]. Promoters such as Co, copper (Cu), Tin (Sn), Pt, Palladium (Pd), Manganese (Mn), Rhodium (Rh), Ruthenium (Ru) and gold (Au) have been found to improve the H_2 selectivity and decrease carbon deposition significantly [210].

Noble metals (Pt, Pd, Rh and Ru) are more resistant to carbon formation than other transition metals [7,45,96]. For example, bi-metallic Ni-Pt supported on ZrO_2 has high and stable activity than monometallic Ni-ZrO_2 materials over prolonged periods. Additionally, the presence of Rh keeps Ni in its metallic form by H_2 spillover, thus reducing NiO formation. The activity and stability of bi-metallic Ni-Pd catalysts are reported to be much greater than a monometallic Ni catalyst [173]. Pakhare et al. [211] found that a Ni-Pd ratio of 4:1 has optimal catalytic stability. Carbon deposition and sulphur poisoning can be mitigated by doping with molybdenum (Mo) and Au, increasing the anodes' conversion and durability at lower temperatures [202,212].

Ni-GDC and 3 wt% Au-Ni-GDC anodes were experimentally prepared and tested by Souentie et al. [183]. Mathematical modelling of SOFC performance under internal MSR conditions was carried out. The surface dissociation of CH_4 to form methyl species was considered, which then reacted with H_2O to produce CO and H_2. Au was found to contribute to a

slightly higher CH_4 dissociation activation energy. The model agrees with experimental results under open- and closed-circuit operation conditions. The study's authors [183] have also found that the anode materials' electrocatalytic activity could be altered by changing the steam to carbon ratio. However, despite the advantages of using noble metal catalysts, their high associated costs prevent large scale adoption within the industry.

Doping Ni-YSZ with ceria is reported to enhance anode performance. Klein et al. [213] noted stable operation of an internally reforming SOFC with a Ni-YSZ anode and a 500 μm thick layer of iridium (Ir) impregnated ceria. This result is particularly promising as it was conducted with a steam to carbon ratio of 1, well under the commonly recommended threshold (1.5) for carbon deposition. Belyaev et al. [214,215] and Ramirez-Cabrera et al. [137] investigated a Ni-Ce-ZrO_2 at 500 °C - 800 °C. The weight per cent of Ni was 10%. It was seen that the catalyst exhibited the highest conversion at the temperature range from 500 °C to 600 °C. When Ni, with the support of $Ce_{0.15}Zr_{0.85}O_2$ was investigated, it was found that ceria increased the capability of transferring, releasing, and storing O_2, thus preventing carbon formation. Reduction of NiO also happened smoothly, as CeO_x promotes the disassociation of H_2O and increases the activity of the reaction. It was noted that this anode showed good performance in terms of stability and resistance to carbon deposition. However, an inhibitory effect on the MSR reaction was observed when a high concentration of CH_4 was present.

Arcotumapathy et al. [216] evaluated the MSR reaction on 1 wt% Ce-promoted 10 wt% Ni/SBA-15 catalysts, and mechanistic considerations for MSR were derived based on single and dual-site associate and dissociate adsorption of one or both reactants. The model considering single-site dissociative adsorption of both CH_4 and H_2O explains the experimental data most adequately. The reaction order on CH_4 and H_2O obtained were 0.94 and −0.16, respectively. The negative order of H_2O reflects the competition between the H_2O and the active sites where the CH_4 reforming occurs. Using Ce as the promotor reduces the ratio of the acid-to-basic site by 12% over Ni/SBA-15.

Flexible composition modification can be realised by infiltration, and Gorte et al. have investigated the catalytic properties of electronically conducting ceramic electrodes prepared by this fabrication process [124,173]. Adding 5 wt% ceria to the anode increased the maximum power density from 105 mW/cm^2 to 300 mW/cm^2. The addition of 0.5 wt% Pd alone or 0.5 wt% Pd and 5 wt% ceria increased the maximum power densities to 500 mW/cm^2 and 520 mW/cm^2, respectively. The addition of Pd and ceria also exhibited a much lower performance loss than only pure ceria addition. Both are much lower than those in the cell without a catalyst.

Cu has been utilized as a modifier for Ni in different studies [171, 217]. Replacing Ni with Cu can reduce carbon deposition as Cu does not catalyse C-C bond formation [156,217]. It was found helpful in preventing carbon deposition due to its inertness towards hydrocarbon oxidation and did not catalyse the breaking of C-H bonds. However, its low thermal resistance is a notable drawback. As copper has a relatively low melting point compared to other metals, it is unsuitable for high-temperature operation, negatively impacting its application in reforming processes.

Additionally, fabrication of a two-phase cermet is required [174]. An infiltration procedure was employed in one study to form the Cu-Ni alloy anodes [217]. In another study, electroplating of Cu onto the surface of a Ni-YSZ composite was implemented to form the anodes [171]. Carbon formation at high temperatures was suppressed on both anodes in the event of exposure to CH_4, although the electrochemical performance was sacrificed.

Sn is another interesting modifier for Ni-based anode materials [129, 210]. Ni-based electrodes with and without the addition of 0.5–1.0 wt% Sn were tested in CH_4 and isooctane in the study reported by Nikolla et al. [129]. It was found that the addition of Sn significantly suppressed the carbon deposition over the anodes. Ni's electrochemical and conduction properties do not significantly change due to the surface alloy
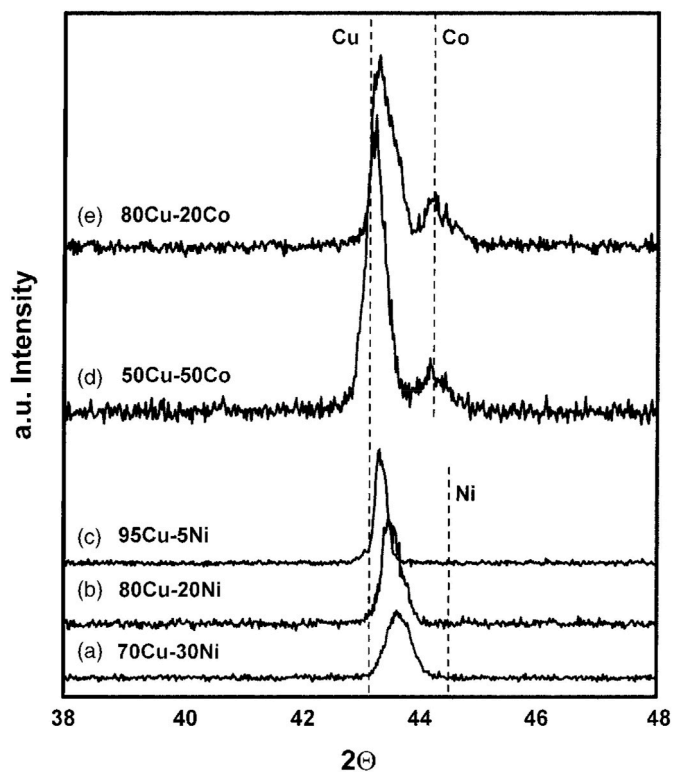

Fig. 5. XRD patterns of Cu-Ni, Co-cermet with various metal compositions [174].

formed with Sn.

Enhanced MSR activity and electrochemical performance of $Ni_{0.9}Fe_{0.1}$-supported SOFCs with infiltrated Ni-TiO$_2$ particles were reported by Li et al. [218]. The reforming activity of the $Ni_{0.9}Fe_{0.1}$ support increases with the presence of the TiO$_2$-supported Ni particles (NTO). 3 wt% is the optimal value of the added NTO, corresponding to the highest reforming activity, electrochemical performance, and much-improved resistance to carbon deposition. Furthermore, the addition of TiO$_2$-supported Ni particles into the $Ni_{0.9}Fe_{0.1}$ support reduces the polarization resistance of the processes attributed to MSR and gas diffusion in the $Ni_{0.9}Fe_{0.1}$ support and functional anode. Progress on the development of anodes with improved sulphur tolerance has been reviewed elsewhere [78].

Efforts in modifications to the catalytic properties of Ni-cermet anodes have also been made to improve their sulphur tolerance [133,219]. Although relatively high H$_2$S: H$_2$ ratios are required to form bulk Ni sulphides, studies have shown that sulphur concentrations as low as 1 ppm have already caused significant degradation over Ni-YSZ anodes due to the sulphides formed on the Ni surface [81,126,140,142,143,150, 153]. Kurokawa et al. [133] modified a conventional Ni-YSZ anode using infiltrated ceria nanoparticles. 40 ppm of H$_2$S in the H$_2$ feed stream caused the unmodified SOFC cell voltage to drop to zero within several minutes. The cell voltage dropped from 0.78 V to 0.6 V under the same concentration of H$_2$S after several minutes. It was then stable for the next 500 h on the modified anode with the addition of ceria nanoparticles. The initial performance of the cell was restored by switching the feed stream back to pure H$_2$.

Besides adding ceria, other material modification strategies for sulphur tolerance are using all-ceramic anode materials and alloying Ni with other metals. Detailed reviews of studies on sulphur tolerance are not expanded here but can be found elsewhere [13,65,66,220]. Many investigations on sulphur poisoning are mostly related to H$_2$S containing H$_2$ fuels and Ni-cased anodes. However, sulphur-containing hydrocarbon fuels react differently from H$_2$ fuels due to the concurrently occurring reforming and WGS reactions potentially affected by sulphur and carbon deposition. Gur et al. [79] discussed the sulphur tolerance on SOFC anodes in CH$_4$ environments and pointed out that it still needs further study.

3.2.3. Addition of an internal reforming catalyst layer

Ni-based anodes could promote the direct utilization of hydrocarbons in SOFCs if the side effects of carbon formation can be avoided or mitigated and the poor sulphur tolerance can be improved. Significant effort has been made to improve the commonly applied Ni cermet properties to benefit from and ameliorate drawbacks. Implementing either a high carbon deposition resistant catalyst or a protective barrier on the external surface of the anode can physically protect Ni from unsafe conditions. In one study, higher-molecular-weight hydrocarbons were first reformed into syngas by a thin outer layer containing a Ru/ceria catalyst before contacting the Ni catalyst [221]. In another study, an electronically conductive oxide, $La_{0.2}Sr_{0.8}TiO_3$ (LST), was applied onto the external surface of the anode as a protective barrier which helps maintain a higher p_{H_2O} around Ni under closed-circuit working conditions [222]. The LST barrier. However, further studies considering the diffusion limitations need to be taken to verify the general effectiveness of this method.

Wang et al. [223] investigated the catalytic activities of Ru loaded Al$_2$O$_3$ in CH$_4$-fuelled SOFCs, as shown in Fig. 6. 3 wt% Ru-Al$_2$O$_3$ loading showed an outstanding catalytic activity towards CH$_4$ reforming and good thermal stability over the Ni-YSZ anode. The electrochemical performance of 3 wt% Ru-Al$_2$O$_3$ anode in various gas mixtures was tested. A peak power density of 1006 mW/cm^2 was achieved on the fuel cell fed with a CH$_4$ and O$_2$ mixture at 850 °C. The result is comparable to the same fuel cell in pure H$_2$ with a power density of 1038 mW/cm^2.

Chen et al. [162] reported that the coking was reduced by infiltrating a thin SDC nano-catalyst layer on the walls of the hierarchically porous
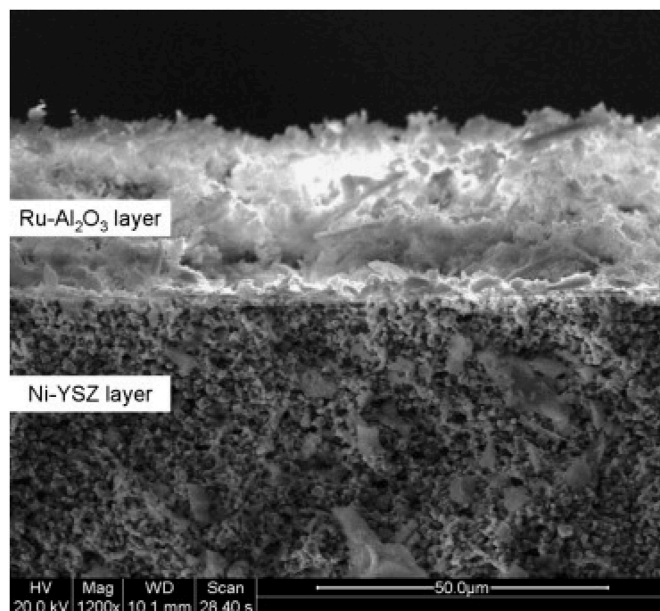

Fig. 6. The addition of an internal reforming Ru-Al$_2$O$_3$ catalyst layer: cross-sectional SEM images of the catalyst–anode interface after the cell stability test [223].

Ni-YSZanode when the SOFC was directly fuelled with CH$_4$. As a result, a power density of 650 mW/cm^2 was achieved at 800 °C. Moreover, stable performance was observed for 400 h. This study thus provides an insight into the development of direct hydrocarbon fulled-SOFCs.

A button cell with an internal catalytic reforming layer was tested in direct ethanol-fed SOFCs by Elharati et al. [42]. The catalytic functional layer consisted of 5 wt% Rh/Ce-ZrO$_2$, which was applied in front of the conventional Ni–YSZ anode. This catalyst layer effectively reformed the ethanol solution into an H$_2$-rich gas stream under harsh operating conditions without coking on the anode in the button cell. The transmission electron microscopes (TEM) and X-ray powder diffraction (XRD) measurements of spent catalysts showed no signs of coking after a 24-h ethanol steam reforming test. In addition, the electrochemical performance of the button-cell with the catalyst layer illustrated much improvement under direct-ethanol feeding conditions.

Direct utilization of CH$_4$ in conventional tubular SOFCs with Ni-YSZ anode support was reported by Yang et al. [212], using MoO$_2$ as a partial oxidation catalyst for CH$_4$ reforming at the fuel cell inlet. The addition of the MoO$_2$/alumina catalyst proved to be an efficient and practically promising method for direct hydrocarbon utilization. Dokamaingam et al. [224] numerically compared the performance of a conventional reformer and a catalyst-coated internal reformer in a SOFC system. The wall-coated internal reformer significantly reduced the local endothermic cooling effect at the entrance of the internal reformer and achieved a smoother CH$_4$ conversion in the SOFC.

The integration of a catalytic microchannel reactor loaded with highly efficient nanofibrous Ni-based composite within the SOFC anodes successfully demonstrated the efficient co-generation of electricity and syngas, as shown in Fig. 7 [225]. The exothermal fuel oxidation reactions and endothermal reforming reactions were thermally coupled on the modified anode. As a result, the peak power density and syngas yield was improved by 25% and more than two times, respectively. The operational stability has also been increased compared to the non-microchannelled-SOFC, implying a good material coupling effect. This innovative design promotes the practical application of methane fuelled-SOFCs.
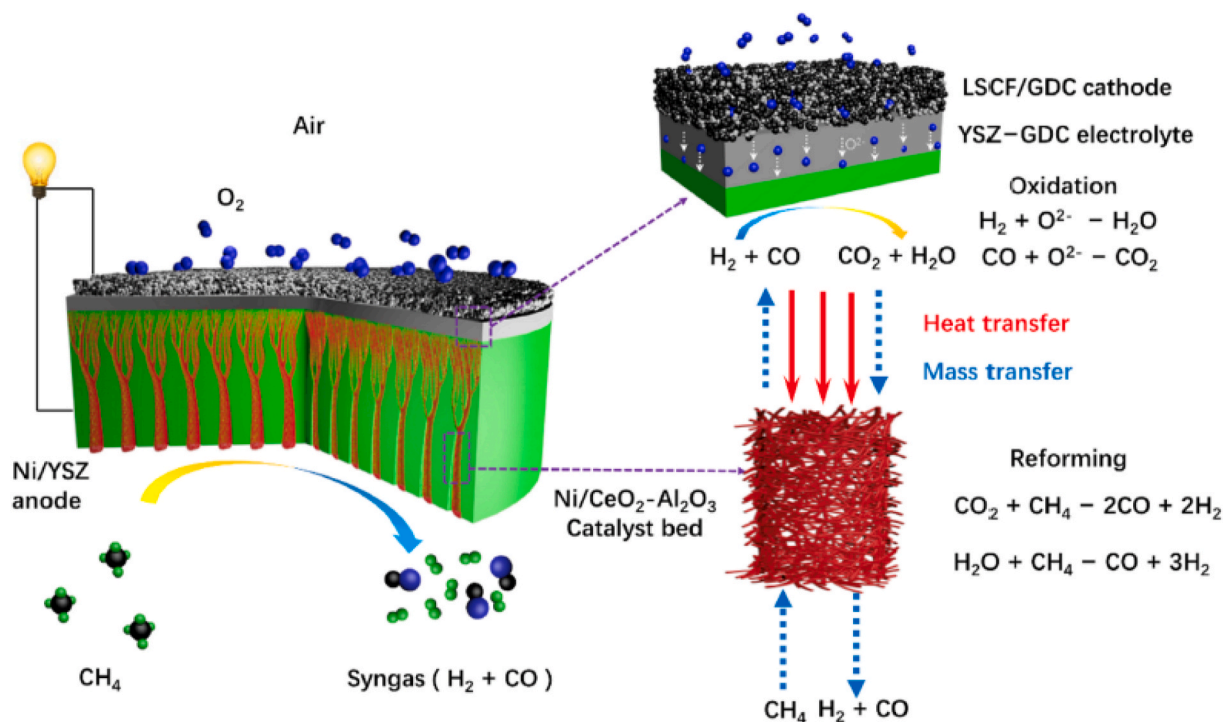
Fig. 7. Schematic presentation of SOFC reactors with materials and thermal coupling within anode supports [225].

3.3. Summary and alternative anode materials

The commonly used Ni-based anodes, such as Ni-YSZ, suffer from carbon deposition due to Ni being an excellent hydrocarbon reforming catalyst that catalyses carbon formation during SOFC operations. While this can be avoided to a large extent by having excess oxidant, such as water, in the system to promote the reforming reactions, however, this will increase the system complexity, such as water management issues. Additionally, the periodical regeneration and recovery of the anode materials in SOFCs would also bring extra requirements to the already complex systems. The ability to utilise the hydrocarbon fuel directly with less or no additional water or oxidant would greatly benefit by reducing the cost. Therefore, an excellent catalyst that can work at low steam to carbon ratios with a long-term stable performance would be ideal for these systems. This can be realised either as a part of direct utilization on the anode itself or as part of a robust pre-reforming catalyst supplying partially reformed fuel to the anode.

When YSZ is replaced by SDC, a promising performance can be expected. When replaced with Al_2O_3, the cost can be reduced while the catalyst shows a fast degradation due to its acidic nature. Ni-TiO_2 effectively depressed the carbon deposition, however, with a high cost of the materials. Therefore, investigations on affordable alternative supporting materials with excellent carbon suppressing performance is one of the critical development in this field. Alternatively, the carbon deposition resistance is significantly reduced when Ni is modified with the promotors, especially the noble metals. However, this is not the preferred method, although the addition of the noble metal is minimum compared with Ni.

Further, when Ni is replaced by Cu, carbon deposition can be alleviated. However, this method is affordable at the sacrifice of the overall performance as Cu is inert to hydrocarbon reformation. Additionally, this also requires the fabrication of Ni-Cu alloy. Finally, Sn is an excellent modifier in Ni-based anode materials as Sn does not form a bulk alloy with Ni and only forms a surface alloy that maintains the actual electrochemical performance while suppressing the carbon deposition significantly.

Another strategy to mitigate the carbon deposition is to modify the catalyst surface with dopants which can lower the population of acid sites on the anode surface. Adding Ce into the anode materials reduces the acid-to-basic site concentrations, leading to carbon deposition reduction. Ni-La doped ceria cermet anode has shown more significant tolerance to carbon deposition than Ni-Ce cermet anode. Likewise, adding alkali oxide promotors also reduce the coking propensity of Ni. Fabrication methods can flexibly modify the composition, and the interested readers can refer to Refs. [78,124,125,172,173]. Adding an internal catalyst layer can physically protect Ni from unstable conditions. The carbon-tolerant catalyst or a diffusion layer on the top surface of the anode, such as the LST barrier, the Ru-Al_2O_3 top layer, SDC thin layer, the MoO_2 at the inlet of the fuel cell and the Ni/CeO_2-Al_2O_3 catalyst bed, have been reported. Implementing the element for pre-reforming on the anode is significant in carbon deposition suppression. However, researchers in this field should still investigate and find a simple fabrication method with a cheap extra reforming layer.

Another strategy involves using perovskite-based mixed proton and oxide ion conductors. For example, a proton-conducting zirconate oxide (BaZr$_{0.8}$Y$_{0.2}$O$_3$, BZY) was applied as an electrolyte and anode material in a proton-conducting SOFCs (H-SOFCs) by Lei et al. [226]. BZY is stable in a CO_2/H_2O-containing atmosphere, and thermodynamic and experimental assessments of internal MSR in an H-SOFC were conducted in the study. As a result, the endothermic MSR process and the exothermic electrochemical process are synergistically integrated into the H-SOFC, increasing fuel flexibility and improving the overall energy efficiency.

The electrochemical performance and durability of H-SOFCs operated with internal CH_4 reforming were comprehensively evaluated. Coking is a severe issue when the CH_4 to H_2O ratio is 1:1 in the fuel, and a significant reduction of the open-circuit voltage was found at 650 °C and 700 °C. Lowering the operating temperature can efficiently suppress carbon formation. However, a reasonable amount of H_2 was produced from CH_4 reforming in the Ni-BZY anode at 550 °C without noticeable carbon deposition due to the good catalytic activity and high coking resistance of the Ni-BZY anode at that temperature.

A titanium-doped (La,Sr)FeO$_3$ ceramic oxide (LSFT) anode was fabricated by Cao et al. [126]. LSFT possesses the advantage of the high durability of titanate perovskite and super electrocatalytic activity of

ferrite-based perovskite. It is an excellent candidate for anode materials for SOFCs when fuelled with H_2S containing CH_4. They investigated the sulphur and coking tolerance of titanium-substituted ferrite perovskite anode. Acceptable activity toward CH_4 direct oxidation, excellent coking resistance and sulphur tolerance up to 750 ppm with good durability were revealed. LSFT holds excellent potential for direct application of hydrocarbon fuels in high-temperature SOFCs.

Another alternative anode material is $La_{0.6}Sr_{0.4}Co_{0.2}Mg_{0.8}O_3$ (LSCM). Conductivity and performance enhancements of LSCM anodes were reported by Kim et al. [124,173] with the addition of Pt, Rh, Pd and Ni. The amount of added metal (from 0.5 to 1 wt%) was too low to provide the electronic conductivity, demonstrating that the added metals function primarily as catalysts. Reasonably stability was observed on the anode containing Pt for at least 24 h when fuelled with CH_4. Carbon deposition occurred on the anode containing 0.5 wt% Pd or Ni, which was significantly improved by adding a 10 wt% ceria as the co-catalyst. The same research group [172,227] obtained identical results by replacing infiltrated LSCM with other electronically conductive oxides, such as LST or ceria. The electrode impedance of all three oxides shows a significant reduction by adding a transition-metal catalyst. The results have important implications for operating SOFCs on hydrocarbon fuels.

4. Perspectives

SOFCs based on O^{2-} conducting electrolytes offer much greater fuel flexibility than low-temperature fuel cells based on proton-conducting electrolytes. Because SOFCs operate at high temperatures, electrode polarization losses tend to be small. SOFCs may find widespread applications for conversion between chemical and electrical energy in the future due to their intrinsically high overall efficiencies. All techniques developed to produce hydrogen through methane reforming can be potentially applied to direct internal reforming SOFCs. The development of hetero-catalytic hydrocarbon reforming in SOFCs has focused a remarkable quantity of research efforts. Researchers across the globe try to understand various relevant factors, such as the reforming catalyst properties, reforming reaction mechanism, and issues encountered when directly fuelling SOFCs with hydrocarbon fuels.

Tolerance of coking and sulphur poisoning is essential for directly utilizing methane in SOFC systems, as was highlighted in this review. Thus the mitigation of carbon deposition through system operation strategies and modification of the anode catalysts were explicitly reviewed. The development of modifications of the existing catalysts, novel designs of the anode (micro-)structure and identification of new reforming catalysts has led to the growth of exploration of more effective catalysts with improved performances for hydrocarbon reforming. The development of new catalysts with low cost, chemical, electrochemical and mechanical stability, tolerance to impurities, and anti-coking with high catalytic activities is highly desired for reforming hydrocarbons from sustainable sources for green hydrogen carbon-neutral power production using SOFC systems. The development of sustainable and affordable methods for the regeneration of the deactivated anode materials is essential for the economic development of this technology needs to be studied more systematically. Furthermore, as sulphurous compounds co-exist with hydrocarbon fuels and the catalyst deactivation process associated with methane oxidation is more complicated than for the cases of H_2S-contaminated H_2 oxidation, coupling the improvement of carbon coking and sulphur poisoning resistance needs investigation as well.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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