Comprehensive Review of Methane Conversion in Solid Oxide Fuel Cells: *Prospects for Efficient Electricity Generation from Natural Gas*

Turgut M. Gür

Department of Materials Science and Engineering

496 Lomita Mall, Durand Bldg.

Stanford University, Stanford, CA 94305-4034

EM: Turgut.gur@stanford.edu

Work: 650-725-0107

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ABSTRACT

Natural gas is an important energy resource for electric power generation and other energy needs. Recent discoveries of vast reserves of shale gas greatly increased its abundance while lowering its cost. Combined with its significantly smaller carbon-footprint than coal, natural gas has increasingly become the preferred choice to generate electrical power even at the expense of converting existing coal fired power plants to run on natural gas. However, most natural gas combustion-based power plants currently operate at efficiencies in the low 30%. Conversion of natural gas in solid oxide fuel cells (SOFC) promises to increase system level conversion efficiencies to above 60%, doubling the current efficiencies and significantly reducing the CO₂ emissions by a factor of 2. Such dramatic improvements in conversion efficiency and ease of CO₂ capture are currently out of reach for the combustion-based power generation technologies. Equally importantly, the CO₂ produced from methane conversion leaves the fuel cell in a highly concentrated form. As nitrogen is blocked off by the impervious ceramic electrolyte of the SOFC from entering the process stream, methane oxidation produces a flue stream that is primarily made of the oxidation products CO₂ and steam. The latter can easily be condensed out to capture CO₂, thus eliminating the need for expensive and energy intensive post separation operations otherwise required to separate CO₂ from N₂ for storage purposes. So if successfully developed and deployed widely, natural gas conversion in SOFCs will greatly reduce CO₂ emissions, help mitigate climate change, and minimize the environmental impact of power generation.

This article organizes and critically reviews the current state of understanding in methane catalysis and oxidation with particular emphasis for electrochemical conversion in SOFCs. It presents a comprehensive review of a vast volume of published work (>600 references) extending from fundamental studies in C-H bond activation and methane catalysis, to basic concepts of electrochemical conversion in fuel cells, to strategies for effective utilization of methane in SOFCs, and associated technical difficulties such as deactivation due to sulfur and carbon yet to be overcome for realizing natural gas conversion, to impactful opportunities provided by recent theoretical advances in computational catalysis and materials screening studies, and innovative concepts such as strain effects and nanostructuring towards enhancing catalytic rates. It provides tutorial-type information at the appropriate level for the uninitiated but interested reader as well as critical discussions of fundamental phenomena and assessment of recent advances for active researchers in the field. The article is weighted around materials and surface properties and provides an in-depth review with emphasis on electronic structure, charge transport and catalysis. It presents an impartial evaluation of the opportunities as well as the challenges to natural gas utilization in SOFCs. Finally, it concludes that natural gas conversion in SOFCs promises very attractive opportunities for efficient and environmentally friendly power generation, while recognizing and offering in-depth discussions of the challenges facing this technology before it can be considered for large-scale power generation applications.

Keywords: Methane oxidation catalysis, solid oxide fuel cell, electrocatalysis of methane, reforming, electricity generation, natural gas conversion

1. Background

Natural gas makes up a significant segment of the global energy portfolio and is rapidly becoming the preferred fuel for thermoelectric power generation partly because of its relatively lower carbon intensity compared to other fossil fuels such as coal and oil. In the U.S., natural gas makes up more than 27% of our energy consumption (see Figure 1). As the least carbon-intensive fossil fuel with abundant reserves, especially after the

Figure 1. U.S. energy consumption in 2012 by energy source (from ref. [2])

recent finds of shale gas reservoirs in the U.S. and around the world, natural gas may serve as the “bridge fuel” during the next several decades to transition into a low-carbon energy economy. Indeed, its share in global electric power generation is expected to increase from 22% in 2010 to 24% in 2040 [1]. It is also expected that the installed capacity for natural gas-based power generation will increase more than 50% during this period.

By all accounts, fossil fuels are expected to dominate both energy consumption and electricity production at the global scale. Table 1 compares the global installed and actual production statistics for electric power generation [3]. Electricity generation relies heavily on fossil fuels, which provide more than 2/3rd of the global electricity that was generated

and consumed in 2012, while the renewable energies such as wind and solar provide only a small fraction. Also note the expected discrepancy between the installed capacity and actual production for wind and solar due to the intermittency of these sources, while electricity production from fossil fuel and nuclear plants are significantly higher than installed capacity share, demonstrating their availability and reliability.

A complementary cut with growth projections by the U.S. Energy Information Administration is presented in Table 2, which summarizes the 2008 global installed capacities for six prominent power generation technologies and their expected capacities in 2035 [4]. It shows that the total electricity production is expected to increase 1.7% annually from 4623 GW in 2008 to 7272 GW in 2035. The table also highlights the large investments expected for non-OECD countries in all forms of power generation

Table.1. Comparison of global installed capacity with actually realized electric power generation in 2012 [3].

	Installed Capacity		Electricity Generation	
	Capacity (GW)	% of World	Generation (billion kWh)	% of World
World Total	5,550	100	21,532	100
Total Fossil Fuels	3,606	65	14,498	67.3
Nuclear	373	6.7	2,345	10.9
Total Renewables	1,438	25.9	4,715	21.9
Hydro	(979)	(17.6)	(3,646)	(16.9)
Wind	(268)	(4.8)	(520)	(2.4)
Solar/tide/wave	(93.6)	(1.7)	(96.3)	(0.4)

technologies to meet the demand for electricity to catch up rapidly with OECD (i.e., Organization for Economic Cooperation and Development - OECD) countries. Table 2 also clearly indicates that fossil-based power generation will likely dominate global electricity production for decades to come, where wind and

solar electricity, albeit their rapid growth rate, are expected to provide only about 9% of the total installed capacity collectively by 2035 with much of that growth happening in wind power generation.

Table 2. World installed electricity production capacity for six prominent power generation technologies for 2008 and their projected capacities for 2035 [4].

Blocks	Coal (GW)		Natural Gas (GW)		Nuclear (GW)	
	2008	2035	2008	2035	2008	2035
OECD	641	633	690	959	313	379
Non-OECD	862	1496	499	866	65	265
TOTALs	1503	2129	1189	1825	378	644

Blocks	Hydro (GW)		Wind (GW)		Solar (GW)	
	2008	2035	2008	2035	2008	2035
OECD	355	432	97	330	14	83
Non-OECD	502	1031	24	203	0	36
TOTALs	857	1463	121	533	14	119

Natural gas-based power generation clearly offers greater benefits in terms of less environmental damage, smaller carbon footprint and lower emissions to the atmosphere when compared to coal-based power generation. The 2013 International Energy

Outlook report concludes that natural gas will be the fastest growing fossil fuel resource, and predicts that the global consumption will increase 64% from 113 trillion cubic feet (tcf) in 2010 to 185 tcf in 2040 [1]. Much of this increase in both production and demand comes from rapidly developing non-OECD countries, which will account for more than 72% of this increase and attain a 59% share in global consumption of natural gas in 2040, from 51% in 2010 [1].

As the world's largest consumer and producer of natural gas, the U.S. consumption is projected to increase by 5.8 tcf in 2040 and is predicted to produce nearly 34 tcf of natural gas in 2040, up from 21.5 tcf in 2010. Much of this production increase is due to the recent discoveries of vast shale gas reserves in the U.S. as well as in other places around the planet. A 2013 Energy Information Administration (EIA) report assessed 137 shale formations in 41 countries and estimated the global recoverable shale gas resources to be 7,299 tcf [6]. Although concerns about the long term environmental impact of hydraulic fracturing (i.e., fracking) are still debated, abundant shale gas resources of natural gas can help meet the energy needs of the growing economies of the world in a cost effective manner. The Henry Hub natural gas spot price, which averaged \$3.73/MMBtu in 2013 and \$4.46/MMBtu in 2014, is expected to average \$3.87/MMBtu in 2015 [7]. The slightly higher natural gas prices in 2014 reduced natural gas consumption in the U.S. thermoelectric power sector by 2% to 21.9 Bcf per day, but this number is expected to increase to 22.Bcf per day in 2015 due to more favorable prices for natural gas.

Figure 2. U.S. electricity generation by fuel source in trillion kWh for 1990-2040 (from ref. [5]).

Currently, natural gas accounts for nearly 26% of the primary energy consumed in the U.S. and was responsible for 27% of the U.S. electricity generation in 2013. More importantly, the abundance, low cost, and low carbon intensity of natural gas has fueled a renewed interest and growing increase in its share in thermoelectric power production in the U.S. and globally as well (see Figure 2). Much of this is the result of retiring or in some cases, converting coal fired power generation capacity and building up natural gas power generation instead. Between 2005 and 2012, while 496 billion kWh of coal fired power generation capacity was retired in the U.S., this was replaced by an increase of 470 billion kWh in natural gas based power generation capacity [8]. This is despite the fact that on unit energy basis, coal remains to be considerably cheaper than natural gas. The average price of coal for thermoelectric power generation was \$2.39/MMBtu in 2011, \$2.35/MMBtu in 2013, and \$2.36/MMBtu in 2014, which is expected to continue unchanged in 2015 [7]. In a way, the increasing rate at which coal fired plants are being converted to natural gas is a testament of the environmental concerns and downhill costs that outweigh price considerations in favor of natural gas power generation.

The most widely employed natural gas-based electric generation process consists of a steam generation unit, where natural gas is combusted in air inside a boiler that produces steam that turns a turbine to generate electricity. However, conversion efficiencies using steam generators are rather low. US. Energy Information Administration (EIA) statistics based on actual testing of heat rates in operating power plants in the U.S. averaged around 10,350-10,400 Btu/kWh during the 2007 and 2012 period [9]. This corresponds to a conversion efficiency of only 32.85%. Similarly, conversion efficiencies derived from tested heat rates of major power generation technologies are summarized in Table 3 for comparison. The numbers clearly indicate inherent inefficiencies in these conversion technologies. It should be noted that the corresponding efficiency values estimated by the World Energy Council are significantly higher than the actually measured efficiency values published by U.S. EIA, and places the global average efficiency for natural gas-fired power generation at 40.6%, while the U.S. average is shown even higher at 47.9 % in 2013 [10]. The reason for such large discrepancies in the efficiency values reported by the two reputable organizations is not clear. As the nature of how the latter data is collected, processed and evaluated by the World Energy Council is unknown, actual measured efficiency data published by the U.S. EIA and presented in Table 3 is accepted to be the more reliable source for this article.

Natural gas-fired combustion turbines are also employed for power generation, especially for meeting peak demands, although their average capacity factors, i.e., their availability, are quite low (~10 - 27%) and they contribute only a small percentage to total generation (3% of the total electricity generated in 2012 [11]). Combined-cycle gas turbines provide higher efficiencies reportedly up to 55%, but the average actually achieved in 2012 was only 44.8% (see Table 3).

Natural gas combustion releases nearly 1/2 the amount of CO₂ than coal power generation. This provides a significant incentive and advantage for natural gas-based electricity generation. Indeed, a recent article assessing the climate benefits of natural gas- versus coal-based power generation reported that over the long run gas-fired plants present significantly greater benefits for mitigating climate change than coal-fired plants [12]. Likewise, recent harmonization [13] studies by the U.S. DOE-National Renewable Energy Laboratory (NREL) on life cycle analyses of green house gas (GHG) emissions

of different power generation technologies [14] estimated median values of 470 g (CO₂)_{eq}/kWh for the combined average of all different natural gas conversion technologies [13] versus 1000 g (CO₂)_{eq}/kWh for the average of all coal power generation [15]. In either case, however, combustion of the fuel in air inevitably produces flue gases that contain diluted quantities of CO₂ (5-15%) in vast amounts of N₂ that necessitate expensive and energy intensive post-separation operations for CO₂ capture.

As stringent emission standards especially for CO₂ is expected eventually to go into effect around the world, there will be increased demand in developing advanced and efficient technologies for conversion of natural gas into electricity with total carbon capture. In this regard, electrochemical conversion in solid oxide fuel cells (SOFC) offers great opportunities to meet efficiency and emission requirements. Most reserves are geographically separated by long distances from populated markets or high volume

Table 3. Comparison of average tested heat rates (and calculated efficiencies) by energy source for U.S. thermoelectric power production in 2012 [9]

	Coal		Natural Gas		Nuclear	
	Heat rate (Btu/kWh)	% Efficiency	Heat rate (Btu/kWh)	% Efficiency	Heat rate (Btu/kWh)	% Efficiency
Steam generator	10,107	33.76	10,385	32.85	10,479	32.56
Gas turbine	-	-	11,499	29.7	-	-
Combined cycle	-	-	7,615	44.8	-	-

industrial customers in Europe, Asia and other places that require transportation of natural gas to points of use, which can add \$3.00-5.00/MMBtu on top of the cost of production [16]. Leakage of CH₄ from natural gas production sources and other industrial or biological

activities may have significant impact on climate change, as CH₄ has 21 times the global warming potential (GWP) as CO₂ over a 100-year horizon [2]. In fact, a recent study estimated that the total amount of CH₄ leaking into the atmosphere from all accounted sources in North America is between 7 and 21x10¹² g/year [17]. On-site utilization and conversion of natural gas can mitigate or minimize many of these concerns. Indeed, SOFCs are ideally suited for distributed power generation at the point of production offering significant cost and environmental benefits.

2. Introduction

This article is motivated by renewed interest in natural gas for power generation, which in part is propelled by the recent discoveries of vast reserves of shale gas in the U.S. [18] and around world, as well as due to the inherently lower carbon footprint for natural gas compared to liquid and solid carbonaceous fuels such as oil and coal. The high H/C ratio of nearly 4 for natural gas, as opposed to that for oil (H/C ~ 2) or coal (H/C ~ 1), translates into much larger amounts of energy generated per unit quantity of CO₂ released into the environment upon combustion. Natural gas is a critically important primary energy source, fuel and chemical feedstock for a wide range of industrial and societal needs, and especially for electricity generation. Nearly 75% of the hydrogen produced globally is derived from steam reforming of natural gas in large-scale centralized plants. After proper adjustment of the CO/H₂ ratio, the reformation product

syngas can subsequently be utilized to make higher hydrocarbons via Fischer-Tropsch synthesis [19,20]. Natural gas is also employed as the starting fuel for many of the fuel cell systems after it is reformed to syngas or water-gas shifted primarily to H_2 , which is then used as the fuel for various types of fuel cells.

Due to its low cost, natural abundance, and low emissions natural gas is also a critical and desirable fuel for electricity production. However, most conventional power generation technologies including those that are based on natural gas are not efficient as indicated in Table 3, which presents actual measured performance data from power plants. While the three conventional technologies, namely, coal and natural gas combustion, and nuclear, have efficiencies in the low 30%, only combined cycle technology offers moderate efficiencies around 45%. Clearly, there is a great need to develop advanced technologies that provide significantly higher efficiencies for natural gas-to-electricity conversion. Compared to the thermoelectric power generation technologies employed today, solid oxide fuel cells (SOFC) offer the highest conversion efficiency along with other environmental benefits, and can play a critical role in our energy R&D strategy [21]. Due to its relatively high operating temperatures, SOFCs also offer exceptional fuel flexibility [22] unsurpassed by any other fuel cell systems for direct utilization of a wide range of fuels, and even switching sequentially from one hydrocarbon fuel to the next in real time with great ease [23]. Examples of such flexibility include gaseous hydrocarbons such as alkanes [24-27], and dimethyl ether [28], liquid fuels such as octane [29] toluene, diesel and n-decane [30], vegetable oil [31], jet fuel and crude oil [32], and solid fuels such as activated carbon [33,34], biomass [35], and untreated coal [36].

Likewise, SOFCs are ideally suited for methane conversion not only into electricity but also to syngas or higher hydrocarbons. There are various ways these outcomes can be accomplished. For combustion and coupling reactions of methane, ceramic membrane reactors can be employed and these may be either mixed ionically electronically conducting (MIEC) [37-41] or primarily ionically conducting membranes [42,43]. Conversion in MIEC membranes is primarily a chemical process driven by the chemical potential difference of oxygen across the membrane, where the electrons as well as either oxide ions or protons may diffuse across the membrane to accomplish the desired chemical reaction of oxygenation or dehydrogenation. Another approach to produce electricity and chemicals consists of employing an electrochemical reactor that utilizes a proton conducting solid electrolyte in a SOFC configuration, where the methane transformation reactions are dominated by proton extraction [44-47]. Both of these schemes, namely, MIEC ceramic membrane reactors and electrochemical reactors based on protonically conducting solid oxide electrolyte membranes, fall outside the scope of this review article and will not be covered here. Likewise, natural gas combustion processes including chemical looping combustion [48-50], oxy-combustion [51,52], and propulsion [53] will not be covered here as they fall outside the scope of this article. However, relevant aspects of catalytic combustion will be discussed briefly below, but only in the context of chemical kinetics of methane oxidation over precious metal and oxide catalysts. This article will primarily focus on SOFC approaches that employ oxide ion conducting solid electrolytes for electrochemical utilization of methane to generate of electricity generation only. The potential benefits as well as challenges to electrochemical conversion SOFCs as opposed to chemical combustion processes will be highlighted in the proceeding sections, and recent advances and progress will be discussed in detail.

Understanding the mechanistic details and technical challenges of methane conversion in SOFCs is the logical first step towards realizing natural gas utilization in SOFCs for electricity generation. Methane chemistry is rich as it can undergo many reactions [54,55]. Several of the industrially important net reactions pertinent to this article and the associated enthalpy changes are listed below.

Full oxidation (or, complete combustion)

Partial oxidation

Steam reforming

Dry reforming

Water-gas shift

Boudouard reaction

In the reaction environment at the SOFC anode, it is possible that several of these reactions may compete or proceed concurrently.

Methane conversion to electricity in SOFCs can be accomplished primarily in three different ways, namely, via external or internal reforming through reactions (3) and (4), or by direct electro-oxidation, i.e., reaction (1). External or internal reforming process produces a mixture of H_2 and CO , i.e., syngas that is subsequently oxidized at the SOFC anode. Direct oxidation, however, is a distinctly different reaction and more difficult to achieve electrochemically. It requires fundamental understanding and development of electrocatalytic anode materials that selectively promote direct electro-oxidation of methane in SOFCs. This article offers a critical review of methane utilization in SOFCs, and discusses the prospects, opportunities as well as technical challenges to efficient conversion of natural gas to electricity.

The first logical step towards utilization and conversion of natural gas in SOFCs requires mechanistic understanding of the electrocatalytic oxidation of methane, as it is the principal constituent of natural gas, which contains up to 90% CH_4 with CO_2 , N_2 and other impurity gases make up the remaining. Electrochemical conversion in SOFCs, however, presents its own set of technical challenges, many of which will be addressed in this article. One difficult challenge relates to the natural occurrence of sulfurous species in natural gas, usually in the form of H_2S , which cause rapid deactivation of the catalytic anode. Another one is presented by coking, or carbon deposition on catalytic surfaces, which blocks off access to surface active sites from the reacting species, causing deactivation of the catalytic activity of the anode and subsequent degradation of cell performance. In addition, there are also demanding requirements related to materials

stability issues at the high operating temperatures of SOFCs and under steep chemical potential gradients across cell components produced by the strongly oxidizing gas environment typically in the form of air at the cathode, while the anode is in direct contact with a highly reducing environment due to the presence of the fuel. Furthermore, cost and lifetime issues for economic competitiveness and practical applications pose additional challenges. Most of these issues are addressed and discussed in the proceeding sections.

This review article is organized to present the interested readers both tutorial level background material to introduce them into fuel cell-based electrochemical conversion systems and materials as well as the fundamental aspects of methane catalysis, electrocatalysis, reforming and conversion in SOFCs. It provides a critical review of the progress made in these areas, identify the knowledge gaps, and discuss strategic approaches and opportunities to bridge and overcome outstanding technical difficulties. It should be noted that the article is primarily focused on methane conversion for the purpose of electricity generation in SOFCs, and will not cover areas related to co-generation and synthesis of chemicals from methane or natural gas. Basic concepts of surface science and catalysis will be presented in this context along with an adequate review of SOFC materials focusing heavily on catalytic anodes. The latter part of this article will discuss major technical and scientific challenges and key hurdles yet to be overcome in order for natural gas conversion in SOFCs can be realized for wide scale practical applications. The article will also present important opportunities that are offered by new theoretical, experimental, and analytical tools for advancing the current state-of-the-art into better mechanistic understanding to methane catalysis, as well as catalyst design and discovery. Finally, prospects of natural gas conversion in SOFCs and the outlook of this exciting approach into the future will be discussed.

2.1. Environmental benefits of electrochemical conversion

Electrochemical conversion of natural gas to electricity in SOFCs offers inherently higher efficiencies than possible by conventional thermoelectric power generation technologies. It also produces a flue stream that is highly concentrated in CO₂ and hence, is easy to capture, as nitrogen is blocked from entering the process stream by the impervious dense solid electrolyte membrane of the fuel cell. So no post-separation operation to capture CO₂ will be necessary. Conversion in SOFCs also offers environmentally friendly and noiseless operation as well as portability and modularity suitable for both distributed or central production of electricity. In addition, SOFCs exhibit their highest efficiency at low loads in contrast to gas turbines, which normally exhibit high efficiency only at high loads. Moreover, the highly exothermic nature of methane oxidation reaction provides high quality waste heat from the SOFC that opens up opportunities for combined heat and power generation, which gives rise to improved efficiencies. In summary, electrocatalytic methane conversion in SOFCs offers the following benefits:

- *High conversion efficiencies exceeding 60%*
- *Correspondingly lower CO₂ emissions per unit of power generated*
- *Capture-ready CO₂ production, as no nitrogen enters the process stream*
- *Significantly lower NO_x production due to moderate SOFC temperatures*

- *Isothermal conversion simplifies plant design and lowers cost*
- *No need for water, if steam reforming is not involved (as in direct oxidation)*
- *Environmentally friendly conversion (no noise, no moving parts, small footprint)*
- *Modular process well suited for distributed generation*

It is important to note that low efficiencies of chemical combustion processes typically carried out using air as the oxygen source also pose major environmental problems in the form of heavily diluted CO₂ emissions (~5%, balance mostly N₂) that makes it difficult and expensive to capture CO₂, as well as produce of NO_x and SO_x, whose formation are favored by the high operating temperatures typically employed in combustion processes. It should be noted that both CH₄ and NO_x are extremely potent greenhouse gases, whose global warming potentials over 100 years are significantly greater than for CO₂ [56] as shown in Table 4.

Table 4. Global warming power (GWP) of common greenhouse gases [56].

Greenhouse gas	GWP
CO ₂	1
CH ₄	21
N ₂ O	310

By contrast, electrochemical conversion of methane in SOFCs offers the prospects of dramatically reducing total emissions into the atmosphere by significantly increasing the conversion efficiency and producing capture ready CO₂ that will help reduce the carbon footprint on the environment. Certainly, lowering the SOFC operating temperature for methane conversion will also be beneficial, and the strategies and advances

made to achieve this goal will also be discussed in this article.

2.2. Efficiency of direct electrochemical oxidation

Combustion processes involve the chemical reaction of the fuel with oxygen. The latter can be supplied to the fuel in various ways, but most commonly via the use of air. Driven primarily by the objective to achieve effective capture of the combustion product and green house gas CO₂, recent developments in combustion technologies explore metal

Figure 3. Calculated theoretical efficiencies for electrochemical oxidation of methane, hydrogen, and carbon monoxide.

oxides as the oxygen carrier in chemical looping [48-50], or oxygen in pure molecular form as in oxy-combustion [51]. Most often, however, air is employed for the oxygen source, which means nitrogen too is carried into the process stream as a passive diluent. This is undesirable for obvious reasons including loss of efficiency due to the latent heating and cooling losses of huge volumes of a practically inert gas, difficulty in separating it from the combustion product gas CO₂ for capture, and the tendency to produce NO_x. More specifically, N₂O formed during

combustion is a deleterious green house gas that is 310 times more potent than CO₂ in trapping infrared radiation from the earth's surface. Consequently, when air is used as the oxygen source, the presence of N₂ in the flue gas stream will require expensive and energy intensive post-separation processes in order to capture the CO₂. The exothermic enthalpy change during the combustion reaction is transferred to a suitable medium such as steam, which turns a turbine that is connected to a generator that produces electricity. The efficiency of this thermal conversion process is rather low as indicated in Table 3.

By contrast, electrochemical conversion of methane in SOFCs offers inherently higher conversion efficiencies. The theoretical efficiency, η , for electrochemical conversion is defined simply by $\eta = \Delta G^\circ / \Delta H^\circ$, where the Gibbs free energy change, ΔG° , represents the maximum possible work available for the conversion process while ΔH° denotes the enthalpy change for the same. For conversion processes where the reaction entropy losses are small, examples including direct oxidation reactions of carbon or methane, exceptionally high theoretical efficiencies are possible. Another advantage of electrochemical conversion is that it occurs isothermally, simplifying process flow and minimizing energy losses otherwise associated with chemical processes, which usually require multiple heating and cooling cycles.

The net cell reaction (1) is thermodynamically downhill with a Gibbs free energy change, $\Delta G^\circ_{298K} = -799$ kJ/mol of CH₄, which represents the maximum work potential for this reaction. Due to the negligibly small entropy change ($\Delta S^\circ_{298K} = -1.3$ J/K.mol of O₂) during the methane oxidation reaction, the free energy change is also identical to the highly exothermic methane combustion reaction with the enthalpy change, $\Delta H^\circ_{298K} = -801$ kJ/mol of CH₄. Consequently, this provides an exceptionally high ceiling of 100% for the theoretical conversion efficiency of electrochemical oxidation of methane, which also is significantly higher than for the typical and preferred SOFC fuel H₂, as shown in Figure 3.

By comparison, thermal conversion of methane for electricity generation using steam or combustion turbines in the conventional way involves many process steps and also offers quite low efficiencies around 30% (see Table 3). It is clear SOFCs can accomplish electricity generation in a single process step with nearly twice the conversion efficiency of conventional thermoelectric power technologies. In fact, product sheets from the commercial SOFC developer and manufacturer Bloom Energy of California, U.S., indicate 52-60% system level conversion efficiencies – based on lower heating value (LHV) - for their 200 kW and 250 kW commercial SOFC units running on reformed natural gas [57].

3. Catalysis of Methane Oxidation

As expected from the sp³ hybridization of the C-H bond, methane is a tetrahedrally coordinated molecule with 3-dimensional symmetry. It has a high ionization potential (12.5 eV) and low electron affinity (4.4. eV). Compared to higher alkanes, the C-H bonds in methane are exceptionally stable with bond energy of 435 kJ/mol. Hence, the high C-H bond strength and the directionality of the sp³ orbital make it difficult for methane to form bonds with other species or with catalytic surfaces. This provides a barrier to activate the C-H bond and for methane to react under mild conditions. For this

reason, high temperatures and effective catalysts are required to activate and transform methane into useful chemicals, products, or electricity.

The oxidation of methane, especially partial oxidation towards producing higher value added fuels and chemicals, has been studied extensively for nearly a century. There is rich literature on the wide range of catalytic reactions that methane can undergo, including interactions and oxidation kinetics on metal [58-61] and oxide surfaces [62,63], combustion [61,64-67], partial oxidation [59,62,68-73], as well as oxidative coupling [74-78], and conversion to useful chemicals [79-84]. Usually, non-selective oxidation takes place when methane and molecular oxygen are co-fed onto the reactor. The design and control of the properties of the catalyst as well as the optimization of the reaction conditions are important consideration to achieve selectivity.

3.1. Catalytic oxidation of methane on metal catalysts

Although methane is the simplest hydrocarbon and its catalytic oxidation kinetics has been studied widely, consensus on the mechanistic pathways of this reaction is still lacking. Even on metal catalyst surfaces, elementary steps of the reaction mechanism are not fully resolved. Many of the catalytic reactions of methane are further complicated by side reactions (3)-(6) and their products CO₂ and H₂O that participate in further reactions with methane.

Kinetic studies [85,86] of methane oxidation on Pt catalyst supported on Al₂O₃ was best described by the Langmuir-Hinshelwood (L-H) mechanism, where the rate limiting step is usually the reaction between the adsorbed atomic oxygen and adsorbed methane according to the following simplified scheme.

Here * denotes the active site on the catalyst surface, and the subscripts in parentheses indicate gaseous and adsorbed states. It is highly unlikely that the pyrolysis reaction proceeds in single step, i.e.,

but may involve several elementary steps. The results of a Monte-Carlo study of methane oxidation on oxidized Pd catalyst were consistent with the L-H type mechanism, but it was proposed that the reaction (9) of the adsorbed species occur not on a single active site, but on two sites [63]. Theoretical simulations combined with experimental verification of the methane oxidation reaction mechanism on Pt and Rh assuming a L-H type desorption model [87] provide a detailed list of possible elementary reaction steps with associated rates constants and activated energies and indicate that the pyrolytic pathway for methane oxidation has a higher activation energy than the oxygen-mediated pathway that involves an oxygenated surface. Under high surface coverage of the catalyst

surface with oxygen at moderate temperatures and oxygen-rich reaction environments, the oxygen-mediated pathway for methane oxidation may dominate overall kinetics over the pyrolytic pathway. A similar study of methane oxidation on Cu- and Ag-modified CeO₂ support reported strong dependence of catalytic activity on the crystallite size of ceria and found the reaction involves L-H type of mechanism [88].

Using solid electrolyte potentiometry for monitoring oxygen activity at the Ag catalyst/solid electrolyte interface during the reaction, the kinetics of methane oxidation on Ag anodes was represented by the Eley-Rideal mechanism [89], where the mobile adsorbed atomic oxygen is the active surface species that reacts with methane in the gas phase. Similar experiments on Ag anodes supported this view and indicated that surface oxygen on the catalytic anode is more effective than oxygen supplied from the gas phase for methane oxidation [90]. The strongly bound surface oxygen site (i.e., Lewis base) is proposed to catalyze the dehydrogenation reaction for the oxidative coupling of methane to C₂ hydrocarbons [91].

On the other hand, a systematic study [92] that considered L-H, Eley-Rideal (E-R) and Mars-van Krevelen (MVK) mechanisms reported that the surface kinetics of methane oxidation over Pd/Al₂O₃ catalysts agree well with the MVK model [93]. This is in agreement with other reports that oxidation proceeds by direct interaction of the adsorbed species with the lattice oxygen in accordance with the MVK mechanism [63], although several inconsistencies have recently been pointed out in applying the MVK model rate expression to oxidation. It was suggested that the reaction steps describing the MVK model are not elementary in nature, and an alternative kinetic model such as L-H can provide similar rate expressions that may fit the data better [94]. Indeed, the product selectivity of methane oxidation seems to depend largely upon the availability of oxide ions on the catalyst surface. Using *in situ* microprobe Raman and time resolved FTIR spectroscopies, others [95] observed that CH₄ oxidation products over Rh/SiO₂ and Ru/SiO₂ catalysts yield CO₂ when the surface concentration of O²⁻ is high, and CO when it is low, although the reaction mechanisms on the two catalysts were found to be different. Similar findings were reported by an isotopic study of methane partial oxidation to syngas reported that CH₄-O₂ and CD₄-O₂ reactions on Rh/ γ -Al₂O₃ catalysts yield CO₂ as the only reaction product at 450°C, indicating complete oxidation is predominant under these conditions [96]. More recent studies on oxygen dosed Pt and Pd surfaces suggested that PdO surface is catalytically more active for CH₄ and CO oxidation than metallic Pt and Pd surfaces saturated with chemisorbed oxygen under near stoichiometric conditions, which severely suppresses methane activation, whereas Pt and Pd surfaces under low-oxygen activity are found to be quite active [97]. Oxygen isotope studies of methane oxidation on metal oxide-supported Pd-based catalysts were found to be consistent with the Pd/PdO redox combustion mechanism, where oxygen adsorbed on the Pd/PdO migrates to the support and participates in the catalytic oxidation of methane [61]. It was observed that the oxygen exchange rate between the support and the catalyst is dependent on temperature as well as on the nature of the support material. For example, oxidation rates over ZrO₂-supported PdO catalyst showed marked increase above 450°C, while MgO- and Al₂O₃-supported PdO catalysts exhibited no improvement over pure PdO catalysts within the same temperature regime [61]. This is consistent with the higher oxide ion mobility in zirconia than in alumina, and the kinetic results were in good agreement with the MVK type redox reaction.

DFT calculations for Pd, PdO and CeO₂-supported Pd catalysts provided insights into the mechanistic pathways and indicated that C-H bond activation remains to be the rate-determining step for the overall reaction with barrier heights ranging from 0.18 eV over Pd_xCe_{1-x}O₂(111), to 0.89 eV for Pd(111), to 1.08 eV for PdO(100) [98]. Over CeO₂ and Pd_xCe_{1-x}O₂, C-H bond activation proceeds via sequential abstraction of H from the adsorbed CH₄ by the surface (lattice) oxygen to form CH_x (x=1-3) adsorbates with the formation of intermediates including HCO, CO and eventually CO₂, when desorbed leaves behind an oxide ion vacancy. DFT studies of methane oxidation on Pt also reported similar reaction pathways that involve surface oxygen [60,71].

3.1.1. Catalyst-support interactions

Interactions between the metal catalyst and the oxide support material during methane catalysis are important as they can affect both the reaction pathways and the product distribution [95,99,100]. Strong metal-support interactions have been widely recognized [101]. For example, the sintering resistance of nanosize precious metal catalysts

Figure 4. Oxygen spillover effects in the extended (bulk) and nanostructured Pt/CeO₂ system, illustrating the significant reduction in the vacancy formation energy for oxygen, E_{vac} , from 2.25 eV for the case of the extended CeO₂(111) surface to 0.80 eV for the Ce₄₀O₈₀ nanocluster. This makes reverse spillover of oxygen from the Ce₄₀O₈₀ nanocluster to the Pt₈ aggregate energetically more favorable, leading to the formation of two Ce⁺³ active centers in the nanocluster. “Reprinted with permission from ref. [109] Vayssilov GN, Lykhach Y, Migani A, Staudt T, Petrova GP, Tsud N, Skala T, Bruix A, Illas F, Prince KC, Matolin V, Neyman KM, Libuda J, Nature Mater. 2011; 10: 310-315. Copyright (2011) The Nature Publishing Co.”

supported on TiO₂ [102], CeO₂ [103,104], Al₂O₃ and SiO₂ [105] have been demonstrated and their enhanced catalytic activity was explained by oxygen adatom transfer from the support to the catalytic particle surface. It is also known that the catalyst particle size at the nanoscale plays an important role not only on catalytic activity, but also on selectivity [106,107].

In the case of ceria supported metal catalysts, it is suggested that the improved sintering resistance of the catalyst particles may be due to the oxygenated metal surface, which improves bonding of the catalyst particle to the reduced ceria surface [108] and retards volatilization of the catalyst [105]. Calorimetric measurements the heat

of adsorption also indicated that Ag nanoparticles < 4 nm in diameter bind more strongly to reduced $\text{CeO}_{2-x}(111)$ surface than to a non-reducible surface such as MgO (100) [108]. Size effect of the support material is also important. Combining resonance photoemission spectroscopy (RPES) with theoretical predictions using Vienna ab initio program (VASP), a recent study on the Pt_8 clusters supported on bulk $\text{CeO}_2(111)$ and $\text{Ce}_{40}\text{O}_{80}$ nanoclusters has shown that the formation of oxygen vacancies is heavily favored by nanostructuring, where energy of oxygen vacancies is reduced significantly from 2.2.5 eV for the bulk $\text{CeO}_2(111)$ surface to 0.80 eV for $\text{Ce}_{40}\text{O}_{80}$ [109]. This is shown in Figure 4.

Catalyst particle size and electronic effects [110] play interactive roles in oxide ion exchange and mobility, and dramatically affect catalytic activity and selectivity. While the metal catalyst may transfer electrons to the support material, the latter may in turn transfer oxygen to the metal catalyst surface. The surface transfer of oxygen and hydrogen between the catalyst and support, or with another catalyst, is commonly observed in catalysis and is called spillover [111]. Surface spectroscopy backed by theoretical calculations provided evidence for two types of interactions involving Pt nanoparticles supported on CeO_2 , namely, electron transfer from Pt to ceria, and oxygen transfer from ceria to Pt [109]. This study also reported that spillover of oxygen to Pt is accompanied by increase in the concentration of Ce^{+3} in ceria, and is a nanoscale effect, which requires nanostructured Pt particles in intimate contact with ceria. Size dependence on catalytic activity and selectivity has been well recognized [106]. Such dependence is reported for water-gas shift reaction (5) on 2-4 nm size Cu catalysts supported on $\text{CeO}_2(111)$ and $\text{ZnO}(0001)$ [112] as well as for dry reforming reaction (4) of methane on Rh catalyst supported on various oxides, which showed high catalytic activity for Rh up to 6 nm with decreasing activity for larger sizes [113]. It also showed strong correlation of catalytic activity with the acidic character of the support material surface, where Rh activity for dry reformation decreased in the order of the supporting materials: yttria-stabilized zirconia (YSZ) > Al_2O_3 > TiO_2 > SiO_2 > La_2O_3 > MgO. This activity ranking correlates qualitatively with oxide ion mobility in these oxides, which is highest for YSZ and lowest for MgO.

Oxygen exchange between the metal and the support material is extensively studied for ceria-supported Pd, which is known as one of the most effective catalyst systems for methane oxidation. The catalytically active phase for this reaction is PdO [114], which is stable up to 650°C but reduces to Pd at higher temperatures. Reducible oxides such as CeO_2 can stabilize the PdO phase. During the reaction, PdO is reduced to metallic Pd by transfer of oxygen to the ceria support, which in turn provides the oxygen back to Pd for methane oxidation [61]. The latter process is usually called reverse- or back-spillover.

In addition to ion exchange or spillover, metal-support interactions also involve donation or back-donation of electrons between the catalyst metal and the surface adsorbate. Such electronic effects play an equally important role in catalysis, as electron transfer alters the strength of the chemisorptive bond of the surface species. In general, adsorbates that donate electrons to the metal catalyst lower the catalyst work function, while those that accept electrons from the metal catalyst increase its work function. Induced by a suitable current or potential applied externally, the migration (i.e., spillover) of the ionic species such as $\text{O}^{\delta-}$ from the solid oxide electrolyte (i.e., support) to the metal catalyst surface is accompanied by its compensating charge in the oxide. This leads to the formation of surface dipoles, which eventually form the electrochemical double layer

Figure 5. Schematic of the interactions between the metal catalyst with the ionically conducting supports a) $\beta''\text{-Al}_2\text{O}_3$, and b) YSZ, illustrating the double layer built by the spillover of ions supplied via the support, for case of CO oxidation. “Reprinted with permission from ref. [124] Vayenas CG, Catal. Lett. 2013; 143: 1085-1097. Copyright (2013) Springer”

hence, altering catalytic activity and selectivity for many hydrocarbon oxidation and oxidative coupling reactions [75,116-119]. Even though there is molecular O_2 in the reaction gas phase, spillover of oxide ions on to the catalyst metal surface driven by a small amount of externally applied current or voltage gives rise to a dramatic enhancement in the oxidation rate of the reactant fuel above and beyond the Faradaic current through the cell. This effect is coined NEMCA, for non-faradaic electrochemical modification of catalytic activity [120-124], where electronegative promoters such as O^{2-} increase the work function of the metal catalyst while electropositive promoters such as Na^+ lower the work function. This behavior is depicted in Figure 6, which also indicates the work functions for the 1st, 2nd, and 3rd row transition metal catalysts [125]. The NEMCA effect has successfully been demonstrated for a long list of catalytic reactions [125] involving many hydrocarbons, CO , H_2 , and NH_3 , where reaction rates were reportedly enhanced by as much as 10^4 beyond the Faradaic limit [116,126-128]. *In situ* measurements of the change in the catalyst work function by Kelvin probe upon electrochemical supply (or removal) of oxide ions made it clear that the catalytic activity is intimately related to the electronic structure of the metal catalyst [115,116,129,130].

on the catalyst surface exposed to the reactant gases composed generally of an oxidizing reactant or fuel such as a hydrocarbon, CO , NO , NH_3 , and an oxidant such as O_2 . As expected, the double layer also contains adsorbed reaction intermediates.

The double layer formation over metal catalysts supported on O^{2-} and Na^+ conducting oxides are illustrated in Figure 5 (a) and (b), respectively. The density of the double layer, which may be as small as 5% of a monolayer [115], is dependent on the applied potential or current that drives the ions on to the metal catalyst surface. This in turn alters the work potential of the metal catalysts and consequently the binding energy or strength of the reactants and intermediates,

The observed spillover effect of $O^{\delta-}$ on catalytic rates is not restricted to O^{2-} -ion conducting support materials only, but was observed also for many important hydrocarbon-involving reactions studied on catalysts supported on H^+ - and Na^+ -ion conducting ceramic supports such as Y-doped $BaZrO_3$ (BYZ) and sodium β'' -alumina, respectively, and even on proton conducting polymeric supports such as Nafion [116,125,131]. It is suggested that the spillover-backspillover of species taking part in the promotion effect of NEMCA at the triple phase boundaries (*tpb*) between the metal catalyst, the electrolyte, and the reacting gas phase serve merely as promoters and not directly participate at the reaction as reactants [124]. In other words, in NEMCA dominated catalysis the observed reaction rates dramatically exceed the Faradaic rates,

Figure 6. Variation of work function, Φ , with respect to the 1st f (circles), 2nd (triangles), and 3rd (diamonds) row transition metal catalysts, and with the addition of electropositive and electronegative promoters such as K^+ , Na^+ , and O^{2-} , Cl^- , respectively. “Reprinted with permission from ref. [125] Vayenas CG, Brosda S, Top. Catal. 2014; 57: 1287-1301. Copyright (2014) Springer”

sometimes by several orders of magnitude, and cannot be accounted for by the ionic current through the solid electrolyte.

Although such dramatic enhancements has been the case for many catalytic oxidation reactions, a recent thermodynamic study indicated that this is usually not the case for hydrogenation reactions, which show a weak NEMCA effect that often approaches the Faradaic efficiency limit [132].

In fact, Faradaic behavior dominates the kinetics of synthesis reactions that involve reduction or the removal of oxygen from

electrode surfaces in contact with the reacting gas phase through the solid electrolyte. A recent study of steam electrolysis in an SOFC arrangement indicates that the rate of H_2 production is proportional to the current through the cell [133]. Obviously, this process requires an externally applied potential imposed on the cell to drive the uphill transport. Uphill reactions that have been enhanced by this approach include NO reduction [134], CO_2 methanation [135,136] and CO hydrogenation (i.e., Fischer-Tropsch synthesis) [135,137]. In these cases, however, the rate enhancements were Faradaic in nature and all correlated well with the ionic flux through the electrolyte, which in turn is directly related to the measured current across the cell.

3.2. Catalytic oxidation of methane on oxides

There is extensive literature on methane oxidation on various oxide catalysts, some of which have been reviewed previously [138-142]. A selective oxide catalyst must perform multiple functions including activation of the adsorbed methane, hydrogen abstraction,

oxygen insertion and regeneration of the catalytic site for the next turnover. Hence, the nature of the catalytically active surface site is important. Oxidation catalysis involves the introduction of gaseous molecular oxygen along with the hydrocarbon reactant, such as methane, into the reactor. It is possible that the surface oxygen can also participate in the reactions. Therefore, it is important to understand the relative roles of adsorbed oxygen from the gas phase vis a vis the lattice oxygen from the oxide catalyst. It was proposed some time ago that the concentration of nucleophilic oxygen, i.e., lattice oxygen - as opposed to the electrophilic, or, adsorbed oxygen, from the gas phase, controls the selectivity of the oxide catalyst for total oxidation [143]. This view is in agreement with the MVK mechanism.

It is generally assumed that gas phase oxygen upon adsorption on the oxide catalyst surface can sequentially accept electrons until fully reduced [144]. This can be described by the stepwise sequence depicted in Figure 7, where the subscript “s” indicates a surface site, and $(O^{2-})_{latt}$ denotes the lattice oxygen. Note that for the latter, presence and the availability of oxygen vacancies near the surface is required for the adsorbed surface oxygen O^{2-} to be incorporated into the oxide lattice.

Figure 7. Sequential electronation of the surface oxygen before it is incorporated into the oxide lattice via an oxygen vacancy. Subscript “s” denotes surface, while “latt” represents lattice oxygen. “Adapted with permission from ref. [144] Panov GI, Dubkov KA, Starokon EV, Catal Today, 2006; 117: 148-155. Copyright (2006) Elsevier”

MgO), so their catalytic activities are quite limited. Electron paramagnetic resonance (EPR) studies of alkane and alkene oxidation on MgO indicated that the surface species O^- , which forms at low temperatures usually when N_2O is employed as the gaseous oxidant, likely plays a significant role in selective oxidation of these hydrocarbons by facilitating the initial hydrogen abstraction step in the

reaction sequence [145,146]. When promoted by the addition of Group IA alkali metal oxides, the catalytic activity of alkaline earth oxides improves greatly. The alkali metal promoters increase the conductivity of MgO by nearly four orders of magnitude, inducing p-type conduction. More importantly, promotion by alkali metal oxides also stabilizes the surface O^- sites. In fact, EPR studies on Li- and Na-promoted MgO and CaO identified the presence of $(Li-O^-)$ and $(Na-O^-)$ centers on these oxide surfaces, which are responsible for the catalytic production of surface methyl groups via hydrogen abstraction from methane by the O^- species [147,148].

However, the view that $(Li-O^-)$ and $(Na-O^-)$ centers are indeed the catalytically active sites on doped alkaline earth oxides was recently challenged [149,150]. Temperature programmed oxidation and theoretical studies have shown that the same sites are

responsible for methane activation on both Li-doped MgO and undoped MgO catalysts, and the nature of the active sites were identified to be the $\text{Mg}^{+2}\text{O}^{2-}$ sites located at the crystal steps and corners which binds CH_4 preferentially [149]. However, the nature of the oxygen-centers on oxides that activate the adsorbed CH_4 via hydrogen abstraction is still unclear. A first principles study on the roles of several surface oxygen centers on lanthanum oxide clusters, reported that the predicted energy barriers for CH_4 activation on O_2^{2-} and O^- sites to be ~ 196 kJ/mol and 33-42 kJ/mol, respectively, and suggested that the peroxide O_2^{2-} site is the active oxygen center for activation [151]. More recently, density functional theory (DFT) studies on methane activation on La_2O_3 clusters indicated the activation barrier for hydrogen abstraction to be significantly less, between 84 and 105 kJ/mol, and inconclusively proposed that both O^{2-} and O^- centers may participate in the activation reaction [152]. Similarly, DFT studies on YAlO_3^{+} clusters demonstrated that yttria-promoted alumina can activate methane at room temperature, where transfer of hydrogen from methane to the oxygen in the YAlO_3^{+} cluster is thermodynamically favorable and almost barrierless [153].

Doping of alkaline earth oxides by lower valence cations is expected to reduce the formation energy for oxygen vacancies [138], and generally make them better oxidants than the undoped host. The situation, however, is different when oxides are doped with high valence dopants. For non-reducible oxides including the alkaline earth oxides, substitution of a higher valence dopant on the cation site in the host lattice creates an extra electron localized at the dopant site, which serves as a Lewis base site. For reducible oxides such as CeO_2 , on the other hand, a higher valence dopant such as Nb^{+5} can donate its excess electron to Ce^{+4} (i.e., Lewis acid site), reducing it to Ce^{+3} . Indeed, a recent study indicated doping with high valence transition metals has shown the existence strongly bound O^{2-} species that form on Mo-doped CaO films [154], which enhanced the oxidative coupling of methane on Au-Fe-doped MgO [155].

Generally, oxygen strong adsorption onto a transition metal oxide surface is facilitated by the overlap between the d-states of the metal atoms and the 2p orbitals of the surface oxygen. As oxide surfaces typically have defects, the interaction of oxygen from the gas phase with such surface defects is important for oxidation reaction. Such defects can be topographic as well as chemical in nature. The latter may be the result of unintentional (e.g., impurities) or intentional (i.e., extrinsic) doping. In this regard, transition metal oxides, perovskites, and reducible oxides offer wide opportunities as well as possibilities for doping strategies to control and increase the concentration of active surface sites such as oxygen vacancies for molecular activation [138]. However, elucidation of the active surface sites and the details of the activation mechanism are obviously more challenging and elusive on these oxides.

Using N_2O as the oxidant, selective oxidation of methane to methanol and formaldehyde on SiO_2 -supported MoO_3 catalysts is activated by the reactive O^- ions coordinated to the Mo^{IV} at the surface [156]. The O^- ions abstract the hydrogen from methane forming the methyl radicals that proceed to form HCHO and finally CH_3OH . Using Raman spectroscopy, catalytic activity on different crystal planes of MoO_3 has identified the terminal ($\text{Mo}=\text{O}$) sites located on the side (100) planes to be catalytically more active for selective oxidation of methane to formaldehyde, while the bridging oxygen ($\text{Mo}-\text{O}-\text{Mo}$) sites on the basal planes were likely to lead to complete oxidation [157], in general agreement with other studies [158].

Reducible oxides such as CeO₂ are generally good oxidant sources for catalytic reactions including partial oxidation of methane [159]. It is known that the fully oxidized surface of undoped CeO₂ (~ 5.5 eV) does not exhibit significant catalytic activity [160]. The situation is completely different for the reduced CeO_{2-x} surface, where the oxygen nonstoichiometry dramatically influences the catalytic activity. When reduced at high temperatures or under reducing environments, stoichiometric CeO₂ has the ability liberate oxygen through the reduction of Ce⁺⁴ to Ce⁺³ for charge compensation. In Kroger-Vink notation, this reaction is expressed as,

For each oxygen vacancy, V^{oo}_O, created at the surface, two cerium cations, Ce^x_{Ce}, located adjacent to the vacant site change their valance state from Ce⁺⁴ to Ce⁺³ (or, Ce'_{Ce}).

Raman spectroscopy of O₂ adsorption on reduced ceria indicated the presence of both superoxide (O₂⁻) and peroxide (O₂²⁻) species on the surface [161], where the peroxide species is significantly more strongly bound to the oxygen vacancy than the superoxide [162]. At sufficiently high temperatures, these species sequentially dissociate into the O²⁻ as depicted in Figure 7, and are incorporated into the oxygen sublattice, thus re-oxidizing the oxide surface. Furthermore, the adsorption energy of O₂ on fully oxidized CeO₂ surface was reported to be endothermic, while it is exothermic on the reduced surfaces of CeO_{2-x} [161]. Although evidence of methane adsorption of fully oxidized CeO₂ is scarce, enhanced dehydrogenation activity for steam reforming of methane was reported for precious metal catalysts supported on CeO₂(111), where the specific rates were higher by a factor of 10⁵ on Pd/CeO₂ than on Pd/SiO₂ catalysts [163]. Methane oxidation on Cu/CeO₂ catalysts indicated an L-H type of kinetics where the rate determining step involves adsorbed methane, but the oxygen partial pressure dependence of the rate expression suggested that perhaps more than one type of surface oxygen species (i.e., O₂²⁻, O⁻, O²⁻) and lattice oxygen likely participate in the activation step [164]. Enhanced catalytic activity for methane was also reported for transition metal oxides and fluorites supported on CeO₂ [165-170].

3.3. Role of lattice oxygen in methane catalysis

In most catalytic oxidation reactions, the oxidant, usually molecular oxygen, is provided to the catalytic surface from the gas phase. However, there is general agreement that most oxidation and oxidative dehydrogenation reactions taking place on oxide catalysts can adequately be described by the MVK mechanism, where the reactant fuel is actually oxidized not by adsorbed oxygen from the gas phase, but by the lattice oxygen atoms from the surface of the oxide catalyst [138]. As the reaction product desorbs, it leaves behind an oxygen vacancy, which then traps the next oxygen from the gas phase. This mechanistic model requires the exchange of gaseous O₂ with lattice oxygen on the surface of the oxide catalyst. In the case of supported metal catalysts, this exchange happens on surface of the oxide support prior to oxygen spillover to the metal catalyst surface.

Exchange of gaseous oxygen with lattice oxygen on oxide surfaces have been known for a long time [171-173], and generally proceeds via two thermally activated mechanistic pathways. Using isotopic labeling for identification purposes, one pathway involves exchange between the molecular oxygen isotope ¹⁸O¹⁸O_(g) and a single surface

atom $^{16}\text{O}_{(\text{s})}$ of the oxide. The other pathway involves two surface oxide atoms ^{16}O - $^{16}\text{O}_{(\text{s})}$ participating in the exchange reaction. The single and double exchange reactions are given, respectively, by,

These reactions most likely involve several intermediate steps during the dynamic exchange process including dissociative adsorption of molecular $^{18}\text{O}_2$ or $^{18}\text{O}^{16}\text{O}$ on the oxide surface, and the associative desorption of $^{16}\text{O}^{16}\text{O}$ or $^{18}\text{O}^{16}\text{O}$ from the oxide surface. It is expected that these reactions also involve electronic and ionic defects, and in the case of CeO_2 , may constitute the following intermediate steps:

Here, $*_{(\text{s})}$ indicates an oxide surface site for adsorption, $\text{O}''_{\text{ad}(\text{s})}$ denotes a doubly electronated oxygen on the oxide surface with a charge of -2, $\text{V}^{\bullet\bullet}_{\text{O}(\text{ceria})}$ represents an oxygen vacancy in ceria with a relative charge of +2, and $\text{O}^{\text{x}}_{\text{O}(\text{ceria})}$ is a lattice oxygen in ceria, where the superscript x denotes neutral charge with respect to the perfect crystal lattice in Kroger-Vink notation.

It is clear that ready availability of both electrons and oxygen vacancies is critically important for fast exchange rates. Using atomic layer deposition (ALD), a recent study systematically varied the oxygen vacancy concentration on the YSZ surface by atomic scale control of yttria-doping levels has demonstrated that optimizing the vacancy concentration on surface engineered YSZ dramatically improves SOFC performance [174]. In a related study, the activation energy for oxygen exchange on gadolinia-doped ceria (GDC) and YSZ at high temperatures ($T > 700^\circ\text{C}$) was reported to be 3.3 eV and 2.3 eV, respectively, while for $T < 700^\circ\text{C}$, the corresponding activation energies were 0.9 eV and 0.7 eV [175]. Similarly, using ultra thin (10-130 nm) yttria-doped ceria (YDC) interlayers deposited by ALD on top of YSZ electrolyte has also improved SOFC performance [176-178]. These results suggest that at high temperatures the availability of electrons is equally important for the oxygen exchange reaction, and may be rate limiting on these oxides. High catalytic activity observed for ceria supported metal catalysts is likely related to its relative ease of reducibility to provide the electrons as well as mobile lattice oxygen required for the exchange reaction. So reducible oxides, and oxides that can sustain large deviations in their oxygen stoichiometries can be employed as either the active catalysts or the catalyst supporting material, and may offer significant advantages.

Usually, oxides with strong metal-oxygen bonds, or large heats of formation, exhibit low catalytic activity, while those with weak bonds favor “deep” or complete oxidation. Selective catalysts tend to be in the intermediate range in terms of their metal-oxygen binding energies. This is an important consideration, as methane oxidation on most oxides proceeds via the MVK mechanism that involves surface redox of the lattice oxygen sites. The reduction step involves the oxidation of methane, while the oxidation step may proceed either via gas phase oxygen exchange, or by bulk transport of lattice oxygen. The latter can be supplied either through a mixed conducting oxide or through an oxide-ion conducting electrolyte.

Mixed ionically electronically conducting (MIEC) perovskites with extrinsically controlled non-stoichiometries in the oxygen sublattice offer attractive opportunities for enhanced catalysis of the methane electro-oxidation reaction. Perovskites have the general chemical formula $ABO_{3-\gamma}$, where the typically lower valance and larger size A-cation is located in 12-fold coordinated interstitial sites among the BO_6 octahedra in the simple cubic crystal structure. As long as the sum of A and B-site cations add up to 6, and the radii of the A, B, and O site ions satisfy the Goldschmidt criteria for structural stability, perovskites offer a vast choice of compositions in the materials space provided by extrinsic doping of appropriate cations on the A and B sites that dramatically alter their physical and chemical properties. For example, A-site doping with a lower valence cation gives rise to the formation of mobile oxygen vacancies for charge compensation, whereas B-site doping generally alters the electronic structure and catalytic properties of perovskites. As expected, oxygen storage capacity i.e., oxygen non-stoichiometry, γ , is important for the lattice exchange reaction and relates to the oxygen vacancy concentration dictated by the oxidation states of the A- and B-site cations. Generally, non-stoichiometry parameter γ increases with increasing temperature and decreasing oxygen partial pressure. It is important to note that the catalytic activity of perovskites is primarily governed by the nature of the B-site cation [66,179]. Indeed, recent work on the perovskite-based $La_{0.75}Sr_{0.25}Cr_{1-x}Mn_xO_{3-\delta}$ anodes demonstrated the critical role of lattice oxygen plays in the rate and selectivity of methane oxidation, where complete oxidation [180] is favored by a small value of γ , i.e., low oxygen vacancy concentration and increasing concentration of the reducible B-site cation Mn, while larger non-stoichiometry favors partial oxidation of methane [181].

Much of the earlier work on perovskite-based catalysts has been reviewed elsewhere [86,141,142,182]. The important role of the storage capacity of lattice oxygen has been highlighted in these studies [183]. Catalytic combustion rates of methane on various doped perovskites of the general composition $La_{1-x}A_xMO_3$ (where, A= Sr, Ba, Ca, Ce, and M= Co, Mn, Fe, Cu, Ni, Cr) indicated that the perovskite composition $La_{0.8}Sr_{0.2}MnO_3$ exhibited reactivity comparable to an alumina-supported Pt benchmarking catalyst for the oxidation reaction at $T < 550^\circ\text{C}$, but became significantly less active above 600°C [86]. At low temperatures, the pressure dependence of the rate expression was consistent with the Eley-Rideal mechanism [86,142], where methane oxidation rate depended on the partial pressures of both methane and molecular oxygen. This suggests that at these low temperatures the weakly bound oxygen adsorbed from the gas phase on to the catalytic perovskite surface is more active in oxidizing methane. Raising the reaction temperature above 600°C diminishes the oxygen pressure dependence, indicating that in this temperature regime methane reacts with the lattice (i.e., intrafacial) oxygen

from the bulk oxide. In fact, the rate of methane oxidation increases dramatically when lattice oxygen becomes available to activate the methane C-H bond [66]. Catalytic combustion of methane was studied on doped lanthanum cuprate-based perovskites of the varying compositions $\text{LaMn}_{1-x}\text{Cu}_x\text{O}_3$ and $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ below 800°C , and found to be effective oxidation catalysts with a first order kinetics for methane producing 100% CO_2 in the product stream [184]. It was also reported in this study that Cu seems to have an adverse effect on catalytic activity in both perovskite compositions, and the Mn-based catalysts have shown higher catalytic activity than the Co-based compositions, in qualitative agreement with the easier reducibility of Mn^{+4} at temperatures lower than that for Co^{+3} . This again highlights the role of the $\text{Mn}^{+4}/\text{Mn}^{+3}$ redox couple in promoting the mobility of the lattice oxygen and hence, the observed catalytic activity.

The lattice oxygen in doped-perovskites is unlikely to be in a uniform state but may exhibit a range of binding energies and desorption kinetics. In fact, temperature programmed desorption (TPD) coupled with X-ray photoelectron spectroscopy (XPS) identified two distinct types of desorbed oxygen, one that is associated with the oxygen vacancy formed upon A-site doping, and the other is ascribed to the partial reduction of the B-site cation valence that liberates an equivalent amount of lattice oxygen [142]. Similar results were reported by others for methane oxidation on perovskite catalysts of the general compositions $\text{La}_{1-x}\text{A}_x\text{MO}_3$ (where, A= Sr, Ce, Eu, and M= Co, Fe, Ni) [66], $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0-0.5$) [185], $\text{La}_{1-x}\text{Sr}_x\text{M}_{1-y}\text{M}'_y\text{O}_3$ (where, M= Mn, Cu, Ni, Co, and M'= Ni, Fe, Co) [186], and $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ [187], where in each study the TPD spectra augmented by mass spectrometry (MS) or x-ray photoelectron spectroscopy (XPS) indicated at least two energetically different oxygen peaks between 200 and 800°C . The low temperature peak was assigned to suprafacial oxygen adsorbed from the gas phase, while the peak at $T > 500^\circ\text{C}$ was associated with intrafacial, or lattice, oxygen. The results indicate that activation of molecular oxygen is relatively easy to achieve at low temperatures, whereas the activation of the C-H bond is more difficult and requires high temperatures. Moreover, increasing the dopant concentration x in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ shifted the gas phase $^{18}\text{O}_2$ concentration to lower temperatures in the TPD spectra, which is in line with increased oxygen vacancy concentration in the perovskite thus facilitating easier exchange of oxygen. Isotopic experiments indicated that the gas phase $^{18}\text{O}_2$ does not react directly with CH_4 , and oxygen exchange with $^{16}\text{O}_s$ in the perovskite lattice precedes the C-H activation step [65]. The reaction rate was first order (> 0.9) with respect to methane [86,141,184,186] and of the order of 0-0.5 with respect to oxygen partial pressure, suggesting kinetic reversibility of oxygen [86,141,142].

It should be noted, however, that the kinetic interpretations implicitly or explicitly suggested by some of these studies, particularly those that involved A-site substitution, were challenged. It was argued that an MVK-type surface redox model assumes the supply of oxygen from the gas phase occurs only when a reduced surface site becomes available (i.e., irreversible), which obviously renders the oxidation reaction to be the rate limiting step in the exchange [188]. As expected, Sr substitution on the A-site greatly impacts the concentration as well as the mobility of oxygen vacancies. This provides better kinetics for re-oxidation of the reduced lattice site, and up to an Sr-content of $x \sim 0.2$ enhances the catalytic activity for methane oxidation [185].

In addition to the attention on lattice oxygen, doped-perovskites containing transition metals show unusual behavior during chemical and electrochemical catalysis, where the

redox activity and stability is generally assigned to the valence change of the transition metal cations [189-191]. Although all evidence above shows that lattice oxygen is a redox partner for the molecular oxygen on doped-perovskites, the transition metal-oxygen bonds also play a key role in this exchange. In fact, X-ray absorption studies of the redox-active surface centers on thin films of $\text{La}_{1-x}\text{A}_x\text{M}_{1-x}\text{M}'_x\text{O}_3$ (where, A= Ba, Sr, Ca, and M and M'= Fe, Co) [192] and MNiO_3 (where M=La, Pr, Nd, Sm, Eu, Gd) [193] compositions have recently provided direct evidence of strong transition metal 3d-oxygen 2p hybridization effects, indicating the highly covalent and directional character of the bonding. The degree of hybridization increases with the d-electron count and the oxidation state of the B-site transition metal ions, which plays an important role in the catalytic activity of the perovskite. Understanding the underpinnings of such electronic interactions in these materials will help develop effective catalysts by designing rational doping strategies.

Although sulfur-poisoning of catalytic anodes is discussed in detail in a later section (see section 5.2. Sulfur Poisoning), the importance of this topic and its potential relation to lattice oxygen in mitigating the deactivation process justifies a brief account. In contrast to metal-based catalytic anodes, oxides with sufficient tolerance to non-stoichiometry in their oxygen sublattice may play an important role for rendering sulfur resistance to the catalytic anodes during methane oxidation in SOFCs when natural gas is employed directly without prior desulfurization. However, the mechanistic understanding of sulfur interactions with lattice oxygen is not well established. A series of surface analytical studies to understand sulfur interaction with lattice oxygen on various chromite-based perovskites including $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) [194], $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0.2, 0.5, 0.8$) [195], and $\text{Sm}_{0.9}\text{Sr}_{0.1}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.2, 0.5, 0.8$) [196] revealed several interesting results. Upon treatment of these oxides in H_2S (balance N_2) environments ranging from 1000 ppm up to 20% at 800°C for several hours in the absence of oxygen in the gas phase, x-ray photoemission spectroscopy (XPS) results indicated the presence of sulfate (SO_4^{2-}) group on the surface, suggesting strong interaction of sulfur with lattice oxygen not only on the surface but also participation from the bulk. The depleted oxygen is supplied from the bulk by diffusion towards the surface. It was also suggested that the adsorbed sulfur is trapped in the oxygen vacancies and binds to adjacent oxygens. XPS results also showed no shift in the binding energies of Cr indicating no valence change upon exposure to reducing H_2S environment, whereas multi-valent Mn ions are detected on the B-sites. It was proposed that the $\text{Mn}^{4+}\text{-O-Mn}^{3+}$ clusters might be responsible for the observed sulfur tolerance in LSCM [195]. The results also suggest that the electronic conductivity and catalytic activity of these doped chromite-based perovskites are governed primarily by Mn and not by Cr, in agreement with others [197]. Catalytic studies of methane oxidation at 700-900°C over $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_x\text{Mn}_{1-x}\text{O}_{3-\delta}$ ($x = 0, 0.25, 0.5, 0.75, 1$) with varying oxygen stoichiometries in a pulse reactor in the absence of gas phase O_2 revealed that high oxygen stoichiometry (i.e., small δ) as well as the availability of reducible B-site cations are necessary to make an effective catalyst for full oxidation of methane [180,181]. The selectivity varied with oxygen stoichiometry from the upper limit of 100% full oxidation at high stoichiometry to 100 % towards partial oxidation at low stoichiometry, pointing to the strong role of lattice oxygen as an active participant in the oxidation reaction. Certainly, higher stoichiometry provides a higher concentration of lattice oxygen on the surface available

to participate in the oxidation reaction, whereas low stoichiometries (i.e., large δ) restrict this supply. It was also observed that the reaction rate and the oxygen stoichiometry regime that provides high selectivity for full oxidation of methane increased with increasing Mn content in LSCM, which also agrees with the earlier views of the catalytic role Mn plays in these structures.

Although not within the scope of this article, it is interesting to point out that the role of lattice oxygen is also being explored as a source for oxygen for the oxidation reaction in the context of chemical looping for combustion and partial oxidation of methane, and even coal. Many different oxygen carriers either as partially reducible oxides such as $\text{CeO}_2\text{-Co}_3\text{O}_4$ [167], and $\text{CeO}_2\text{-Fe}_2\text{O}_3$ [50,169,170,198], or transition metal oxides [48,67,199,200] have been investigated for methane combustion. In this process scheme, combustion is totally separated from the carrier re-oxidation step and hence, no nitrogen enters the combustion stream in the first place. Thus, chemical looping eliminates the need for post-separation operations to capture CO_2 .

4. Electrochemical Conversion of Methane in SOFCs

Electrochemical conversion provides unique opportunities above and beyond catalytic conversion discussed in previous sections. This is illustrated in Figure 8, which

Figure 8. A typical chemical reaction energy profile (dotted red curve) along the reaction coordinate. The dashed (blue) curve illustrates the effect of catalysis in lowering the activation barrier, while solid (green) profile denotes the impact of potential, η , on altering the energy profile. Here, F is the Faraday constant, z is the charge of the electroactive species, symbol α is the symmetry factor, ΔG_{rxn}^0 denotes the free energy change for the reaction, ΔG_f^0 is for the forward reaction while ΔG_b^0 is for the backward reaction, and E_{act} is the activation barrier for the reaction.

qualitatively represents the energetics of the transition state profile along the reaction coordinate for reactants and products of chemical reactions. The free energy change, ΔG_{rxn} , during the chemical reaction is given by the difference in the forward and reverse reaction minima. The presence of an effective catalyst helps reduce the activation barrier, E_{act}^* , for the reactants to overcome, thus accelerating the reaction rate. However, the presence of the electrical potential, η , can dramatically alter the energy profile of the chemical reaction, by lowering the activation barrier for the forward reaction by $\alpha zF\eta$, where α is the symmetry factor for the transition state, F is the Faraday constant, and z is the charge of the electroactive species. It may also increase the barrier for the reverse reaction by the amount $(1-\alpha)zF\eta$. Such effective control makes electrochemical conversion significantly more advantageous over chemical catalysis.

Fuel cells are essentially electrochemical engines that convert the chemical energy of fuels directly into electrical energy. Figure 9 illustrates several major types of fuel cells, indicating the net half-cell electrode reactions as well as the primary ionic species that transport charge through the electrolyte while electrons travel through the external circuit performing useful electrical work. The basic process involves oxidation of the fuel at the anode and shuttling the electrons released during electro-oxidation reaction through the external circuit to the cathode, where they are consumed in reducing the molecular oxygen (in air) to ionic form. In all cases, methane or natural gas is likely the starting fuel stock, but methane-derived hydrogen is the desired and most extensively employed fuel for most fuel cells, despite the fact that H_2 is not a primary energy source but an energy carrier, which must be produced in the first place. This preference is primarily because hydrogen can readily be oxidized, while methane activation is sluggish and challenging. Hence, both high temperatures and highly active catalytic electrodes are required to activate methane. But even molten carbonate fuel cells (MCFC) employing typically a eutectic mixture of alkali metal carbonates as the molten electrolyte at 650-750°C, or alkaline fuel cells (AFC) with a molten hydroxide electrolyte such as NaOH operating at ~ 600°C can utilize methane only after external reforming. Also, because of the low solubility of methane in liquid electrolytes, low temperature fuel cells are unsuitable for direct use of methane as the fuel at the anode.

Moreover, the hot corrosive electrolytes of MCFC and AFC pose major challenges for the stability of cell materials and components including the dissolution of the NiO cathode in the molten carbonate electrolyte and precipitating it in the form of Ni elsewhere eventually causing electrical shorting of the MCFC. It is also difficult to achieve internal steam reforming in the MCFC due to lack of effective and stable

Figure 9. Schematics of major fuel cell systems illustrating their operating temperature regimes, net half-cell reactions, and the primary charge carrying ionic species. In most cases, methane-derived hydrogen is employed as fuel, except for SOFCs, which are capable of utilizing methane directly.

reforming catalysts that can withstand poisoning by the alkali metal attack from the molten carbonate electrolyte [201-203]. Typical reforming catalysts such as Ni show rapid decrease in intrinsic catalytic activity by Li^+ and Na^+ poisoning, and even more severe by K^+ . Furthermore, MCFCs require tight management of CO_2 formed at the anode, 2/3 of which needs to be recycled to the cathode in order to sustain the carbonate formation reaction as

indicated by the cathode reaction for MCFC (see Figure 9). Similarly, the molten hydroxide AFC suffers from the parasitic reaction between the anode product CO_2 and the molten hydroxide that precipitates the solid carbonate that eventually clogs up the cell and degrades cell performance.

So SOFCs are considered more suitable to employ methane directly as the fuel, with or without reformation. They promise clean, efficient and environmentally friendly conversion [204], and also offer an unusually wide range of fuel flexibility including not only gaseous fuels but also liquid fuels [29], and even solid fuels including carbon [34], untreated coal [36] and biomass [35].

Electrochemical conversion in SOFC provides effective control and tuning of the oxygen activity on catalytic electrode surfaces in order to enhance catalytic activity [205]. In fact, electrochemical monitoring of the activity of electroactive surface species during heterogeneous catalysis by the use of solid electrolytes is not a new concept, but proposed several decades ago [206]. The principle concept was implemented successfully in solid-electrolyte-potentiometry (SEP) measurements for ethylene oxidation [207,208] as well as methane oxidation on catalytic anodes including Pt [209], Ag [89] and Pd [210] deposited on YSZ electrolyte. The SEP technique was also used successfully for other reactions such as the oxidation of hydrogen on nickel anode [211] and for SO_2 oxidation on Pt, Ag, and Au anodes [212] on solid oxide electrolytes.

It is important to note that SOFC configurations not only provide passive monitoring of catalytic activity as in SEP, but also allow active control and tuning of the oxygen activity at the metal/electrolyte interface as well as the transport of oxide ions from the metal catalyst surface in order to “cleanse” and avail the catalytic metal surface for the next turnover. Such control of oxygen activity has been demonstrated to dramatically affect catalytic rates. Reaction turnover frequencies, up to several orders of magnitude for many industrially important reactions including NO reduction [134], CO_2 methanation [135,136], and CO hydrogenation (i.e., Fischer-Tropsch synthesis) [135,137] have been reported previously.

Attempts to electrochemically convert methane and other hydrocarbons on precious metal anodes in SOFCs have been reported previously for cells employing solid ion conducting solid electrolytes such as YSZ [213-219], as well as for proton conducting solid electrolytes such as Y_2O_3 -doped BaCeO_3 (BYC) [44,46,220]. Much of this early work on electrochemical reactor systems to oxidize and transform methane on various catalytic electrodes in SOFC arrangements has been reviewed extensively [42,43,131,221].

4.1. SOFC operating principle and materials

SOFCs are quiet, environmentally friendly engines that achieve efficient energy conversion isothermally, and with significantly reduced CO_2 emissions that is almost capture-ready. There are primarily three major SOFC architectures, namely, cathode-supported, anode-supported and electrolyte-supported. A single complete unit of the cathode-electrolyte-anode structure is usually called the membrane electrode assembly, or MEA for short. Stacking of MEAs make up the SOFC stack, or module. The different MEA architectures, as well as materials properties, requirements and challenges for the SOFC science and technology have been discussed and reviewed in great detail

elsewhere [204,222-230]. In each, the thick support material serves as the mechanical and structural scaffold upon which the other functional cell components are built. In the electrode-supported MEA geometries, the porous cathode or anode thickness is nominally 1 mm, where the electrolyte membrane is nominally 10 μm in thickness. Conversely, in electrolyte-supported MEA architecture, the dense impervious electrolyte membrane whose thickness can be somewhere in the range of 200-500 μm provides the mechanical stability for the cell structure. Thin film anode and cathode layers are subsequently deposited on both faces of the electrolyte membrane. Yet a different MEA architecture employs ultra thin (100-1000 nm) electrolyte membranes built on silicon-based substrates using micromechanical machining and lithography techniques. The latter approach for fabricating ultra thin membrane SOFCs has been reviewed recently [231,232]. As there have been many excellent reviews on various aspects of SOFCs materials and performance, only the basic principles and materials that are pertinent to methane oxidation are presented below.

4.1.1. SOFC basics

Typically SOFCs consist of an oxide ion conducting dense ceramic electrolyte membrane sandwiched in between two catalytic electrodes that serve as the anode and the cathode, as shown schematically in Figure 10 for the simplest case of a cell operating on H_2 fuel.

In principle, the operation of SOFCs involve the reduction of molecular oxygen at the cathode into ionic form, transport of O^{2-} ions through a solid oxide electrolyte membrane to the anode where the fuel reacts with the O^{2-} ions to oxidation products. The electrons released during this charge transfer reaction travel through the external circuit from the anode to the cathode, performing useful electrical work along the way. Finite rates of the electrode processes (i.e., activation losses) as well as the finite electrical resistance of the cell components (i.e., ohmic losses) naturally decrease the available cell voltage, which in turn reduces cell efficiency and performance. At very high polarization (i.e., high current densities), transport limitations of the reacting and product species give rise to mass transport losses. In the case of macroscopic or even microscopic cracks in the cell structure, gas leakage across the cell can cause chemical shorting (i.e., cross over) of the fuel and/or the oxidant, and lower the useful cell voltages (i.e., measured) from the theoretically expected value of the open circuit voltage (OCV). In a similar manner, if there is electronic contribution to the total current through the electrolyte membrane, this may also lower the measured OCV due to electronic semipermeability.

Assuming no chemical shorting or semipermeability, and that equilibrium exists between the gas phase species and the catalytic electrode surfaces, the useful cell voltage under no-current conditions will otherwise be the same as the theoretically expected OCV. Figure 10 qualitatively indicates the regimes of dominant loss mechanisms in SOFCs.

Previously, precious metal electrodes - mostly Pt [233-239] were employed routinely in SOFCs for their high catalytic activity both for the fuel oxidation as well as the highly activated and sluggish oxygen reduction reaction (ORR), namely,

As reaction (18) involves species from three different phases, namely, molecular oxygen from the gas phase, oxygen vacancies from the electrolyte, and electrons residing only in the metal electrode, it can occur only at the triple phase boundaries (*tpb*) bounded by the respective phases. In other words, the *tpb* defines the electrochemically active zone. It was reported that the estimated *tpb* width at the metal electrode /solid electrolyte interface is quite narrow, of the order of 1 μm [240,241]. The results of Secondary Ion Mass Spectrometry (SIMS) coupled with oxygen isotope exchange experiments on cathodically biased Pt/YSZ interfaces indicated that electrolyte grain boundaries are also active sites for oxygen exchange on YSZ [242], as well as doped YDC [243]. Since the cell current is preferentially restricted to these practically one-dimensional boundaries, decreasing the grain size improves cell performance in the Pt/nanocrystalline YSZ system with YSZ particle sizes < 20 nm [244].

As the polarization resistance is inversely proportional to the *tpb* length, extending the *tpb* from a one-dimensional narrow zone to 2- or 3-dimensional space naturally

Figure 10. (Left) SOFC schematic illustrating major cell components and half-cell reactions. (Right) Typical current-voltage behavior of the cell and voltage losses associated with activation, ohmic, and mass transport limitations, in addition to any possible chemical shorting due to leaks in the cell architecture. If equilibrium prevails at the electrodes and there are no leaks or chemical shorting, then E_{OCV} and E° will be the same.

maximizes its density and greatly improves cell performance. In this regard, subsequent developments in metal/ceramic cermets and mixed ionically electronically conducting (MIEC) oxides as effective catalytic electrode materials have presented attractive opportunities to expand the *tpb* into 2- and 3-dimensions, respectively. As expected, mixed conduction of both oxide ions and electronic species broaden the electrochemically active region away from the current collector by small polaron hopping and thus enhance cell performance [245,246]. When slightly reduced under the reducing environment at the SOFC anode, ceria is a mixed conductor and a popular cermet anode component. *In situ* photoelectron x-ray spectroscopy of CeO_{2-x} during SOFC operation has shown the electrochemically active region can expand out to nearly 150 μm away from the Au current collector and this active region is defined by the presence of the

$\text{Ce}^{+4}/\text{Ce}^{+3}$ redox couple [247]. Contingent on independent verification, this exciting finding of such a remarkably wide *tpb* zone is important for designing optimized electrode microstructures for practical applications. As MIEC materials and their composites allow the *tpb* zone to extend in three dimensions, there has been much attention and activity in exploring and developing doped-perovskites for cathode materials in the recent decades [245,248-256], and much of this work has been reviewed elsewhere [257-261]. By comparison, the width of the *tpb* zone for the MIEC $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ cathode is estimated to be only 0.03-0.07 μm [262]. However, it must be noted that it is extremely difficult to make accurate experimental determination of the *tpb* width and length, which are parameters very difficult to define and measure. So these widths are often inferred from isotopic oxygen exchange measurements and polarization behavior of model or patterned electrodes [240,246,262-266].

Naturally, the *tpb* concept is also important for an effective anode, and requires maximization of the electrochemically active area. Cermets, which are mixtures of catalytic metal particles dispersed inside an ionically conducting porous solid oxide aim

to maximize the density of *tpb* in the anode structure.

Figure 11. Typical architecture of state-of-the-art SOFC showing (a) cross-sectional view of cell materials, and (b) cell component stacking. “Reprinted with permission from ref. [267] Homel M, Gür TM, Koh JH, Virkar AV, J. Power Sources 2010; 195: 6367-6372. Copyright (2010) Elsevier, and by courtesy of MSRI)”

State-of-the-art SOFC designs usually employ anode-supported planar cell architecture, which consists of a cermet anode, typically made of a ~1

mm thick porous sintered mixture of Ni and YSZ fabricated by tape casting that provides mechanical stability for the cell structure. A thin film of dense YSZ layer of 10 μm in nominal thickness is deposited on the support structure. Finally, 50-100 μm thick porous film of mixed ionically electronically conducting (MIEC) doped-perovskite - typically $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM), $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ (LSCF) or mixtures with YSZ – deposited on top of the YSZ membrane serves as the cathode. A typical example of this architecture is illustrated in Figure 11, courtesy of Materials and Systems Research, Inc. of Salt Lake City, Utah [267]. For electrode supported MEAs, the porous composite of one or more oxides are co-sintered at high temperatures to make mechanically robust a porous structure. In the case of anode-supported cells, the sintered mixture is typically made of NiO and YSZ particles. Regardless of whether the cell structure is anode- or cathode-supported, the porous cermet anode must be reduced prior to obtaining a fully operational MEA. This is accomplished by the chemical reduction of NiO in the porous cermet anode to metallic Ni in H_2 atmosphere at high temperatures.

It should be pointed out that despite intense efforts in materials research and development, there have only been gradual but no groundbreaking advancements in SOFC performance in the last fifteen years, when a series of studies reported record high power densities of 1.7-1.9 W/cm² using H₂ fuel at 800°C for Ni/YSZ cermet anode-supported SOFCs with YSZ thin film electrolyte of about 10 µm in thickness and LSM

Figure 12. Schematic illustrating the diffusion of lattice oxygen by exchanging sites (vertical block arrow) with an adjacent oxygen vacancy ($V_{O''}$) created upon extrinsic doping of the ZrO₂ crystal lattice with Y₂O₃, which leads to creation of one vacancy for every two Y³⁺ ions to maintain charge neutrality of the crystal. The two dots on the vacancy notation, $V_{O''}$, designate its relative charge of 2+ with respect to the perfect lattice.

cathodes [268-272]. Since then, there has been one notable exception that exceeded these record performance values. An anode-supported SOFC architecture that employed humidified H₂ fuel and a bilayer electrolyte made of 10 µm thick gadolinia-stabilized ceria (Gd_{0.1}Ce_{0.9}O_{1.95}) and 4 µm thick erbia-stabilized bismuth oxide (Er_{0.4}Bi_{1.6}O₃), and a bismuth ruthenate-bismuth oxide composite cathode has achieved an exceptionally high power density of 2 W/cm² at the low operating temperature of

650°C, setting a new record [273]. There have also been predictive attempts to guide SOFC research to minimize polarization losses and pave the pathway towards achieving high cell performance [274,275]. The models predict that even with thin film electrolytes (nominally ~ 10 µm thick YSZ), ohmic losses, which partly arise from the finite electrical resistivity of the electrolyte membrane, may still dominate performance. Overcoming this hurdle may require advanced solid electrolytes with superior ionic conductivity as well as catalytic electrodes that exhibit excellent electronic conductivity. As expected, these arguments emphasize the need for new materials discovery, which will benefit from predictive theoretical tools to guide materials selection, and advanced synthesis and processing tools to design and structure materials for targeted properties. In other words, materials properties and behavior is key to achieving high SOFC performance, especially for methane conversion.

4.1.2. Solid oxide electrolytes for SOFCs

The most common electrolyte material used in SOFCs is 8mol% Y₂O₃-stabilized ZrO₂ (YSZ) of the cubic fluorite crystal structure, which transports O²⁻ ions selectively through vacancies in the oxygen sublattice that are generated upon the extrinsic substitution of an aliovalent dopant (in this case, Y³⁺ ions) on Zr⁴⁺ sites in the cation sublattice. For every two Y³⁺ ions substituted on Zr⁴⁺ sites, an oxygen vacancy ($V_{O''}$) forms in order to maintain charge neutrality of the solid. Oxide ion vacancies provide a transport pathway for lattice oxygen to diffuse through the crystal lattice and carry its ionic charge. The formation of oxygen vacancies upon doping, and the vacancy

Figure 13. Ionic conductivity of yttria-stabilized zirconia (YSZ), gadolinia-doped ceria (CGO), and Sr-doped lanthanum magnesium gallate (LSGM). “Reprinted with permission from ref. [267] Jacobson AJ, Chem. Mater. 2009; 22: 660-674. Copyright (2010) American Chemical Society”

exchange mechanism for ion transport is illustrated in Figure 12. Although, Sc_2O_3 -stabilized zirconia provides by far the highest ionic conductivity among the other rare earth dopants [276], the highly activated nature (~ 1 eV) of the oxide ion transport through the crystal lattice in all doped zirconias necessitates high operating temperatures to attain sufficient ionic conductivity for meaningful fluxes. Nevertheless, their excellent chemical stability over a very wide range of oxygen chemical potentials commensurate with the highly oxidizing and highly reducing conditions at the cathode and anode, respectively, as well as their negligibly small electronic conductivity due to their wide (>5 eV) band gap make this material the preferred electrolyte for most SOFC applications.

Other important members in the family of fluorite-based oxide ion electrolytes are doped CeO_2 and the

intrinsic oxide ion conductor $\delta\text{-Bi}_2\text{O}_3$, both of which in fact have higher conductivities than YSZ especially at temperatures lower than 800°C . Indeed, $\delta\text{-Bi}_2\text{O}_3$ exhibits the highest ionic conductivity of >1 S/cm at 800°C , but is only stable in a narrow temperature regime between 730°C and its melting temperature of 804°C . This stability regime can be extended to lower temperatures by extrinsic doping of the Bi-sublattice typically by Y_2O_3 or Er_2O_3 , although usually at the expense of lower conductivity. Electrolytes based on these doped oxides have been considered for low temperature SOFC applications [273,277] but their major shortcoming is their chemical instability in the reducing environment at the anode side of the SOFC. This usually leads to onset of p-type electronic conduction in the case of doped-ceria due to the reduction of Ce^{+4} to Ce^{+3} thus reducing the useful cell voltage, and, in the case of doped- Bi_2O_3 , possible shorting or failure of the cell by the reduction of Bi_2O_3 to metallic Bi or by volatilization [259,278,279]. However, in many cases, this shortcoming can be circumvented by the use of bi-layer electrolyte architecture. Indeed, thin film YSZ interlayers deposited on the anode faces of the doped- CeO_2 or - Bi_2O_3 electrolytes physically isolate the electrolyte from the reducing gas environment and helps prevent electrolyte stability problems associated with the effect of reduction reactions [273,280,281].

Conversely, doped ceria has been successfully employed to serve as the chemical barrier layer to prevent interdiffusion, interfacial reactions, and secondary phase formation between SOFC components both at the cathode and at the anode interfaces. [259,278,282]. Doped-perovskites such as $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$ (LSGM) based on the LaGaO_3 parent formula [283-285] have also been proposed and employed as electrolytes

for low temperature SOFCs [277]. Figure 13 provides a comparison of the ionic conductivities of three different solid oxide electrolytes belonging to the fluorite (YSZ and CGO) and perovskite (LSGM) families. Wide range of materials properties of different cell components employed in SOFCs including catalysts for anodes and cathodes, as well as different classes of electrolyte membranes have been extensively reviewed elsewhere [259,286,287,288].

4.1.3. Typical materials for catalytic electrodes

It is possible to reduce ohmic cell losses by employing thinner electrolyte membranes without resorting to new materials. On the other hand, activation losses at the electrodes are governed by materials properties and microstructure as well as the nature of the electrode reactions and processes, and hence demand superior materials with inherently high catalytic activity and transport properties. In other words, electrodes are arguably the most critical and demanding components of SOFCs that dominate cell performance. Their primary function is to catalyze the fuel oxidation reaction at the anode and the oxygen reduction reaction at the cathode in the most efficient manner and at high turnover frequencies. Besides catalytic activity, they must possess high electronic conductivity to efficiently transport the electrons to and from the external circuit. They must exhibit chemical, structural and thermal stability in the highly reducing environment of the fuel at the anode, and the highly oxidizing environment, typically, of air at the cathode, while operating at elevated temperatures. Typically, the electrode morphology is porous to expose high surface area to the reacting species, and has a complex microstructure that consists of percolating catalytically active metal or a mixed conducting oxide, supported on an oxide ion conducting solid electrolyte (see Figure 11). The interfaces between the electrolyte and composite electrodes components must be stable and nonreactive, as they play important roles in the charge transfer reaction that typically takes place at the triple phase boundaries (*tpb*). Functional cell components must have closely matching thermal expansion coefficients to avoid thermal mismatch that can lead to mechanical failure during thermal cycling of the SOFC. Consequently, discovery and development of superior electrode materials that meet these demanding requirements pose challenges.

Understandably, precious metals are too expensive to be considered as catalytic electrode materials for practical purposes, although a recent report has demonstrated that functional Pt/YSZ cermet electrode structures can be fabricated by atomic layer deposition (ALD) at low Pt loadings $< 0.1 \text{ mg/cm}^2$ [177]. Because of its low cost and high catalytic activity, nickel is the most widely employed active catalyst in SOFC anodes in conjunction with YSZ or ceria to make up the composite cermet structure. Similarly, mixed conducting doped-perovskites have typically been employed as the active cathode material in SOFCs.

A major challenge to efficient SOFC operation is to reduce the large activation loss associated with the sluggish oxygen reduction reaction (18) at the cathode. This reaction has an activation barrier as high as 1.5 eV [258,289] and constitutes a major fraction of the cell losses in H_2 -fueled SOFCs. There has been enormous volume of work to understand, design and develop advanced catalytic cathode materials aimed at reducing or minimizing this large activation loss. Unfortunately, the development of high

performance catalytic cathodes for SOFCs has been slow, partly because it demand the right combination of materials properties including high catalytic activity, high electronic and ionic conductivity, mechanical robustness, chemical, structural and thermal stability both in the oxidizing gaseous environment at the cathode compartment as well as against interdiffusion or solid state reaction with the electrolyte that can lead to the formation of secondary phases or blocking layers. Only few materials may be able to meet these stringent requirements. Much effort and focus have been on MIEC doped-perovskites. In particular, LSM and LSCF compositions have been among the most studied, and currently been employed in state-of-the-art SOFC cathode designs. Fundamental studies on perovskite-based MIEC cathode materials and their transport and kinetic properties have been reported elsewhere [257-261,289-298], and will not be reviewed here. Among the challenges, however, Sr-segregation to the surface has been a persistent problem that results in the degradation of cell performance [299-301]. In addition, effects including interdiffusion and reactions of the cathode material with the electrolyte (e.g., blocking CoZrO_3 phase formation at the LSCF/YSZ interface) also contribute to the cell degradation mechanism [282,302-304].

Anode is a critical component of SOFCs that allows versatility and flexibility for different fuels to be employed for oxidation. Among many of the materials requirements, anode must possess high catalytic activity for oxidizing the fuel, provide sufficient electronic conductivity to collect the electrons released during the oxidation reaction, and have chemical, thermal and mechanical stability to endure the highly reducing anode environment. Since its discovery and introduction more than four decades ago, Ni/YSZ cermet has been the most commonly employed SOFC anode material [305]. Certainly, a wide range of other anode materials has been under investigation towards practical applications. Recent advances in anode materials development are extensively reviewed [306-309]. The challenges that still remain today for effective and direct utilization of hydrocarbon fuels in SOFCs were discussed elsewhere [26,309-314].

Because of its high catalytic activity and low cost, Ni is routinely used as the active anode material for most SOFC studies and applications. It is usually employed as a sintered composite mixture of fine grain NiO powder in an ionically conducting oxide matrix such as YSZ to make a porous cermet microstructure, which extends the *tpb* into three dimensions when NiO is subsequently reduced to metallic Ni that also serves as a 3-dimensional current collector for the electrons. However, impurities such as SiO_2 , Na_2O , etc. present in Ni and/or YSZ may alter the nature of the interface between them by segregation or secondary phase formation, thus blocking the *tpb* sites and increasing interfacial resistance that lead to polarization losses [303,315,316]. A recent review extensively discusses all aspects of Ni-cermet anodes for methane conversion in SOFCs [317].

Much of the focus for the remaining of this paper will on anode materials for SOFC, with particular emphasis on methane oxidation. It should be pointed out, however, that much of the work to date have involved the investigation and development catalytic anode materials targeting the oxidation reaction of H_2 , which has overwhelmingly been the preferred SOFC fuel of choice. In this regard, various cermet compositions including Ni/YSZ and Ni/ceria [316,318-320], as well as single phase or composite mixtures of perovskite-type MIEC oxides [197,321-324] have been developed and employed as anode materials in SOFCs.

For example, SrTiO₃-based doped perovskites attracted attention as potential catalytic anodes for SOFCs due to their structural stability over a wide oxygen partial pressure range and reasonably high electronic conductivity under reducing atmospheres. Investigation of the physical and electrocatalytic properties of La_xSr_{1-x}TiO₃ (x= 0.1, 0.2, 0.3, 0.35, 0.4) indicated that sintering in H₂, as opposed to in air, greatly improved electrical conductivity, where H₂-sintered La_{0.3}Sr_{0.7}TiO₃ (LST) showed a conductivity value of ~ 500 S/cm at 500°C in P_{O2} < 10-20 atm, while the conductivity of the same composition sintered in air was almost 2 orders of magnitude lower at the same reducing atmosphere even at 1000°C. Moreover, LST was stable over a wide oxygen pressure regime down to 10⁻³⁰ atm, dimensionally and chemically stable to multiple redox cycling, and had an average thermal expansion coefficient of 11-12x10⁻⁶ C⁻¹ (between 500 and 1000°C) that is compatible with YSZ [323].

The electrical conductivity and structural stability of the parent strontium titanate perovskite structure was investigated using rare earth dopants (Y, La, Pr, Sm, Nd, Gd, YB) where the highest value of the n-type electrical conductivity was 64 S/cm for Sr_{0.88}Y_{0.08}TiO₃ at 800°C and improved to 82 S/cm by slightly increasing the Sr-vacancy concentration to Sr_{0.86}Y_{0.08}TiO₃, which was also found to be structurally stable over a wide oxygen partial pressure regime from 1 atm down to 10⁻²⁰ atm at 1400°C [325]. Separately, the structural and phase stability, reversibility of electrical conductivity between oxidation-reduction cycles, chemical and thermal compatibility with common electrolytes YSZ and LSGM with no phase change or new phase formation after co-firing with each at 1400°C for 10 hours, and a high electronic conductivity of 82 S/cm composition at 800°C and at an oxygen partial pressure of 10⁻²⁰ atm was reported for the yttrium-doped strontium titanate of the Sr_{0.86}Y_{0.08}TiO₃ (YST) composition [326].

Nevertheless, high catalytic activity and cell performance require optimization of microstructural parameters such as porosity, tortuosity, and particle size, spatial distribution and relative loadings of the active metal or MIEC catalyst with the ionically conducting solid electrolyte component of the composite anode so that good electronic percolation is achieved to assure both maximum *tpd* density and electrical connectivity in the 3-dimensional porous structure, as well as chemical and thermal stability of the materials against the highly reducing gas environment at the anode compartment. A more detailed discussion of numerous catalytic anode materials reported for methane conversion reactions are provided below in section 4.2.

4.2. Strategies for methane conversion in SOFCs

Methane and natural gas are naturally occurring primary energy and fuel sources. Unlike the common SOFC fuel H₂, which needs to be produced from other sources in the first place, methane and natural gas are highly desirable fuels for SOFCs. The environmental cost of production, compression and transportation, as well as lack of ready availability of hydrogen pose major obstacles for successful commercialization and wider deployment of fuel cells in general. By contrast, conversion of methane, or natural gas, directly or indirectly in SOFCs would overcome these major limitations of efficiency, availability, reliability and cost. However, the key to achieving efficient electrochemical conversion lies with the development of advanced electrocatalytic anodes for methane, or

natural gas that exhibit high activity, efficacy, durability, and low cost to accomplish the difficult challenge of methane electro-oxidation to CO₂ and steam.

Several approaches have been proposed and pursued for methane utilization and conversion in SOFCs. The major ones include partial oxidation, oxidative coupling, external or internal reforming, and direct oxidation. Partial oxidation and oxidative coupling largely aims for co-generation of power, and chemicals or syngas. As the thrust of this review article is entirely on power generation and not chemical co-production, only the last three approaches will be discussed and reviewed below. Also, the term “direct” conversion in this article will refer to introducing dry methane directly into the SOFC without any additives such as O₂, H₂O, and CO₂ that can otherwise serve as the oxygen source. This is elaborated later in section 4.2.3.

4.2.1. SOFCs fueled by externally reformed methane

Steam reforming of methane to syngas can be achieved either by external or internal reforming. The syngas is a mixture of H₂ and CO formed by the highly endothermic reforming reaction,

Reaction (3) is typically carried out at elevated temperatures of 800-1000°C in the presence of a Ni-based catalyst, and usually at a pressure of about 35 bar. Most commercial SOFCs employ external reforming (3), which is carried out in an external

Figure 14. Schematic of SOFC system fueled by syngas from external reforming of methane, with optional (dashed lines) water-gas shift (WGS) reactor to produce more hydrogen for the fuel cell stack.

stand-alone fuel processor unit as depicted in Figure 14. If desired, the reformation products of reaction (3) may undergo a mildly exothermic (-41 kJ/mol) two-stage water gas shift (WGS) reaction (5) to increase the fraction for H₂ in syngas while converting most of the CO to CO₂ by further reaction with steam over Fe-Cr alloy catalysts. The first stage of WGS is accomplished at 300-500°C, while the second stage is carried out at lower temperatures around 200°C to benefit from the Le Chatelier shift to achieve complete conversion of CO to CO₂. As a result, methane is

converted primarily to H₂ for ease of electro-oxidation in the SOFC and to obtain high cell performance. Naturally, these extra process steps lead to loss of conversion efficiency as the steam reforming reaction requires an endothermic enthalpy change of + 206 kJ/mol.

Both external and internal reforming of methane has been under consideration and development by SOFC developers to supply syngas to the cell stacks. As internal

reforming integrated with a SOFC is considered to be a more efficient system than coupling to external reforming, there has been more attention to the former approach. In internal reforming, the endothermicity of the reforming reaction helps provide part of the cooling needed for the cell stack, where the highly exothermic oxidation reactions occur at the anode. Additional stack cooling is accomplished by recycling excess air employed at the cathode up to 3.5 to 4 times more than the stoichiometric requirement.

For external reformer-SOFC systems, on the other hand, the only means for cooling the cell stack is by dramatically increasing the airflow through the cathode to about 7.7 times the stoichiometric amount. This suggests that external reforming will require nearly twice the amount of excess air at the cathode as internal reforming, which places external reforming at a disadvantage. However, a modeling study that assumed a hybrid external reformer/SOFC configuration, which is pressurized by a gas turbine and utilizing a cathode recycle can be as efficient as the internal reforming SOFC system [327].

The stand-alone fuel reformer technology for external steam reforming of methane is mature and commercially available, and falls outside the scope of this article. Some of the commercial reformer designs have been reviewed elsewhere [328], and it will not be discussed here.

Hydrogen derived from external steam reforming of methane or natural gas has been the desired fuel of choice for most fuel cells including SOFCs [328]. Kinetic studies of hydrogen oxidation on metal, cermet, as well as MIEC oxide anodes have been published widely. Although hydrogen is arguably the simplest and easiest fuel to oxidize, the mechanistic details of its oxidation kinetics remain unresolved. Kinetic mechanisms that have been proposed to date are comparatively reviewed elsewhere [308,329]. As a formal review of prior work on hydrogen oxidation in SOFC anodes also lies outside the scope of this article, only the pertinent aspects will be highlighted below.

Ongoing debate about the mechanistic nature of H_2 oxidation on SOFC anodes involves different interpretations of the kinetic results, which were based mostly on the behavior of observed cell performance (e.g., current density, overvoltage, electrode impedance, etc.) measured as a function external parameters such as cell voltage, temperature, or partial pressures of reactants. The rate of oxidation was reported to be governed by the reaction of gaseous H_2 with the adsorbed oxygen on thin film well-defined Ni anode surfaces that were patterned in 5- μm wide strips on YSZ electrolyte by photolithography, suggesting an Eley-Rideal type of reaction mechanism [330]. This group suggested that the oxidation reaction occurred at the *tpb*, and the rate-determining step was proposed to be either the dissociative adsorption of reactants or the surface diffusion of adsorbed species on the Ni surface [331]. In a different study that also employed patterned Ni anodes, reaction kinetics was found to be governed by a process with a large activation barrier of about 0.88 eV, and the proposed catalytic mechanism involved H_2O leading to a hydroxylated YSZ surface that allows the migration of protons along the YSZ surface towards the *tpb* to react with the surface oxygen [265]. For H_2 oxidation on Pt anode on YSZ electrolyte, the rate determining process was proposed to be the exchange of hydroxyl radicals between the Pt and the YSZ surface at *tpb* [332]. A similar conclusion is recently obtained by an *in operando* spectroscopic study that employed electrochemical imaging of the Pt/YSZ system at 300 mTorr total pressure and between 550 and 750°C by spatially resolved x-ray photoelectron spectroscopy (EC-XPS), which reported that the rate determining step (rds) involved the diffusion of adsorbed H

from Pt to $O^-(\text{YSZ})$ on the YSZ surface to generate $OH^-(\text{YSZ})$ [333]. The study unambiguously established that the rate-determining step involves H spillover from Pt to YSZ. This sluggish process is purely chemical in nature, and as expected, not accelerated by the electrical field or cell voltage. The charge transfer step involves electron hopping from $OH^-(\text{YSZ})$ to Pt across the Pt/YSZ interface, which of course is accelerated by electrical fields. Based on the EC-XPS results, the study proposed the following reaction pathway for H_2 oxidation on Pt/YSZ:

Electrode kinetics studies using electrochemical impedance spectroscopy (EIS) technique also gave divergent results. While H_2 oxidation on patterned Ni anodes resulted in one semicircular arc [331], it resulted in two clearly separated arcs in the case of Ni/YSZ cermet anodes, indicating two rate limiting processes at the anode that are in series. The low frequency arc was attributed to hydrogen dissociation and diffusion on Ni, and the high frequency arc was ascribed H transfer from Ni to zirconia surface followed by charge transfer near *tpb* [334]. Yet a different study on Ni/YSZ cermet anodes reported, this time, three semicircular arcs in their EIS spectra, suggesting three different rate-limiting processes such that the low frequency arc was associated with a two-electrons transfer process, while the medium arc was attributed to adsorption of water on Ni [319]. In contrast to the low and medium frequency arcs that exhibited strong dependence on reactant concentration and anodic overvoltage, the high frequency arc was sensitive to the cermet microstructure but almost insensitive to reactant pressures and cell potential, and hence, was attributed to transfer of protons across the Ni/YSZ interface. In this regard, it is important to maintain control of the electrode microstructure, and patterned electrode studies are helpful to isolate or minimize the complications arising from microstructural differences and their respective impact on electrode kinetics.

A thermodynamic modeling study invoking equilibrium potentials has considered three reaction pathways for H_2 oxidation on Ni anodes, including oxygen spillover, hydrogen spillover, and interstitial hydrogen transfer, with an intent to reconcile differences in the reported results [335]. This study suggested, albeit inconclusively, that the strong nonlinear dependence of gas phase H_2 and H_2O concentrations is consistent with a rate determining step involving charge transfer during hydrogen spillover from the Ni surface to a hydroxyl group on YSZ. Recently, an isotopic study employing Pt, Cu and Ni catalytic cermet anodes with YSZ and GDC electrolyte supports concluded that H_2 surface exchange and dissociation occurs primarily on the metal catalyst surface of the cermet anode structure, and spillover to the inert oxide support [336].

A direct result of using an external reformer for methane is the production of syngas, which is the fuel fed into the SOFC stack for conversion. In that regard, oxidation kinetics of $CO+H_2$ mixtures have been investigated on various catalytic metal and cermet

anode materials as well as MIEC-based anodes [311,337,338]. As expected, the oxidation kinetics of CO and H₂ are equally important from the point of view of internal reforming of methane. Naturally, there is also water-gas shift reaction (15) taking place at the anode, but the rate of this reaction has been reported to be much faster than the rates of oxidation reactions at the anode [339]. This assessment may have important implications for SOFC operation by virtue of the water-gas shift reaction equilibrium. When operating at high fuel utilization, the local fuel mixture downstream of the anode increasingly shifts to CO-rich compositions resulting in increased polarization losses along the fuel flow path, while the increased H₂O formation shifts the reaction in favor of H₂ formation. In other words, the fast water-gas shift reaction helps reduce concentration polarization [340]. Such dynamic equilibrium that shifts spatially along the anode requires proper control of fuel composition, gas flow rates, and cell operation.

It is generally agreed that H₂ oxidation kinetics proceed much faster than CO as represented by a higher polarization resistance for CO-CO₂ mixture on Pt anode than for H₂-H₂O mixtures [332]. At high CO content exceeding 20% at 800°C, it is reported that CO retards the overall anode kinetics for syngas oxidation. As anode kinetics is strongly dependent on oxygen partial pressure, i.e., oxygen activity, kinetic experiments that were carried out with H₂/H₂O and CO/CO₂ gas mixtures at carefully controlled constant oxygen activity reported that the electrochemical oxidation rates for H₂ are nearly 2 times faster than for CO at 800°C [339]. This study also reported that the oxidation reaction rates obtained for reformed CH₄ on the Ni/YSZ cermet anode at T~800°C is almost equal to that for H₂-H₂O at the same effective oxygen activity, suggesting that H₂ oxidation governs overall cell performance for S/C ratio > 1. Ni is inherently a good catalyst for CO oxidation, but unlike hydrogen, the inferior kinetics for CO may be due to its inability to spillover from the metal catalyst on to the YSZ surface. The effect of composition and dilution effects of H₂/H₂O and CO/CO₂ fuel gas mixtures were studied on Ni/YSZ cermet anodes using multi-component gas transport models with experimentally measured electrochemical kinetic parameters [341]. The results showed that as long as the H₂ content of the H₂+CO syngas fuel mixture is high (i.e., > 50%), the electrochemical performance of the fuel cell is not affected by the presence of CO, where the water-gas shift reaction plays a major role in reducing anode polarization losses. Regardless, however, higher binary diffusivities (i.e., lower concentration polarization) of H₂-H₂O and faster oxidation kinetics of H₂ provide significantly better cell performance than by CO.

Although CO by itself is not considered a desirable fuel for SOFCs due to its slower oxidation kinetics than H₂ and its propensity for coking, it has recently been demonstrated that it is nevertheless a viable fuel for SOFCs, achieving high power densities approaching within 10% for H₂ on Ni/YSZ anodes, as well as cell stability with no carbon deposition under constant current conditions, operating continuously for nearly 400 h at 850°C [267]. This is in agreement with other studies [342]. A recent study on patterned Ni anodes on YSZ indicated only slightly higher polarization losses for CO than for H₂ oxidation, suggesting similar oxidation mechanisms for these fuels that challenge the validity of the proton diffusion pathway [343]. A separate study that comparatively investigated the diluent effects and oxidation kinetics of H₂, CO, and syngas on Ni/YSZ and Cu/GDC cermet anodes reported faster rates for CO oxidation on Co-added Cu/ceria cermet anodes, where the maximum SOFC power density for CO was

370 mW/cm² at 700°C, while it was 310 mW/cm² for H₂ on the same anode [344]. This result, however, is in contradiction with others that consistently reported higher cell performance with H₂ oxidation on Ni/YSZ anodes than with CO, suggesting that the Co-added Cu/ceria cermet anode has better catalytic properties than Ni/YSZ. The implication is that SOFCs employing dry syngas and Ni/YSZ anode structures can possibly utilize only the H₂ components of syngas effectively.

4.2.2. Internal reforming of methane in SOFCs

Internal reforming overcomes the need for an external reforming for fuel processing, which adds cost and complexity to the SOFC operation, and also reduces overall efficiency of the system as discussed previously in sections 2.2 and 4.2.1. The heat released by the electrochemical oxidation reactions of the fuel at the anode helps drive the endothermic reforming reactions (3) and (4). Under typical SOFC operating conditions, the heat produced at the anode is significantly larger than the heat consumed for the reforming reactions. Similarly, the cooling load for the cell that is normally provided by excess air through the cathode compartment is reduced by 50% for internal reforming as compared to external reforming (see section 4.2.1. above). As the reforming product H₂ (and CO) is readily oxidized at the anode and removed from the reaction environment, the reforming reactions can proceed well beyond the thermodynamic equilibrium, as dictated by the Le Chatelier principle. Another advantage of internal reforming is that H₂O and CO₂ generated by the electrochemical oxidation of the reformation product syngas serves as internal reforming agents for methane, eliminating the need for an external steam generator. The high operating temperature of SOFCs also help promote the endothermic reforming reactions (5) and (6) to proceed faster. On the other hand, internal steam reforming poses technical challenges in several areas; 1) high propensity for carbon deposition, or coking, that deactivates the catalysts and anodes, 2) requirement for the use of large steam-to-carbon (S/C) ratios generally ≥ 3 to minimize or eliminate coking, 3) thermal stresses due to large temperature gradients that can develop across the cell by the cooling effect of the reforming reactions.

Several terminologies are frequently employed in the literature to distinguish different internal reforming configurations. Pre-reforming is sometimes used to describe partial

Figure 15. Schematic of the cell configuration showing, (a) the pertinent reactions across the fuel cell as well as in the reforming catalyst added on top of the anode to accomplish gradual internal reforming (GIR) of methane, (b) a design concept for adapting GIR to a planar SOFC. “Reprinted with permission from ref. [345] Klein JM, Henault M, Roux C, Bultel Y, Georges S, J. Power Sources, 2009; 193: 331-337. Copyright (2009) Elsevier”

reforming of methane prior to introduction on to the catalytic SOFC anode. In indirect internal reforming (IIR), most of the reforming reaction takes place in a catalytic passage generally located in between the cells before methane enters the anode. The advantage of IIR is that the physically separated catalytic anode may be made of a different material than the reforming catalyst used in the passage. This situation is quite different from direct internal reforming (DIR), where the anode serves the dual function as both the reforming catalyst and the oxidation catalyst to accomplish the chemical reforming reaction as well as the electrochemical oxidation of the reforming products H_2 and CO . Another configuration, called gradual internal reforming (GIR), involves a porous catalytic layer for the reforming reaction added on top of the anode, whereby separating the catalytic reactions from the electrochemical oxidation reactions as depicted in Figure 15. In fact, this approach has been tested successfully for nearly 200 h of stable operation with humidified CH_4 under current carrying conditions, although with modest cell performance of less than 60 mW/cm^2 of maximum power density obtained at 900°C [345].

Ni-based cermet anodes have been used widely for this purpose, as Ni is a good hydrocarbon cracking catalyst and is inexpensive. But by the same token, Ni promotes coking, or carbon deposition, which leads to rapid deactivation of the anode and degradation of cell performance. For this reason, excess steam with steam-to-carbon ratios (S/C) that may be as high as 3.0 or above are employed to minimize coking by moving the overall gas composition outside the thermodynamic carbon deposition region in the C-H-O equilibrium diagram (see section 5.1. Carbon deposition). Beside thermodynamic considerations, the catalytic effect of the anode material also plays a role in carbon deposition, as well as the nature of the support material due to metal-support interactions discussed above (see section 3.1.1. Metal-support interactions). For example, carbon deposition during methane internal reforming over Ni/scandia-stabilized zirconia (ScSZ) cermet anode was found to be significantly less than for Ni/YSZ cermet anodes, which was still less than the Ni/samaria-doped ceria (SDC) cermet anode, while the Ru/YSZ cermet anode gave the overall best results possibly because, unlike Ni, Ru does not dissolve carbon [346]. Naturally, the use of high S/C ratios that may avoid or discourage carbon deposition also comes with several negative consequences. Strong adsorption of H_2O becomes more pronounced at high steam partial pressures, which results in deactivation of the catalytic Ni surface, or in extreme cases, may even lead to the formation of NiO. Maintaining such a high S/C ratios in the SOFC may require the use of an external steam generator, which demands additional energy for steam generation and hence, reduce overall efficiency.

Most studies on internal reforming of methane on SOFC catalytic anodes have preferentially involved steam as the gasifying agent. However, dry reforming with CO_2 was also employed, and reviewed recently elsewhere [347-350]. Rhodium catalyst-support interactions during dry reforming of methane studied systematically by varying the acidity character of the support oxide, not only highlighted the role of lattice oxygen spillover on to the Rh surface but also achieved the highest conversion with Rh/YSZ catalyst system while the MgO support, which is a basic oxide, provided the lowest activity [113,351].

The reforming product syngas components undergo oxidation at the anode, which involves both H_2 and CO oxidation kinetics and their competing reaction mechanisms to

access surface active sites. This also involves diffusion and mass transport to and from the catalytic sites of the reactants CH_4 , H_2 and CO , and their oxidation products H_2O and CO_2 within the pores of the cermet anode structure. In addition, the reaction products H_2O and CO_2 undergo further reforming reactions with methane on the catalytic anode surface as well as in the gas phase.

Optical *in situ* spectroscopies such as Raman and infrared imaging developed in the last decade have been extremely helpful in examining surface intermediates and temperature variations during hydrocarbon and H_2 oxidation reactions on SOFC anodes [352]. Indeed, a recent study using electrochemical measurements coupled with gas phase vibrational Raman [353] and Fourier transform infra red emission (FTIRES) spectroscopies of both methane and ethanol internal steam reforming on Ni/YSZ cermet anode at 700-800°C indicated that reforming proceeds both in the gas phase and on the catalytic anode surface [354], and that adsorbed $\text{CO}_{2\text{ad}}$ on the Ni surface is identified as an intermediate of the CH_4 oxidation reaction as well as the for the oxidation of the surface carbon via electrochemically pumped oxygen [355,356].

A comparative study of methane internal reforming with S/C ratios between 0 and 3 on Ni/YSZ and Ni/GDC cermet anodes indicated no difference in the reforming activities of the two anodes at 950°C and the gas compositions were in chemical equilibrium [357]. At this temperature, most of the endothermic reforming reactions were nearly complete within the first half of the anode length along the flow direction, which may lead the cell cracking due to deleterious thermal stresses. Indeed, achieving complete reforming can induce large temperature gradients, some of which can be mitigated by a pre-reforming operation. Temperature distribution measurements using near infrared thermal (NIR) imaging of anode surfaces in a 10 kW SOFC stack indicated local variations in temperature average around 4°C/mm for S/C= 4 and 6 along the Ni/YSZ cermet anode, but for the case of S/C=3, the variation was > 20°C within the first 4 mm of the anode length [358]. These large thermal gradients are certainly of major concern for the structural and thermal stability of stack design.

Similar results were reported by an independent study involving *in situ* measurement of gas phase compositions at 700°C during steam internal reforming of methane using vibrational Raman spectroscopy, where surface temperature differences between the anode entrance and exit may reach 30-35°C [359]. NIR and FTIRES studies of methane and biogas oxidation on Ni cermet anodes, the cooling effect of the endothermic reforming reactions for methane and biogas have dropped the local anode surface temperature, respectively, by 1-4°C and 12-14°C, regardless of cell polarization [360]. Much of the *in situ* analytical and diagnostic methods to probe the SOFC anode kinetics have recently been reviewed [352].

Figure 16. Plots of forward CH_4 reaction and turnover rates at 600°C for dry and steam reforming of methane on clusters of metal dispersions on oxide supports using $\text{CH}_4\text{-H}_2\text{O}$ and $\text{CH}_4\text{-CO}_2$ mixtures at 100 kPa total pressure (balance He) on Pt// ZrO_2 (top panel), Ru/ Al_2O_3 (middle panel), and Ni/ MgO (bottom panel) catalysts, indicating the linear dependence of reforming rates with respect to CH_4 pressure, but insensitivity to steam, CO_2 , H_2 and CO partial pressures. “Top panel reprinted with permission from ref. [368] Wei J, Iglesia E, J. Phys. Chem. B, 2004; 108: 4094-4103. Copyright (2004) American Chemical Society”, “Middle panel reprinted with permission from ref. [369] Wei J, Iglesia E, J. Phys. Chem. B, 2004; 108, 7253-7262. Copyright (2004) American Chemical Society”, “Bottom panel reprinted with permission from ref. [366] Wei J, Iglesia E, J. Catal. 2004; 224: 370-383. Copyright (2004) Elsevier”

An experimental study of cell stability and performance back by modeling of SOFC transport, chemistry and electrochemistry on oxidation of humidified CH_4 ($\sim 3\%$ H_2O), dry reforming ($75\% \text{CH}_4 + 25\% \text{CO}_2$), and methane partial oxidation ($75\% \text{CH}_4 + 25\%$ air) reactions reported that cell stability is greatly affected by coking and thermal gradients that can lead to mechanical cracking [361]. Stable cell operation was observed under galvanostatic conditions at 800°C over 8 h for both $75\% \text{CH}_4 + 25\% \text{CO}_2$ and $75\% \text{CH}_4 + 25\%$ air mixtures at high current densities ($> 1 \text{ A/cm}^2$), but increasingly more severe cell degradation with decreasing current density. On the other hand, decreasing the cell operating temperature helped enhance cell stability, as expected. These results were in agreement with coking being responsible for the observed cell degradation. The modeling results also indicated that there are significant temperature gradients as much as 6.6°C/mm (or, 4°C over 0.6 mm) across the anode, which is in good qualitative agreement with the gradients measured by NIR above. This modeling study also showed that such thermal gradients, which are primarily due to the endothermic nature of the internal reforming reaction, could be eliminated by employing an inert interlayer

(such as, partially stabilized zirconia) between the YSZ electrolyte and the porous anode [361,362]. This inert interlayer also mitigates coking by impeding the transport of CH₄

Table 5; Forward reaction parameters for CH₄ reforming on various catalysts at 600°C for a total pressure of 100 kPa. (Data compiled from references # 366-369).

Catalyst	Co-reactant	Turnover rate (s ⁻¹)	Activation Energy (kJ/mol)	Ref.
Pt/ZrO ₂	CO ₂	12.8	83	[368]
	H ₂ O	13.1	75	
	None	12.4	78	
Ru/Al ₂ O ₃	CO ₂	3.9	96	[369]
	H ₂ O	4.2	91	
	None	3.8	99	
Rh/Al ₂ O ₃	CO ₂	4.2	111	[367]
	H ₂ O	4.1	109	
	None	3.9	108	
Ni/MgO	CO ₂	4.0	105	[366]
	H ₂ O	4.1	102	
	None	3.8	99	

into and H₂ out of the porous Ni/YSZ anode structure, thus slowing down the reforming reaction and decreasing the critical current needed for stable cell operation without coking. This is an important consideration from a practical point of view for employing SOFCs for generation of electricity and production of syngas/chemicals using methane oxidation, reforming or transformation reactions on Ni/YSZ anodes without coking problems.

Despite much progress, there is yet no consensus on the internal reforming reaction pathways and mechanisms due to the complexity of the reaction system and the difficulty in determining the individual elementary steps [363]. Several reaction mechanisms, including first order kinetics with respect to methane, L-H type kinetics [364], as well as power law expressions [365] have been proposed. In a series of

rigorous studies using isotopic measurements, it was reported that the reaction kinetics was first order with respect to the methane partial pressure but practically independent of the respective partial pressures of reforming agents H₂O or CO₂. This is depicted in Figure 16 for Pt/ZrO₂, Ru/Al₂O₃, and Ni/MgO supported catalysts, and shows linear behavior of reaction rate for CH₄ pressure but indicates lack of dependence on H₂O, CO₂, H₂ or CO partial pressures. In all cases studied, the C-H bond activation was found to be the slow step for both reforming reactions as well as the CH₄ decomposition reaction on Ni/MgO catalysts [366], Rh catalysts supported on Al₂O₃ and ZrO₂ [367], and on other noble catalysts including Pt and Ir, and Ru [368,369]. The results suggest that the water gas shift reaction is sufficiently fast and equilibrates readily, as the reformation rates were practically unaffected by the CO₂ or H₂O contents. Based on their systematic study of isotopic effects and reaction kinetics on several supported metal catalysts, this research group proposed a first order reaction rate with respect to methane. The activation energies and turnover rates, i.e., frequencies, for methane internal reforming on Pt, Ru, Rh, and Ni catalysts are summarized in Table 5. Clearly, Pt is the best performing reforming catalyst among the others studied, with significantly lower activation energy. A reaction mechanism that includes a sequence of elementary steps for hydrogen abstraction towards the formation of chemisorbed carbon and hydrogen species on the catalyst surface. The following elementary steps and surface intermediates on that Ru/Al₂O₃ catalyst were proposed [369]:

However, this view was challenged by other studies that reported dependence of the reaction rate on the partial pressure of both the products and the reactants [218,365,370]. A detailed analysis considered a large number of reaction mechanisms for methane steam reforming on Ni/MgO catalyst, and proposed a L-H type of mechanism [371] that postulated the reaction rate is dependent on the partial pressures of methane, hydrogen and water vapor, and also the rate determining step is governed by the reaction between the adsorbed carbon and oxygen species according to the reactions below.

Steam reforming kinetics on catalytic Ni film and Ni/YSZ cermet anodes in SOFCs indicated a L-H type dependence on the partial pressures of methane and water vapor, and suggested competitive adsorption of carbonaceous and oxygen species, or OH [364]. Much of the previously reported studies have been reviewed recently [203,363,372]. Kinetic studies of methane internal steam reforming reaction on Ni/YSZ cermet anode in a plug-flow tubular SOFC at 700-1000°C and for partial pressures P_{CH_4} =2-40 kPa, P_{H_2} =10-70 kPa, and P_{steam} = 10-70 kPa at $P_{\text{total}} = 1$ atm, indicated that the reaction rate expression was first order with respect methane, and showed a weak dependence on hydrogen but a strong negative dependence on steam [370]. Oxidation as well as steam reforming of methane on Ni/YSZ cermet anodes exhibited significantly different kinetic behavior than that on Fe/YSZ anodes [373]. While only small amounts of H_2 and CO was produced on Fe/YSZ anode due possibly to oxidation of Fe, the catalytic activity of Ni/YSZ anode exhibited high activity producing large quantities of H_2 and CO under low humidity ($0 < \text{H}_2\text{O}/\text{CH}_4 < 1$) conditions, and no carbon deposition was observed under current carrying conditions, indicating the role of lattice oxygen in removing surface carbon.

It is clear from the preceding discussion that there is still no consensus yet on the mechanistic details of the internal reforming kinetics on metal catalyst surfaces. The degree of catalyst dispersion on the support material and catalyst particle size, diffusional and mass transport effects, metal-support interactions, and operational parameters used in these studies may all influence the kinetic results and the proposed reaction mechanism.

Another important consideration has to do with significant variations in the temperature distribution in the cell during internal reforming [358-360]. The endothermic enthalpy change of the reforming reaction as well as carbon deposition due to cracking, or pyrolysis, of methane on the catalyst surface leads to degradation in cell performance. Hence, it was suggested that some degree of external reforming may be helpful to remove particularly higher hydrocarbons that inherently have higher propensity for cracking than methane [202].

Coking, or carbon deposition due to the cracking of methane, and other hydrocarbons, presents one of the major technical difficulties in achieving effective internal reforming without cell degradation and loss of performance. This problem becomes detrimental especially at low current densities and low steam-to-carbon (S/C) ratios. However, oxidation of simulated steam reforming gases of CO and H₂ on Ni/YSZ cermet anodes indicated that the best SOFC performance was achieved with S/C ratio = 0.5 at 950°C, and single cell experiments over several weeks showed only slight carbon deposition on the reference electrode at the anode side and on the Ni current collector, again suggesting the role of lattice oxygen in removing surface carbon [342]. Stability of the Ni/YSZ cermet anodes were also tested galvanostatically in dry flowing methane at 400 mA/cm² current density at 950°C for with only 70 mV reduction in performance over 1000 h. On the other hand, it has been reported in the literature that S/C ratios sometimes as high as 3-5 may be required to avoid carbon deposition over Ni/YSZ anodes [374]. Several SOFC cermet anode compositions were investigated for carbon tolerance for internal steam reforming of methane and propane, and indicated that Ru/ScSZ cermet anode has better carbon tolerance than Ni/YSZ [346]. It was also suggested that electrochemical pumping at sufficiently high current densities could effectively remove the carbon deposits from the anode surface via oxidation [227,375]. Indeed, no carbon deposition was observed during CO oxidation on Ni/YSZ anodes under galvanostatic conditions at 414 mW/cm² at 850°C for 375 h of continuous operation without any discernable degradation in SOFC performance [267]. Using internal steam reforming with 97% CH₄ + 3% H₂O fuel mixture on Ni/scandia –stabilized zirconia cermet anode, a maximum power density of 640 mW/cm² was achieved at 900°C, and the cell performance was stable over 150 hours at 500 mA/cm² current density, while degradation of cell performance due to carbon deposition was observed at 800°C operation [376]. The results suggest that the collective actions of high temperatures and high current densities may be required for electrochemical removal of carbon deposits.

As an effective cracking catalyst for hydrocarbons, Ni has sufficient solubility for carbon that promotes coking on Ni-cermet anodes in SOFCs. One strategy to reduce the propensity for coking is to reduce the activity of Ni by alloying it with a metal such as Cu or Au that lacks catalytic activity for cracking or for activation of C-H bonds. Indeed, NiAu alloy-cermet anode containing 1 at% Au was tested for methane rich steam reforming conditions in the SOFC at temperatures 700-900°C and showed high tolerance to coking even at a methane-to-steam ratio of 3 [377]. At a constant cell voltage of 500

mV corresponding to a cell current density of about 300 mA/cm², the cell current remained practically unchanged during the 60 hours of stability testing at 850°C, indicating lack of degradation and improved carbon tolerance. Similarly, YSZ- and

Figure 17. Oxidation of 2:1 mixture of CH₄ and H₂O, respectively, on Ni/La_{0.1}Ce_{0.9}O_y cermet anode giving nearly 850 mW/cm² peak power density at 650°C. ‘Reprinted with permission from ref. [383] Zhu H, Wang W, Ran R, Shao Z, Intern. J. Hydrogen Energy, 2013, 38: 3741-3749. Copyright (2013) Elsevier”

CeO₂-based cermet anodes containing Cu or NiCu alloy have been developed for oxidation of hydrocarbons with stable cell performance over hundreds of hours [23,311-314,378-380]. Cu-Co-ceria anode also showed stable SOFC operation in simulated biogas environment at 750°C with humidified H₂, CH₄ and H₂S additions for nearly 740 hours, but the anode was found to be a mixture of the fluorite structure Cu_xCo_yCe_{1-x-y}O_{2-γ} phase with CuO and Co₃O₄, making it difficult to identify the active phase responsible for the observed stability [381]. In general, Cu-based anodes have been effective in mitigating hydrocarbon cracking and minimizing carbon deposition in SOFCs as Cu is a

poor catalyst for C-C bond formation and does not dissolve carbon, but at the same time, Cu is a poor catalyst for activating the C-H bond and hence requires the addition of an active catalyst to achieve methane oxidation. In most cases, CeO₂ is employed in connection with Cu as the catalytically active component of the cermet anode composition.

Catalytically active MIEC-based oxide anodes provide another opportunity to move completely away from the conventional Ni-based anodes, or other transition metals such as Fe, that promote cracking and carbon deposition on the SOFC anode surface during steam internal reforming of methane. It was reported that Ni-free La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃ anode material was redox stable and exhibited electrochemical performance (200 mW/cm² at 900°C for CH₄ with 3% H₂O) comparable to that of Ni/YSZ cermets for methane oxidation without the need for excess steam [197]. Despite its redox stability, however, the electronic conductivity of this material is not sufficiently high under reducing conditions (~1 S/cm at 900°C in wet H₂) but has tolerance to sulfur especially for the high Cr content composition La_{0.75}Sr_{0.25}Cr_{0.6}Mn_{0.4}O₃, but shows several decomposition products when the lower Cr-content composition La_{0.75}Sr_{0.25}Cr_{0.4}Mn_{0.6}O₃ is exposed to 10% H₂S containing humidified H₂ at 950°C for 5 days [321]. Improvement in cell performance and sulfur tolerance was reported by employing Sr₂Mg_{1-x}Mn_xMoO_{6-δ} double-perovskite anodes on the 300 μm thick LSGM electrolyte. Best cell performance with methane was obtained with the Sr₂MgMoO_{6-δ} composition, which achieved a maximum power density of 438 mW/cm² at 800°C for dry CH₄ and 338 mW/cm² for wet

(3% H₂O + 97% CH₄) methane [322]. La substitution on the Sr-site in Sr₂MgMoO_{6-δ} (SLMM) has provided further improvement in cell performance, where the maximum power density values for the Sr_{1.2}La_{0.8}MgMoO_{6-δ} anode composition increased from the previous 438 mW/cm² to 543 mW/cm² at 800°C for dry CH₄, and from 338 mW/cm² to 550 mW/cm² for wet (3% H₂O + 97% CH₄) methane [382]. It was proposed that the Mo⁺⁶/Mo⁺⁵ redox couple, as well as cation ordering are important for catalytic activity, and that La-substitution decreased the Mg/Mo ordering parameter rendering the less ordered LSMM electrochemically more active. Significantly better SOFC performance and coking resistance was obtained for Ni/La_{0.1}Ce_{0.9}O_y cermet catalytic anodes employed for internal steam reforming of methane that resulted in high power densities up to 850 mW/cm² at 650°C [383], as shown in Figure 17. Nearly complete methane conversion was achieved for T > 800°C, and methane conversion at a low steam-to-carbon ratio of 0.25 remained stable for nearly 280 hours over Ni/La_{0.1}Ce_{0.9}O_y catalytic anode at T < 650°C. High catalytic activity for methane conversion under low humidity conditions was also demonstrated on a member of the titanate-based perovskite family, namely in La₄Sr₈Ti₁₁Mn_{0.5}Ga_{0.5}O_{37.5} (LSTMG)-based YSZ composite anodes, which exhibited a high concentration of disordered oxygen defects in its crystal lattice that was key to its redox properties [384]. Furthermore, the study demonstrated a remarkably low polarization resistance of 0.36 ohm.cm² for this anode material giving a maximum cell power density of 350 mW/cm² at 950°C in 97.7% CH₄ + 2.3% H₂O fuel mixture, which was not much lower than the 500 mW/cm² obtained for 97.7% H₂ + 2.3% H₂O fuel mixture on the same composite anode at the same temperature.

Effect of catalytic promoters based on alkaline earth metal oxides added in small quantities up to 10 mol% to Ni/YSZ cermet SOFC anodes for steam internal reforming reported that SrO and CaO addition was effective in reducing coking, while promoting the methane reforming reaction nearly as effectively as the control Ni/YSZ cermet anode [385]. At 800°C, methane conversion was nearly complete at > 99% on all tested anodes, and carbon deposition was significantly reduced by the addition of CaO and SrO to Ni/YSZ cermet. It was proposed that the addition of these strongly basic oxides modified the electronic structure of metallic Ni to a more cationic state, thus suppressing coking. However, the benefits gained by the addition of these alkali earth oxides came at the expense of slight reduction in fuel cell performance.

There have also been modeling studies to understand and map out the parameter space for optimum operating conditions for SOFCs fueled by internally reformed syngas [386,387]. A thermodynamic study of a tubular SOFC stack fueled by internally reformed methane provided insight into the importance of effective management of heat losses in the stack, and assuming an efficient stack design for air preheat and heat recovery from flue gases have predicted a first law conversion efficiency of 52% based on lower heating value (LLV), and a second law efficiency of 86% (LLV) [388]. The mismatch between the moderately endothermic internal steam reforming reaction (3) and the highly exothermic oxidation reactions of syngas components H₂ and CO gives rise to non-uniform temperature distribution in the SOFC that may lead to mechanical failure of the cell due to induced thermal stress. A mathematical model was developed to investigate the benefits of adding small amounts oxygen to internal steam reforming of methane in the feed to maintain autothermal reaction [389]. Although oxygen addition was found to be beneficial for lowering the demand for steam while achieving smoother temperature

distribution and reduced cooling at the reformer entrance, it resulted in lowering the electrical cell efficiency.

Most modeling studies for internal reforming in SOFCs usually employ empirically derived rate expressions and omit surface chemistry of intermediates. To bridge this knowledge gap, a recent modeling study revealed for the first time that incorporating the surface chemistry during the reforming reactions provides a more detailed understanding and helps explain the capacitive effects previously observed by EIS for anode polarization [390]. A related modeling study for co-generation using partial oxidation of methane in an anode-supported tubular SOFC geometry explored the benefits of introducing a chemical barrier layer on top of the Ni-based anode catalytic layer that can impede the outward diffusion and trap the electrochemically generated steam inside the pores of the anode structure [362]. As this is expected to maintain a sufficiently high S/C ratio on a local basis, the addition of the chemical barrier layer indeed helps prevent coking on the Ni cermet. The model also suggested that the barrier layer should not cover the entire anode length of the tubular SOFC but only a section at the upstream of the anode surface, and that the cell operational parameters would largely dictate the length of the barrier layer. Although the barrier layer is expected to compromise cell performance especially along the downstream section of the anode surface, this approach nevertheless presents the possibility of utilizing methane as the primary fuel directly in SOFCs without significant coking.

Another study considered counter-flow and co-flow configurations in their model to achieve autothermal operation of SOFC by thermally coupling the loads for the endothermic steam reforming reaction with the exothermic anodic oxidation reaction, and reported cooling at the reformer entrance, which is undesirable for SOFC operation [391]. Methane internal reforming study modeled for 75% methane utilization in SOFCs operating at 750°C predicted a power density of 330 mW/cm² and 47% fuel efficiency [392].

A 3-dimensional model was developed for an anode-supported planar SOFC operating at 800°C with internal reforming to understand the role of recycling the anode product gases back to SOFC in order to lower the temperature gradients and to reduce the amount of coking at the anode [393]. A co-flow system with 75% methane utilization at 0.65 A/cm² of current density and 0.7 V were considered in this model. The results indicated large temperature gradients exist both along the length of the cell (up to 16°C/cm) and across the thickness of the cell (up to 35°C/cm) particularly near the gas inlet, which can be reduced significantly to 10°C/cm and 11°C/cm, respectively, by recycling 75 % of the anode exhaust. However, this high recycling ratio lowers cell performance by reducing the relative amount of H₂, and instead, 60% recycling was suggested as an optimum value.

Anode gas recycling not only lowers temperature gradients in the cell but also eliminates the need for an external steam generator as the product gases provide the internal steam cycle [394]. Unlike direct internal reforming (DIR) that requires large quantities of steam at the fuel inlet, a modeling study predicted that the gradual internal reforming (GIR) approach, which internally generates its steam through the electrochemical oxidation of the reformation product H₂ at the SOFC anode, gives better outcomes than DIR with no loss of cell performance, lower temperature gradients, and reduced carbon deposition [395]. However, an experimental study reported that steam-

rich conditions at the of Ni-YSZ-CeO₂ anode led to cell degradation due to NiO formation, while its catalytic activity was found to be still higher than the Ni-YSZ cermet anode [365].

Possibility of recycling the anode product CO₂ provides opportunities for innovation and has generated renewed interest in dry internal reforming using CO₂ as the gasifying agent, especially for the prospects of using biogas. In experiments using CH₄-CO₂ mixtures simulating biogas on Ni-cermet electrodes, internal reforming SOFC performance reached maximum performance at the CH₄/CO₂ feed ratio of unity, resulting in a modest power density of only 51 mW/cm² at 875°C [396]. For CO₂/CH₄ < 1, no deactivation due to carbon deposition was observed. Methane conversion rate consistently showed a maximum with methane partial pressure of around 5 kPa suggesting competitive adsorption of CO₂ and CH₄ on the Ni catalyst, which is indicative of L-H type kinetics. In similar dry internal reforming experiments using CH₄-CO₂ mixtures, 50 hours of stable SOFC operation at 1000°C and 200 mA/cm² was reported on Ni/scandia –stabilized zirconia cermet anodes without carbon deposition, suggesting that carbon deposits can be removed electrochemically from the anode surface [375].

4.2.2.1. *Electrochemical promotion of methane by NEMCA effect*

As discussed in detail in section 3.1.1, the NEMCA effect can significantly enhance catalytic rates of methane oxidation on the anode electrocatalysts beyond the Faradaic limit by tuning the work function of the metal catalyst and hence the surface binding energy of adsorbates via an externally applied current or potential to the electrochemical cell. An early study employed a methane-oxygen mixture with respective partial pressures of P_{CH₄} = 2.6 kPa and P_{O₂} = 1.9 kPa over Pd film catalysts deposited on the YSZ electrolyte of an electrochemical cell configuration CH₄, O₂, CO₂, Pd/YSZ/Au, CH₄, O₂, CO₂, where the catalytic rate of methane oxidation at 400°C was enhanced by electrochemical pumping up to a factor of 150 higher than the Faradic rate otherwise expected from the electrochemical supply of oxide ions on to the Pd catalyst [397]. This was attributed to the reverse spillover of oxide ions under the influence of the positive overvoltage from the YSZ on to the Pd catalyst, almost fully covering its surface. These reverse spillover oxide ions that form a neutral double layer on Pd/gas interface (see Figure 5) are strongly bonded to Pd and less reactive towards CH₄ than chemisorbed oxygen, and merely serve as promoters to affect the binding strength of chemisorbed O₂ and CH₄ on Pd. As the positive potential increases, the work function of Pd also increases which leads to weakening of the Pd-O binding strength of the dissociatively chemisorbed oxygen. Decreased coverage of the Pd surface from strongly bonded oxygen makes room for dissociative chemisorption of CH₄. The reaction was also reported to obey the L-H mechanism with first order kinetics with respect to methane and zero order with respect to oxygen.

More recently, similar results of electrochemical promotion of methane oxidation reaction on Pd/YSZ anode with enhanced CO₂ formation were reported, where an enhancement ratio of 18 was achieved for CH₄ consumption with Faradic efficiencies up to 1400 [398]. Electrochemical promotion of methane oxidation was further extended to include ceria as part of the anode cermet component. Methane oxidation in excess oxygen at 320-450°C using a 1.3%CH₄+4.5%O₂ reaction gas mixture on Pd-impregnated

Pd-CeO₂/YSZ and Pd/YSZ anodes reported enhanced electrochemical promotion on Pd/YSZ anode under electrochemical pumping, and reasonable catalytic activities for the two anodes under OCV conditions with improved OCV values in the presence of ceria, but failed to achieve electrochemical promotion, i.e., the NEMCA effect, on the Pd-CeO₂/YSZ anode at either anodic or cathodic potentials, unless a small amount of C₂H₄ at 0.3 kPa pressure was also co-fed into the cell along with the methane-oxygen mixture [399]. The high catalytic activity but lack of electrochemical promotion on the Pd-CeO₂/YSZ anode was attributed to the intrinsically high activity of ceria that can thermally supply the reverse spillover oxide ions to the Pd surface possibly faster than the electrochemical migration rate driven by the potential, such that the electro-migration effect did not play a significant role in the overall rate of reverse spillover.

Expanding the temperature regime this time to 470-600°C, similar results were reported for electrochemical promotion of methane oxidation in excess oxygen (0.4%CH₄+1.0%O₂) on Pd-CeO₂/YSZ and Pd/YSZ anodes, where catalytic activity under OCV conditions of the Pd-CeO₂/YSZ anode was found to be nearly 14 times higher than that for Pd/YSZ, and a NEMCA effect of 1.33 was observed at 470°C for the Pd-CeO₂/YSZ anode [400]. Recently, electrochemical promotion was extended to natural gas oxidation and using an inlet gas composition of 15%O₂, 5.3%CH₄, 0.24%C₂H₆, 0.07%C₃H₈ (balance He) over impregnated Pd/YSZ anode at 340-420°C, NEMCA enhancement factors of 2.7 and 2.1 were reported for CH₄ oxidation and CO₂ formation rates, respectively, demonstrating that electrochemical promotion of natural gas combustion is possible at such low temperatures [401].

Interestingly, the general concept of electrochemical promotion was extended into a primarily catalytic MIEC-based membrane reactor, where the operating principle of ion transport is not electrochemical but entirely chemical in nature and is based upon the oxide ion transport through the mixed conducting oxide under the chemical potential difference of oxygen across the membrane. Employing such a chemical reactor made of hollow fiber La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ tubular membrane coated with a thin film Pt catalyst layer exposed to an ethylene-oxygen reaction gas mixture of P_{C₂H₄} = 0.5 kPa and P_{O₂} = 1.5 kPa at 500°C, a modest enhancement in non-faradaic modification of ethylene oxidation rate was reported using this wireless-NEMCA effect [402]. It was envisioned that the mixed oxide ion and electron hole transporting La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ would supply the reverse spillover oxide ions to the Pt catalyst surface to accomplish the oxidation reaction, albeit with a rather limited NEMCA effect.

4.2.3. Direct electro-oxidation of methane

There have also been great interest direct utilization and electro-oxidation of methane and other hydrocarbons in SOFCs for power generation [28,29,131,197,216,312,403-405] as well as to achieve electrochemical transformations for chemical synthesis [42,43,131] in SOFC-based electrochemical reactors. Naturally, direct conversion eliminates many of the inefficiencies of external and internal reforming that complicate the overall process by the additional steps and a more complex balance of plant. Direct electro-oxidation is conceptually simple as depicted in Figure 18, but from mechanistic and practical points of view it is challenging to achieve. In principle, the oxygen needed to oxidize methane is supplied through the solid oxide electrolyte such that the product flue gases after

conversion are made primarily of H₂O and CO₂, where the latter can be readily captured for storage after condensing out the steam. This is obviously a desirable outcome, but by the same token, these very same products may in turn undergo steam and dry reforming reactions with methane in the gas phase as well as on the catalytic anode surface, which are primarily chemical steps in nature and introduce complications in selectively constraining the electrochemical reaction only to methane oxidation, as both CO and H₂ are also rightful fuels for the anodic reactions.

For the ideal case of direct electro-oxidation of methane, the net half-cell reactions at the cathode and anode, as well as the overall cell reaction are given by,

As the electrochemical oxidation of methane would involve the transfer of eight electrons as indicated in the half-cell net reaction (39), it is quite likely that the electro-oxidation reaction can only be accomplished in a sequence of elementary steps [23,404]. Furthermore, it is clear from the discussions of methane catalysis in the earlier sections that the first step in methane oxidation involves the activation of the C-H bond followed by successive abstraction of hydrogen to form carbonaceous surface species. These are purely chemical steps and not electrochemical in nature. So, the mechanistic sequence for methane electro-oxidation involves both chemical reactions and electron transfer steps at the anode. It was hence, argued that the terminology of “direct electrochemical utilization” can be used in this broad sense, even for internally reforming SOFCs [312].

Figure 18. Simplified schematics highlighting the anode rate processes for direct electro-oxidation of methane on catalytic MIEC (left panel) and cermet (right panel) based anodes, illustrating oxygen and electron transport pathways, the *tpb* locations at the two different anode interfaces, and the net half-cell reactions at the electrodes. Note the *tpb* covers the interfacial area for the MIEC anode, while it is along the metal particle/ionic conductor boundaries in the cermet anode. The oxygen needed for the oxidation reaction is provided through the YSZ electrolyte.

It should be noted that in sections preceding this, discussions about methane oxidation or reforming always involved co-feeding of reactants O₂, H₂O, or CO₂ along with methane into the SOFC. In this section and hereafter, however, the term “direct” electro-oxidation implies that no reactants other than the methane fuel is fed directly into the anode chamber of the SOFC, and that the oxide ion flux through the solid oxide electrolyte of the SOFC is the only source for oxygen needed for

the electro-oxidation reaction. This interpretation of “direct” oxidation may be slightly more restrictive but in principle in line with other suggestions made previously for the use of proper terminology regarding the utilization of gaseous [23,312], liquid [23,406], and solid fuels [407] in SOFCs. In some cases, though, the terminology “direct conversion” is employed in the literature even when a small amount ($\leq 3\%$) of O_2 or H_2O is co-fed along with methane into the SOFC. To avoid confusion, these studies will be explicitly identified as such in the flowing discussion.

Figure 19. Activation energy, E_a , for methane dehydrogenation as a function of the reaction (i.e., dissociative chemisorption) energy, ΔE , over fcc (211) and (111) surfaces of transition metals, denoted by red and black colored fonts and symbols, respectively. Also note that the stepped surfaces (upper left inset) in general show slightly higher dissociation barrier than the closed packed (111) flat surface (lower right inset). However, the electronic effect (indicated by arrow) is significantly more pronounced than the geometrical effect. “Reprinted with permission from ref. [411] Nørskov JK, Bligaard T, Hvolbaek B, Abild-Pedersen F, Chorkendorff I, Christensen CH, Chem. Soc. Rev. 2008; 37: 2163-2171. Copyright (2008) Royal Society of Chemistry”

positively charged [410].

In general, metal atoms located in low coordination number sites such as steps, edges, kinks and corners interact more strongly with adsorbates than atoms located on close packed surfaces with high coordination number sites such as flat surfaces and terraces. DFT calculations for methane dehydrogenation over various transition metal surfaces indicated that electronic effects largely dominate the catalytic behavior [411]. This is illustrated in Figure 19, where for example, the step atoms on Ni (211) shift the adsorption energy slightly to the left of the flat Ni (111) surface. It should be noted that when the change in geometry shifts the point for any metal along the

As documented in previous sections, theoretical and experimental evidence agree that the biggest energy barrier on the reaction pathway to methane oxidation is posed by the initial breakage of the first C-H bond to form an adsorbed methyl group, followed by subsequent hydrogen abstraction. Density functional theory (DFT) calculations for CH_4 oxidation on the Ni (111) surface indicated that C-H activation occurs on top of the surface Ni atom and its energy barrier is found to be 105 kJ/mol [408,409]. The sequential dehydrogenation of methane on Ni surface indicated that the adsorbed CH_x (where, $x = 0-3$) species prefer 3-fold sites on Ni (111) and also lower the work function of Ni, indicating that electrons are transferred from the adsorbed CH_x species into Ni that leaves the adsorbed species

□□□□□□□□□□ axis, then this indicates a purely electronic effect, or likewise, purely geometrical if shifted along the vertical axis. The step atoms on Ni (211) have lower metal coordination numbers than those on the close packed (111) surface, and make stronger bonds with intermediates as well as the transition state, and hence decrease the activation barrier. It is clear from Figure 19 that C-H bond activation for methane oxidation is largely governed by electronic effects, and not particularly sensitive to geometrical factors. From a practical point of view, this would imply that design and surface engineering of many metal catalysts may not have a major impact on catalytic activity.

Figure 20. Comparison of (a) electrochemical impedance spectra, and (b) cell performance of $\text{La}_2\text{Sn}_2\text{O}_7\text{-Ni-Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) versus Ni-GDC anode-supported SOFC at 650°C in H_2 (100 sccm) and dry CH_4 (25 sccm).

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sulfur weakens the binding energy of CH_x and increases the energy barrier for activation [408]. Interestingly, this inhibiting effect was exploited for suppressing carbon deposition on Ni/YSZ cermet anodes, where the highly active Ni edge sites were blocked off intentionally by sulfur deposition prior to ethanol oxidation. The resulting Ni-S_x surface showed significant resistance to coking and still had good catalytic activity due to the active sites available on the terraces, generating a significant power density of 400 mW/cm^2 at 850°C in ethanol fuel [412].

It is clear that the nature of the catalytic anode material, its electronic structure, composition, microstructure, and surface properties are important considerations for successful electro-oxidation of methane with practically significant SOFC performance. The salient features and requirements for effective anode materials are already discussed in detail in excellent reviews published earlier [311,313,314,317,380]. A wide variety of catalytic anode materials have been reported for methane oxidation in SOFCs including oxides. One of the early, perhaps the first, study reported for methane oxidation on an oxide anode in SOFCs, employed the electronically conducting anode material $\text{Bi}_2\text{O}_3\text{-Pr}_6\text{O}_{11}$ [216]. Dry methane oxidation on pyrochlore-structure $\text{La}_2\text{Sn}_2\text{O}_7\text{-Ni-Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) composite anodes was investigated and high catalytic activity with a significant power density of 910 mW/cm^2 at 650°C in dry methane was reported [413]. This is shown in Figure 20, which favorably compares the cell performance running on

DFT

studies also predicted that the barrier height for C-H activation is significantly lower at step edges where the CH_x is bound more strongly than on a terrace site, and that blocking the step edge sites with

dry CH₄ and H₂, with and without the La₂Sn₂O₇-pyrochlore phase in the Ni-GDC composite anode. It was reported that the pyrochlore containing anode showed significantly higher coking resistance even after 20 h of operation under 0.3 A of constant current. By comparison, x-ray diffraction analysis of the Ni-GDC anode indicated the presence of carbon under the same conditions.

As pointed out earlier, MIEC oxides possess the unusual ability to sustain large nonstoichiometries in their oxygen sublattice without phase transformations in their crystal structure. Depending on the MIEC oxide composition, charge compensation to maintain neutrality may be accomplished by either electronic transitions such as changes in the oxidation state of cations, and/or by creation of lattice point defects such as vacancies that are ionic in nature. Experimental and theoretical studies [63,92,97,98] have already indicated the importance of surface oxygen for activating the C-H bond. In this regard, the wide non-stoichiometric window offered by doped-perovskites can serve as a source and supply lattice oxygen to the catalytic surface in order to facilitate and enhance C-H bond activation. To achieve this outcome, a variety of perovskite-based catalytic anode materials including LaCoO₃ [90] La_{0.08}Sr_{0.92}M_xO_{3-δ} (where M= Mn, Fe, Co) [414] La₄Sr₈Ti₁₁Mn_{0.5}Ga_{0.5}O_{37.5} (LSTGM) [384] , and La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM) [415] were employed in order to oxidize mildly humidified (< 3% H₂O) methane in SOFCs. The latter two compositions LSTGM and LSCM were reported to be redox stable anodes with low polarization losses that rival the performance of metal-based catalytic anodes, and also showed high catalytic activity for full oxidation of methane in SOFCs. The electrode impedance of LSCM anode was improved by making a composite anode by mixing 50-60 wt% LSCM with YSZ, which improved both adhesion to the underlying YSZ electrolyte membrane as well as the anode performance for the oxidation of humidified (3% H₂O) methane [416]. However the high activation energy of 160 J/mol for methane activation suggests that the oxide ion transport is the dominant factor governing the overall rate of the oxidation reaction. Similarly, various doped-SrTiO₃ based [417,418] and La_{0.7}Sr_{0.3}VO₃ –based [419,420] perovskite anodes have successfully been employed for mildly humidified methane oxidation in SOFCs. The vanadate-based ceria-Pd anodes exhibited considerable conductivity (2 S/cm at 700°C), had low electrode polarization resistance (0.4 ohm.cm² in CH₄ at 600°C), and gave a substantial power density of 510 mW/cm² in humidified CH₄ at 800°C.

Catalytic anodes based on precious metals were also employed for methane oxidation or transformations in SOFCs [75-77]. Although the number of reports is relatively low, some of the earlier studies have been reviewed elsewhere [46,209]. Complete conversion of electrochemically pumped oxygen to syngas was achieved on Pt anodes during partial oxidation of methane at 800°C in a SOFC featuring YSZ solid electrolyte [421]. Similarly, Ru-based cermet anodes have been employed previously for propane oxidation [24,25]. With its significantly higher melting temperature of 2334°C than for Pt (1768°C), Ru offers better microstructural and morphological stability. Ruthenium also offers good catalytic activity for the oxidation reactions of methane and other hydrocarbons. The possible reaction pathways during methane oxidation on Ru catalytic anode are illustrated schematically in Figure 21.

Figure 21. Schematic illustration of various reaction pathways of methane oxidation reaction on Ru anodes over YSZ electrolyte: (a) methane cracking followed by indirect oxidation, (b) partial oxidation, reforming, and full oxidation of intermediate species. "Reprinted with permission from ref. [424] Takagi Y, Kerman K, Ko C, Ramanathan S, J. Power Sources, 2013; 243: 1-9. Copyright (2013) Elsevier"

resistance upon methane oxidation, while in the case of hydrogen oxidation the Ru grains seem to spread and coalesce possibly due to hydrogen-assisted surface diffusion with corresponding reduction in the Ru sheet resistance. Although the root cause of this observation has not been identified yet, its practical implication may relate to the fact that *tpb* density during methane oxidation is largely preserved, while it is apparently reduced in the case of hydrogen oxidation.

Arguably, Ni-based cermets have been the most widely used anodes not only for the typical fuel hydrogen but also for methane conversion in SOFCs. Much of the recent progress made in this area as well as the challenges posed by the fabrication, microstructural control, catalytic activity, stability and performance of Ni-based anode materials for conversion of methane and other hydrocarbon fuels in SOFCs have been reviewed extensively [317]. The review drew attention to the need for more research for better understanding of the reaction mechanisms and catalytic activity, and concluded that oxidation of methane on Ni-based cermet anodes pose significant challenges such as coking and sulfur poisoning that lead to deactivation and cell degradation. These shortcomings unfortunately represent the inherent vulnerabilities of Ni that are difficult to overcome. The review discussed both engineering solutions that have been pursued or implemented such as pre-desulfurization and co-feeding of O_2 or steam along with CH_4 ,

Recent studies have explored Ru as an alternative catalytic anode material. MEAs with nanoporous Ru [422] and Pd [423] anodes deposited on ultra thin film YSZ membranes were fabricated, and oxidation of humidified CH_4 in this micro-SOFC resulted in 450 mW/cm^2 at 500°C for Ru and 385 mW/cm^2 at 550°C for Pd anodes, respectively, without any detectable evidence of coking. However, the OCV in these studies were reported to be much lower than expected, at around 0.7 V . The total thickness of the MEA was about 180 nm , with 30 nm thick Ru, 80 nm thick YSZ and 70 nm thick Pt cathode layers. The cross section of the MEA and the plan view of the Ru anode film are shown in Figure 22. Interestingly, the microstructure of Ru seems to react differently to methane than to hydrogen fuel, where the granular Ru microstructure is largely preserved with increase in the anode sheet

Figure 22. SEM cross-sectional image of the thin film MEA, showing the 30 nm thick Ru anode, 80 nm thick YSZ electrolyte and 70 nm thick porous Pt cathode (top layer), (b) plan view optical image of the wrinkled Ru anode layer of the micro-SOFC of (a). “Reprinted with permission from ref. [422] Takagi Y, Lai BK, Kerman K, Ramanathan S, Energy Environ. Sci. 2011; 4: 3473-3478. Copyright (2011) Royal Society of Chemistry”

V constant cell voltage over 5 hours [405]. The results shown in Figure 23 indicate how even a slight alloying with Sn brings about a dramatic improvement in the carbon tolerance of the Ni catalytic anode. The impact of 25 vol.% WC addition on the catalytic behavior and stability of 5 wt% Ni-based ceria cermet anodes during the oxidation of humidified methane at 850°C was investigated using porous YSZ anode structures impregnated with Ni-WC-ceria mixture [425]. The study reported modest catalytic behavior but improved coking resistance by WC addition. The stable operation of the composite anode with the WC phase in humidified (3% H₂O) methane at 850°C for 48 hours under OCV condition was also confirmed, although the x-ray diffraction spectra indicated the presence of WO₃ in the anode mixture and the cell power density dropped to more than ½ of its initial value during the first few minutes of a 24-h run, after which the power density was practically unchanged. Moreover, WC is expected to oxidize under

Figure 23. Stability of Sn-Ni alloy/YSZ anode versus Ni/YSZ in pure CH₄ at 740°C under constant cell voltage of 0.6 V. “Reprinted with permission from ref. [405] Nikolla E, Schwank J, Linic S, J. Electrochem. Soc. 2009; 156: B1312-B1316. Copyright (2009) The Electrochemical Society”

as well as more fundamental solutions that were undertaken such as increasing the basic site population for the catalytic reaction by adding oxide catalysts or alkali promoters to Ni, or by alloying the Ni with a less active metal such as Sn to lower its activity and hence its propensity for coking. Indeed, Ni-YSZ anodes loaded with 0.5-1.0 wt% Sn showed dramatically improved stability over Ni/YSZ anode in pure CH₄ at 740°C at 0.6

oxide ion flux and may not be a suitable anode material, as is the case with other metal carbide anodes employed as SOFC anodes at elevated temperatures [426].

Another study tested the validity of the hypothesis that increased S/C ratio within the porous anode by coating it with an inert gas diffusion barrier layer composed of a porous layer of partially stabilized zirconia and ceria mixture with 1:1 weight ratio, may improve anode stability by impeding the tendency for coking [427]. It was reported that cells with uncoated Ni/cermet anodes can maintain stable

operation in humidified CH_4 for long periods only at current densities larger than 1.8 A/cm^2 at 800°C , while those with the diffusion barrier indeed showed stable performance down to about 0.6 A/cm^2 , albeit at the expense of overall cell performance which dropped nearly 20% from 1.0 W/cm^2 at 0.7 V without the barrier layer to 0.8 W/cm^2 with the barrier layer.

Attempts to promote the oxidation of dry methane by BaO incorporated into the porous Ni/YSZ cermet matrix by microwave irradiation indicated BaO incorporation into Ni/YSZ anode lowered carbon accumulation but also exhibited inferior cell performance and lower kinetic rates at 800°C [428]. Another study coated a Ni-MnO reforming catalyst overlayer on top of the Ni/YSZ cermet anode by *in situ* reduction of the spinel MnNi_2O_4 , such that upon reduction the anode microstructure composed of fine-grained Ni particles imbedded in an MnO matrix [429]. The EIS results in humidified (3% H_2O) methane indicated that the anode impedance was significantly lower for the Ni-MnO/YSZ than for Ni/YSZ anode, which became even more dramatic at longer times where the impedance under open circuit conditions for the uncoated cell increased to 20 ohm.cm^2 after 6 hours at 800°C due to carbon deposition, while the impedance for the Ni-

MnO anode went up to less than 2 ohm.cm^2 , more than 10-fold improvement in anode performance due to lower degree of graphitization.

As a more desirable alternative to Ni/YSZ cermets, ceria-based SOFC anodes have been investigated for methane oxidation for more than two decades [403,430-432]. Ceria offers important advantages, as it becomes a mixed ionic electronic conductor (MIEC) at the reducing atmosphere of the anode environment, which extends the electrochemically active zone beyond the electrode/electrolyte interface. It can sustain nonstoichiometry in its oxygen sublattice, and serve as a source for lattice oxygen needed for the electro-oxidation reaction. It also has a higher ionic conductivity than the more commonly employed YSZ electrolyte. Exploiting these advantages, an early study for electrochemical oxidation of methane successfully employed a 1 mm thick porous LSM cathode-supported SOFC design with $8 \mu\text{m}$ thin film YSZ electrolyte, and a Ni/YSZ cermet anode deposited on top of a $0.5 \mu\text{m}$ thin yttria-doped ceria (YDC)

Figure 24. (Top) Performance of SOFC with Ni/YSZ cermet anode during oxidation of humidified methane. (Bottom) Long-term cell stability test at 800 mA/cm^2 constant current in humidified methane fuel at 700°C . "Reprinted with permission from ref. [434] Lin Y, Zhan Z, Liu J, Barnett SA, Solid State Ionics, 2005; 176: 1827-1835. Copyright (2005) Elsevier"

catalytic interlayer [432]. The presence of the YDC interlayer helped lower the anode interfacial resistance by a factor of 6, and no carbon deposition was observed below 700°C using slightly humidified (trace H₂O) methane that produced a considerable power density of 370 mW/cm² at the low operating temperature of 650°C. This time using an anode-supported SOFC architecture with Ni/YSZ cermet anodes, this research group has steadily improved their cell performance first to about 1 W/cm² at 800°C [433], and subsequently to 1.27 W/cm² at 800°C [434]. The cell was operated under 800 mA/cm² of constant current at 700°C for more than 160 h, and showed no sign of significant coking or cell degradation. Experimental results of cell performance and stability in humidified methane fuel on Ni/YSZ cermet anodes are shown in Figure 24. Catalytic activity and coking resistance of Ni/samaria-doped ceria (SDC) cermet anodes were compared to Ni/YSZ cermet anodes for methane oxidation [435]. It was suggested that the mixed conducting SDC might be a more suitable and effective anode support than the purely ionically conducting YSZ. Although coking resistance of the Ni/SDC cermet anode was superior to Ni/YSZ, degradation in cell OCV in methane and considerable carbon deposition on the anode top surface as well as at the anode/electrolyte interfacial regions were observed.

The inherent catalytic property of ceria in the cermet anode was investigated by using catalytically inert metals. One study compared the catalytic behavior of 25 wt% Cu or Au loaded ceria and SDC composite anodes for the oxidation of H₂ and n-butane at 650°C [436]. The results indicated that both Cu and Au served as current collectors and did not participate in the oxidation reaction, while the addition of ceria to the cermet mix improved the overall catalytic activity of the anode, possibly due to mixed conduction in and the catalytic role of the lattice oxygen supplied by ceria. Another study investigated the role of ceria for direct oxidation of methane in a SOFC configuration at 1000°C using a gadolinia-doped ceria (Ce_{0.6}Gd_{0.4}O_{1.8}) anode in connection with catalytically inert Au particles mixed in a GDC matrix serving as the current collector for the cell [437]. It was reported that GDC provided an important advantage in suppressing carbon deposition during 350 hours of testing at 1000°C. On the other hand, it exhibited only minimal catalytic activity for steam reforming or methane oxidation. These results provide strong evidence that the role of Cu in the cermet anode is not catalytic, but merely to provide electronic conductivity as an effective current collector. Moreover, the addition of ceria clearly enhances anode performance in all these Cu-based cermet anode cells and hence serves an important catalytic role [438], and has been found to be catalytically more effective than either La₂O₃ or MoO_x additions to the Cu-based cermet anodes [439]. Nevertheless, the catalytic activity of ceria for methane activation is not sufficiently high for practical interest. Hence, the results highlight the need to employ an effective catalyst such as Ni, Pt or Ru that possess the intrinsic ability to break C-H bonds. As Pt and Ru are expensive catalysts, and Ni poses major problems with carbon deposition on the anode structure resulting in rapid degradation of cell performance, ongoing search in this area aims to identify more suitable anode materials that exhibit catalytic activity comparable to these known active catalysts but without the limitations posed by materials costs or carbon deposition.

Catalytic propensity of Ni for pyrolytic carbon formation during methane oxidation is closely related to its ability to catalyze C-C bond formation as well as the considerable solubility of carbon in Ni. Indeed, the ability of Ni to dissolve carbon is exploited

industrially to produce man-made diamond particles in the presence of group VIII metal catalysts using the high pressure, high temperature synthesis technique developed by General Electric in the 1950's [440,441]. Indeed, point defects associated with Ni impurities have been identified in synthetic diamond crystals that are remnants of Ni incorporation into the diamond structure from the Ni-based catalyst solvent that dissolves the carbon during synthesis [442,443].

An obvious strategy to reduce the tendency for carbon formation is to lower the thermodynamic activity of Ni by alloying with another metal such as Sn [405] or Cu [378,444]. In fact, Ni-alloy based cermet significantly reduced coking on the anode in dry methane, but did not eliminate it completely. It is interesting to note that the power densities of the cells that employed Cu-Ni alloy based cermet anodes for the oxidation of dry methane have improved significantly over time at temperatures below 800°C, and this was ascribed to better electronic connectivity established at the anode due to carbon formation [378,444]. An extension of this strategy towards lowering the thermodynamic activity of Ni in the cermet anode explored a non-Ni based anode. Indeed, pure Cu-based cermet anodes were developed and investigated in detail [312-314,380]. Cu offers several unique advantages. It does not catalyze C-C bond formation and thus does not promote coking. It is a cheap metal with excellent electronic conductor and has better stability to oxidation than Ni. On the other hand, Cu and its oxides have relatively low melting points (1085°C, 1232°C, 1326°C for Cu, Cu₂O, and CuO, respectively), and thus making the cermet fabrication process, which typically requires sintering of the mixed oxides at high temperatures, difficult. The low melting points also lead to grain coarsening, sintering and microstructural changes in the Cu-based anodes due to the elevated operating temperatures of SOFCs, which eventually lead to loss of percolation and electrical connectivity to collect the electrons released during the oxidation reaction. Fabrication of Cu-based cermets requires modified process steps such as wet impregnation or infiltration followed by carefully selected temperature treatment procedures during the preparation of the porous anode structures [445-447]. More importantly, Cu is a poor catalyst for oxidation reactions, so requires the addition of an active catalyst to the cermet composition in order to achieve reasonable cell performance when methane or hydrogen is employed as the fuel. SOFC performance of H₂ oxidation on Cu/YSZ and Cu/ceria/YSZ cermet anodes studied at 800°C were reported to be similar to that of Ni/YSZ anodes, suggesting that the catalytic activity of the metal component of the cermet played an insignificant role [379].

Arguably, the first successful attempt to employ Cu-based cermet anodes with dry methane has validated direct oxidation by gas analyses, which showed CO₂ as the primary reaction product with minor quantities of CO [379]. In methane fuel, the Cu/YSZ cermet anode performed quite poorly with negligibly small power density and a low OCV of only 0.5 V vs air at 800°C, confirming the poor catalytic activity for Cu as well as the YSZ for the oxidation or the reforming reactions. By contrast, the addition of 0.2 g of ceria per gram of the Cu/YSZ cermet, which originally contained 40 wt% Ni or Cu, has greatly improved the catalytic activity and increased the power density more than 3-fold to 32 mW/cm² at 800°C with stable cell operation for nearly 72 hours [379]. Similarly, the addition of ceria to the Cu/YSZ composition greatly improved cell performance, where the short circuit current densities in CH₄ at 800°C increased from ~120 mA/cm² for Cu/YSZ to 480 mA/cm² for Cu/ceria/YSZ composite cermet, pointing

to the important catalytic role played by ceria as the primary catalyst for oxidizing methane [26]. The Cu-based cermet anodes provided stable cell operation at constant current in CH₄ for 3 days with no deactivation, while the Ni-based anode deactivated rapidly within 30 minutes in CH₄ fuel, where the reactor tube was completely filled with filamentary carbon deposits. Moreover, CH₄ conversion was reported to increase linearly with the current density, indicating that the direct oxidation process is Faradaic nature.

While the catalytic activity of Cu-YSZ cermet anodes were comparable to that of Ni/YSZ anodes for H₂ oxidation, Cu/YSZ anodes were practically inert for the oxidation of dry methane, giving power densities much lower than 10 mW/cm² at 800°C. The results suggest again that Cu serves merely as an efficient current collector to transfer the electrons from *tpb* to the external circuit, and not as an effective catalytic agent for methane activation, while ceria does, although it should be noted that Cu-Zn is known to be an effective catalyst for the GWS reaction (5).

In a related study using Cu/ceria/YSZ cermet anodes for the oxidation of methane, propane, butane, decane and toluene at 700°C, cells that contain less than 20 wt% Cu in the cermet anode structure showed enhanced cell performance that improved over time, which was attributed to extended electrical connectivity materialized by the formation of tar-like carbonaceous deposits inside the pores of the cermet anode that link together the Cu particles [448]. This finding is in agreement with similar reports on improved cell performance due to carbon deposits during methane oxidation on Cu-based anodes [378,444].

4.2.3.1. Efficiency for direct oxidation versus steam reforming

To work around the difficulty in activating the stable C-H bonds, much of the development work on electrochemical utilization of methane in SOFCs employed either external or internal steam reforming to produce a syngas that is then oxidized at the SOFC anode [449]. The production of syngas, which is a mixture of H₂ and CO, is often followed by a water gas shift (GWS) process step given by reaction (5) in order to further increase the H₂ content in syngas while converting CO to CO₂ by reaction with steam. So in most cases, methane is converted primarily to H₂ for ease of electro-oxidation and to obtain high cell performance. Naturally, these extra process steps lead to loss of conversion efficiency as the steam reforming reaction

is highly endothermic with an enthalpy change of $\Delta H^\circ_{298\text{K}} = + 206 \text{ kJ/mol}$.

Hence, direct electro-oxidation of methane in SOFCs offers efficiencies inherently higher than for either H₂ or CO (see Fig. 3). The negligibly small entropy change (-1.3 J/K.mol of O₂ at 298K) during the methane oxidation reaction (1) provides an exceptionally high ceiling of 100% for the theoretical conversion efficiency. By contrast, significantly large entropic losses associated with the H₂ oxidation and CO oxidation reactions are correspondingly, -88.48 J/K.mol of O₂ at 298K for H₂, and -172.27 J/K.mol of O₂ at 298K for CO, highlighting the thermodynamic losses expected for utilizing methane reformates.

It is clear from Figure 3 that the thermodynamic ceiling for the conversion efficiencies of the syngas components H₂ and CO formed by either external or internal

reforming of methane are significantly smaller than the 100% theoretical value for direct electro-oxidation of methane. Such a gap between the efficiencies for methane versus H_2 and CO is an important consideration relevant to the choices for utilizing methane in SOFCs. Although, H_2 has been the preferred and most frequently used fuel in SOFCs due to its fast oxidation rate and high power density, and CO is also a competitive and viable SOFC fuel with cell performance comparable to that of hydrogen, as demonstrated recently in a 1 kW SOFC stack [267] significantly lower conversion efficiencies for these reforming products provide the required incentives for direct electrochemical oxidation of methane over reforming processes (see Figure 3). Conversion efficiencies of 52-60% LHV reported [57] by SOFC manufacturer Bloom Energy of California, U.S., for its BloomBox 200-250 kW power units running on reformed natural gas is a testament that there is room at the top for efficiency improvement by research and development for direct electro-oxidation.

5. Major Challenges for Methane Conversion on Catalytic Anodes

Figure 25. Ternary equilibrium diagram for the C-H-O system, indicating the boundary contours of the carbon deposition region as a function of temperature. Note that the deposition region expands with decreasing temperature. Carbon deposition becomes thermodynamically favorable for mixtures whose overall composition falls inside the deposition region. The dotted blue and green lines denote the loci of the change in the overall gas compositions for steam and dry reforming processes, respectively. As CH_4 is electrochemically oxidized at the SOFC anode, the overall gas composition follows the trajectory indicated by the thick red dashed arrow. “Adapted with permission from ref. [450] Sasaki K.; Teraoka, Y. J. Electrochem. Soc. 2003; 150: A885-A888. Copyright (2003) The Electrochemical Society”

Among various challenges facing methane conversion in SOFCs, only two major ones that pertain to methane conversion in SOFCs are discussed below, as these pose persistent problems and their solutions will require fundamental advances in materials discovery, and SOFC design and operation. The others, including microstructural changes or degradation of the electrodes, defect segregation, aging, solid state reactions and interdiffusion among fuel cell component materials, chemical stability issues, fabrication and materials costs, current collection and interconnect materials are common to all SOFC designs regardless of the fuel, and these issues have been discussed fully in excellent reviews [204,222-230].

5.1. Carbon deposition

One of the major challenges to direct methane conversion in SOFCs is catalyst deactivation due to carbon deposition, or coking, on the catalytic anode. This problem

has its mechanistic origins in both thermodynamic and kinetic contributions. The degree of coking depends on temperature, gas phase composition and the S/C ratio, and also the

Figure 26. Optical images of carbon deposition on Ni/ScSZ cermet anode structures: (1) pristine cell, and after 10 hours of operation at, (2) 500 mA/cm² at 900°C, (3) 500 mA/cm² at 800°C, and (4) OCV at 900°C. “Reprinted with permission from ref. [376] Gunji A, Wen C, Otomo J, Kobayashi T, Ukai K, Mizutani Y, Takahashi H, J. Power Sources, 2004: 131: 285-288. Copyright (2004) Elsevier”

Figure 27. Equilibrium gas phase compositional changes as a function of current density during electrochemical oxidation of dry CH₄ (10 sccm) in N₂ (150 sccm) at 750°C. “Reprinted with permission from ref. [452] Koh JH, Kang BS, Lim HC, Yoo YS, Solid-State Lett. 2001; 4: A12-A15. Copyright (2001) The Electrochemical Society”

nature and catalytic properties of the SOFC anode material. The carbon occupies catalytic sites by forming strong bonds and rapidly deactivates the anode. In extreme cases, it can clog up the entire reactor and debilitate cell operation.

5.1.1. Thermodynamic considerations

The thermochemistry of the gas phase equilibrium in the C-H-O system is a useful thinking tool to understand the thermodynamic driving force for carbon deposition. As evident from the C-H-O ternary equilibrium diagram [450] of Figure 25, the composition of CH₄ resides well inside the thermodynamically favorable region for carbon deposition. This makes it difficult to directly oxidize dry methane in SOFCs, and hence the incentive to employ reforming with steam or CO₂ to drive the overall gas composition out of the deposition region. The dotted tie lines between CH₄ and H₂O and CO₂ indicate the overall composition of their corresponding gas mixtures during steam and dry reforming processes. From a purely thermodynamic point of view, the intersection of the CH₄-H₂O tie line with the high temperature ($T > 800^{\circ}\text{C}$) carbon deposition boundary indicate a minimum S/C ratio of 0.5 is required even at these temperatures to pull the overall composition out of the deposition boundary. In practice, however, high S/C ratios > 3 are usually employed [358,374]. Nevertheless, moving the overall composition outside the deposition boundary does not necessarily negate the possibility of coking, which can still happen due to kinetic reasons. Such is the case for Ni, which is widely used as an anode catalyst material in SOFCs because of its high catalytic activity, good electronic conductivity, low cost, and good thermal and mechanical properties. It is typically employed in the form of a porous sintered Ni/YSZ cermet. Unfortunately, Ni readily promotes graphitic

carbon deposition at low S/C ratios that leads to rapid degradation of cell performance. In extreme cases, the porous anode structure can be clogged up and deactivated by carbon deposits if left uncontrolled, e.g., under open circuit conditions. This is highlighted in Figure 26, where the cell operating on humidified (3% H₂O) methane at lower temperature and OCV conditions accumulate excessive carbon deposition [376] as shown in Fig. 26(4), while the use of high current densities mitigate the effect [451]. The observations were complemented by a thermodynamic study, where almost 98% of dry CH₄ in the feed gas converts to carbon deposits under open circuit conditions, as shown in Figure 27, and the current density required to remove the deposited carbon is estimated to be 85 mA/cm² at 750°C [452].

5.1.2. Spectroscopic observation of carbon formation

SOFC experiments using *in situ* spectroscopy provide convincing evidence in support of the results and observations of carbon deposition under various operating conditions. *In situ* Raman spectroscopy studies on Ni/YSZ cermet anodes on a working MEA exposed to hydrocarbon fuels have indicated confirmation of carbon deposition under

Figure 28. Figure 17. *In situ* Raman spectra of carbon deposits on Ni/YSZ cermet anode at 715°C showing the building up of graphitic G mode at 1585 cm⁻¹ upon exposure to 5 cm³ ethylene under OCV conditions (left panel), under mild polarization at 0.75 V cell voltage (center panel), and under strong polarization at 0.45 V cell voltage (right panel), as a function of time.

Carbon removal, or disappearance of the G band at 1585 cm⁻¹ increases as the oxygen flux increases with cell polarization. The featureless red spectrum encircled with a dashed trace in the center top denotes the clean, reduced Ni/YSZ anode surface prior to exposure. “Reprinted with permission from ref. [453] Pomfret MB, Marda J, Jackson GS, Eichhorn BW, Dean AD, Walker RA, J. Phys. Chem. C, 2008: 112: 5232-5240. Copyright (2008) American Chemical Society”

shown in Figure 29, which illustrates the removal of surface carbon from Ni entirely by the chemical action of steam without any electrochemistry. It should be noted that prolonged exposure of Ni to steam-rich environment eventually oxidizes it to NiO and renders the catalytic anode inactive. In these circumstances, the persistent problem of carbon deposition under OCV conditions requires active control.

OCV conditions, which may subsequently be removed from the Ni surface by the oxygen flux through the YSZ electrolyte [352,355,356,453]. Figure 28 illustrates the accumulation of carbon on a Ni/YSZ cermet anode upon exposure to a single burst of 5 cm³ of ethylene under OCV, and the disappearance of the graphite G mode peak at 1585 cm⁻¹ with increasing time and cell polarization. In a similar manner, *in situ* Raman spectroscopy provided direct evidence on the efficacy of chemical removal of carbon from the Ni surface by steam gasification [454]. This is

Naturally, the critical current density needed to completely remove the deposited

Figure 29: *In situ* Raman spectra of carbon species on Ni/YSZ cermet surface in CH₄ at 715°C. The featureless black spectrum at the top is for pristine Ni before exposure to CH₄ gas. Graphite built up on Ni with appearance of D and G bands of graphite upon exposure to CH₄ (blue trace). Partial removal of graphite and onset of Ni oxidation upon exposure the Ni surface to humidified (4% H₂O) Ar flow for 3 minutes (green trace). Further exposure to humidified (4% H₂O) Ar removes all graphite and full oxidizes Ni to NiO (red trace). “Reprinted with permission from ref. [454] Pomfret MP, Owrutsky JC, Walker RA, J. Phys. Chem. B, 2006; 110:, 17305–17308. Copyright (2006) American Chemical Society”

carbon by electrochemical oxidation with the oxygen flux through the electrolyte depends strongly on the conditions selected initially for the fuel mixture and cell operation parameters. This critical current density is nevertheless a useful measure to manage and mitigate the coking problem for individual operational cases. However, this can vary widely depending on the test conditions. For example, carbon deposition from dry methane on Ni/YSZ cermet anodes that featured a chemically inert diffusion barrier layer of partially stabilized zirconia and ceria placed between the anode surface and the fuel compartment required current densities in excess of 1.4 A/cm² at 800°C [361] [427]. This is illustrated in Figure 30, where cell degradation is clearly obvious even at 1.0 A/cm² at 800°C. In any case, however, high oxide ion fluxes, or current densities, do not necessarily guarantee complete removal of carbon deposits from the Ni surface. Only those carbon particles deposited within the close (several micrometers) proximity of the *tpb* may possibly be removed by the O²⁻ flux through the YSZ electrolyte, but those farther away will rapidly build filamentary carbon deposits that

eventually deactivate the active sites on the Ni/YSZ cermet anode and clog up the reactor.

A more detailed atomistic level understanding of carbon formation energetics and mechanisms is facilitated by first principles calculations, which are discussed in the next section below.

5.1.3. Strategies to mitigate carbon deposition

Significant progress towards minimizing coking during methane conversion in SOFCs was made in the last decade using several strategies. One involved catalytic oxides that offer oxygen storage and release capacity through their wide tolerance to nonstoichiometry in their oxygen sublattice. Most are poor catalysts for the promotion of C-C bond formation, and hence help prevent coking. They also offer opportunities to remove carbon deposits on the catalyst surface by reaction with lattice oxygen and maintain high catalytic activity. This can happen as spillover of oxygen from the oxide support material, or directly using a catalytic oxide with significant nonstoichiometry,

such as doped ceria and perovskites. This strategy has been pursued by many, especially with ceria-based cermets [23, 449,455]. The electronic conductivity ($< 10^{-2}$ S/cm) of these oxides and their catalytic activity to promote C-H bond activation can be improved by adopting appropriate doping strategies. For example, ceria doped with rare earth oxides such as Gd_2O_3 or Sm_2O_3 have shown to activate methane oxidation in SOFCs with improved carbon tolerance and cell stability [312,403,456].

The second strategy evolves in part from insights from DFT studies of methane adsorption and reforming on Ni surfaces, which indicated the Ni(211) edge sites bind carbon strongly and are primarily responsible for promoting carbon formation [457]. As Ni(211) edge sites have a lower activation barrier and are more reactive to CH_x species than the close-packed Ni(111) surfaces, the stepwise abstraction of hydrogen during the

Figure 30. Operational stability of SOFC with Ni/YSZ cermet anode and chemical barrier layer in pure dry methane at 800°C and under constant current conditions. “Reprinted with permission from ref. [361] Pillai M, Lin Y, Zhu H, Kee RJ, Barnett SA, *J. Power Sources*, 2010; 195: 271-279. Copyright (2010) Elsevier”

dissociation of methane is energetically more favorable at Ni(211) sites with the eventual nucleation of graphite. Moreover, the dissociative production of carbon and hydrogen is endothermic on planar surface, while it is exothermic on the stepped surface, where the exothermicity provides the driving force for graphite formation. Based on these insights, the DFT calculations suggested that preferential binding of promoters such as K, S, and Au to the Ni(211) edge sites should reduce the propensity for coking. Indeed, follow-up experiments that employed K and S promoters on Ni

have shown increased tolerance to graphite formation by blocking the stepped edge sites, as observed by both kinetic and spectroscopic evidence [458].

Another DFT study compared CH_4 dissociation on planar and stepped Ni and Cu surfaces, where the adsorption energies of surface CH_x species followed similar trends on Ni and Cu as shown in Figure 31, which compares the energy profiles of CH_x intermediates along the reaction pathway on Ni and Cu surfaces. This study also indicated that the exothermicity of the reaction on Ni(211) stepped edges favors carbon formation, while other surfaces of Cu and Ni do not [459], which agrees well with the poor catalytic activity but superior carbon tolerance observed on Cu. Accordingly, it was proposed that tolerance to carbon can be improved by selective adsorption of Cu on Ni stepped edges.

The third strategy aiming to reduce coking adopted the use of Cu in place of Ni [312-314,379,380,438], which has been effective in preventing carbon deposition, but provided only modest power densities in most cases. Among these, Cu-ceria cermet anodes seem to eliminate the coking problem all together. Unlike transition metal catalysts, Cu does not dissolve carbon and is also a poor catalyst material for C-C bond

formation, C-H activation, and methane reforming, and hence, serves merely as a passive electronic conductor in the cermet anode structure.

Another strategy involves chemical engineering of the catalyst surface. On oxide surface, coking is promoted usually at acid sites, and doping strategies that lower the population of acid sites on the oxide surface can mitigate carbon deposition. For example, Ni/La-doped ceria cermet anode was reported to be significantly more tolerant to carbon

Figure 31. Energy profiles for CH₄ dissociation on stepped Ni(211) and Cu(211) compared to that on planar closed-packed Ni(111) and Cu(111) surfaces, with carbon as the end points for all cases. However, it is exothermic only on the Ni(211) surface, while endothermic on others. (Top) Carbon formation is clearly favored by the stepped Ni(211) surface and not by the planar Ni(111). (Bottom) Dissociation of CH₄ on Cu is highly unfavorable, as each intermediate step requires more energy. The stepped Cu(211) seems slightly more reactive than the planar Cu(111) surface. These theoretical results are in agreement with the poor catalytic activity and lack for coking observed on Cu. “Reprinted with permission from ref. [458] Galea NM, Knapp D, Ziegler T, J. Catal. 2007: 247: 20-33. Copyright (2007) Elsevier”

formation than the Ni/ceria cermet anode, while Ni/Sm-doped ceria cermet displays even better tolerance to coking than its La-doped counterpart [383]. Likewise, additions of strongly basic alkali oxide promoters, or non-catalytic metals like Au alter the coking propensity of Ni, respectively, by reducing the population of acid surface sites to discourage graphitic carbon formation [385] or blocking the active step edge sites on the Ni surface [459]. Furthermore, replacing Ni with another catalytically active metal such as Ru that does not possess sufficient solubility for carbon, also improves the carbon tolerance of the anode material [346] without sacrificing on catalytic activity. A DFT study supplemented by scanning tunneling microscopy (STM) examination of ethylene activation on Ni(111) surface indicated the pronounced role that step edges play in promoting C-C bond formation, and demonstrated that blocking these active edges with Ag favored the selective activation of the C-H bond without carbon formation [460]. Alternatively, up to 1.5wt% sol-gel coating of porous Ni/YSZ cermet anode with a thin film of samaria-doped ceria (SDC) of the composition Sm_{0.2}Ce_{0.8}O₂ has greatly improved its coking resistance and provided stable cell operation under OCV conditions at 700°C in a 25% CH₄+75% air mixture as the fuel for nearly 500 hours [461].

Yet another strategy involves the use of perovskite-based mixed proton and oxide ion conducting oxides of the doped-BaZrO₃ and BaCeO₃ families as SOFC anodes [462-464]. Proton transport in these doped

oxides starts with the incorporation of OH groups from adsorbed H₂O into oxygen vacancies in the perovskite structure followed by proton transport via the Grotthuss mechanism through the oxygen sublattice [461,465]. Hence, they require sufficient humidity to sustain protonic transport regardless of whether they are employed as electrolytes or electrode materials in SOFCs. This naturally requires active water management that may lower the overall efficiency. However, their ionic conductivities, shown in Figure 32, are more than one order of magnitude higher than YSZ, especially at $T > 500^{\circ}\text{C}$ [465]. These materials are mixed ionically conducting oxides that transport primarily protons at low and moderate temperatures with a gradual transformation into a

Figure 32. Comparative ionic conductivities of the perovskite-based protonic conductors $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) and $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY), with the oxide ion conducting fluorite oxides GDC and YSZ measure in wet oxygen containing ~3% H₂O. “Reprinted with permission from ref. [462] Yang L, Wang SZ, Blinn K, Liu ML, Liu Z, Cheng Z, Liu ML, Science, 2009; 326: 126-129. Copyright (2009) The American Association for the Advancement of Science”

predominantly oxide ion transport mode at high temperatures with the cross-over from one dominant ion transport mode to the other occurring in a temperature range around 600-800°C depending on the perovskite composition and the nature of the dopants [466-468]. A composite anode made of Ni/ $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$ (BZCYYb)/ $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) achieved a power density of 580 mW/cm² at 700°C operated with methane fuel and showed stable operation for 120 hours [469]. Stable cell operation of the $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$ anode in humidified (3% H₂O) methane at 750°C was also reported, and the post-mortem Raman spectroscopic analysis of the anode surface confirmed the absence of the 1350 cm⁻¹ and 1580 cm⁻¹ peaks associated with the D and G modes for graphitic carbon [470]. The BZCYYb oxide is combined with catalytic metals such as Pd, Cu, Ni, and NiCu alloys to make cermet anodes and tested for

methane activation at 750°C. All cermet compositions were resistant to coking in humidified (3% H₂O) methane. While Pd/BZCYYb and Ni/BZCYYb anodes showed indications of coking established by Raman spectroscopy during 12 hours of operation in dry methane, NiCu/BZCYYb cermet showed excellent resistance to coking after 24 hours exposure to dry methane and 130 hours to humidified methane all under OCV conditions [471]. Modification of the basic Ni/YSZ cermet structure by BaCO₃ addition for *in situ* formation of a mixed ion conducting $\text{BaZr}_{1-x}\text{Y}_x\text{O}_3$ (BYZ) interlayer on YSZ and nano-islands of BaO on the Ni surface gave promising results for direct oxidation of octane with substantial power density of 600 mW/cm² at 750°C [29]. The anode showed moderate resistance to coking in humidified (3% H₂O) octane where the current density at 0.7 V dropped initially from 1.1 A/cm² to about 0.5 A/cm² within the first few hours but then held steady for nearly 90 hours of continuous operation, while in dry octane

coking resulted in rapid cell degradation within the first few hours. The high catalytic activity for octane was ascribed to the nanosize BaO/Ni interfaces that promote reforming of octane and the subsequent oxidation of the reformat components. Independently, *in situ* Raman studies of Ni/YSZ cermet anodes infiltrated by 1% BaO and 1% Sn via an aqueous salt impregnation method showed resistance to carbon deposition in dry methane under OCV and fuel cell modes [472]. Sn-doped Ni/YSZ showed inhibition of carbon deposition around the electrochemically active regions of the anode, while the undoped Ni/YSZ showed carbon deposition throughout the anode structure. By contrast, BaO infiltrated anode greatly inhibited carbon formation throughout the anode structure, but it also inhibited methane activation giving significantly lower power densities than the undoped Ni/YSZ cermet anode. The gasification power of the oxidants to remove the surface carbon was found to be $\text{H}_2\text{O} > \text{CO}_2 > \text{O}_2$ in effectiveness. However, the Raman spectra also indicated that the use of O_2 , and to some degree CO_2 , to remove carbon led to the oxidation of the Ni in the anode resulting in degradation of the cell performance.

Despite great progress and creative advances made in anode materials, it is clear that there is still need for developing catalytically more superior and non-coking anode materials especially for direct dry oxidation of methane in SOFCs. While high operating temperatures reduce the thermodynamic compositional boundary for carbon deposition, catalytic effects and enhanced rates at elevated temperatures still give rise to carbon deposition problems. Lowering the cell temperature, on the hand, leads to poor cell performance, creating a dilemma to find the sweet spot in the operating conditions, and demanding a materials-based solution also. In this regard, catalytic metal oxides, and in particular, MIEC perovskite-based anodes offer a wide range of doping strategies for tuning and optimizing materials transport and catalytic properties to effectively activate C-H bonds for methane oxidation.

Alternatively, one can take advantage of the coking problem instead and turn it around for beneficial use of generating electricity, albeit with limitations. In this regard, SOFCs are ideally suited to effectively utilize the deposited carbon and convert it efficiently to electrical energy via internal reforming or direct electrochemical oxidation [34,36,227,473-475]. Much of the progress made in this topical area of solid carbon fuel conversion in high temperature fuel cells has been discussed extensively in recent review articles [476,407]. It should be noted, however, that this approach has severe constraints, which limit the electrochemical removal of carbon to the immediate vicinity of *tpb* only, and any excessive carbon deposited elsewhere in the SOFC cannot be removed electrochemically, unless invoking a chemical step such as gasification.

5.2. Sulfur poisoning mechanisms and mitigation strategies

Sulfurous species are generally present in all naturally occurring fossil fuels including natural gas, where this is usually in the form of H_2S at quantities that may vary widely from trace amounts up to 1% depending on the origin of the gas. Even when absent, about 10 ppm of sulfur-containing odorants are typically added to hydrocarbon gases for ease of leak detection. As sulfurous species are highly potent poisons or deactivation agents for catalytic materials, sulfur poisoning of the catalytic anode remains one of the major hurdles, perhaps the Achilles' heel, that stand in the way of developing commercial SOFCs that can directly be fueled by natural gas.

The unusually wide range of fuel flexibility offered by SOFCs cannot possibly be realized for practical purposes unless the sulfur problem is abated and resolved. One strategy is to employ a priori desulfurization step for the sour gas (i.e., sulfur-containing natural gas) to remove sulfurous species before reforming or direct utilization in SOFCs, which of course adds cost and complexity to the process and reduces overall conversion efficiency. The other strategy is to develop catalytic anodes with sufficient sulfur tolerance. This is critically important to realize the fuel flexibility and cost effectiveness of SOFCs, regardless if they are fueled by natural gas, biogas, coal gas, or syngas without the need for extensive pretreatment and desulfurization.

Sulfur can exist in different oxidation and chemical states, and interacts with most metal and oxide surfaces. For example, a recent *in operando* study investigated the interaction of 5 ppm H₂S/H₂ mixture with the Ni/GDC cermet anode in SOFC by using sulfur K-edge x-ray absorption near edge structure (XANES) analysis, and reported the presence of several surface sulfur species with different oxidation states, namely, +6, +4, 0, and -2. Although these oxidation states are characteristic of -SO₄²⁻ (or, SO₃), -SO₃²⁻ (or, SO₂), molecular S₂ or adsorbed S atom, and Ni or Ce sulfides, respectively, the study failed to make definitive identification of the chemical species associated with the corresponding oxidation states [477].

Poisoning and deactivation of catalysts, especially those based on nickel, by sulfurous species in the reaction environments is a well recognized and persistent problem for many industrial catalytic processes [478,479] and the development of poison-resistant industrial catalyst is a never ending task [480]. This challenge is equally important for catalytic anodes in the context of direct utilization and conversion of fossil fuels in SOFCs. Progress in the understanding and development of catalytic anode materials tolerant to sulfur and other impurities that may be present in real, untreated fuels has been reviewed elsewhere [481] [482].

5.2.1. Interaction of Ni-based catalytic anodes with sulfurous species

Most of the work related to sulfur poisoning has been conducted in the context of H₂ fueled SOFCs, as this has been the most preferred fuel. So the discussion in this section necessarily draws upon work performed in H₂ fuel environments, but many of the mechanistic findings and conclusions reported are also applicable to CH₄ fueled SOFCs, albeit with reduction in the reforming activity on the catalytic anode by the added complications of the C-H-O-S gas phase equilibrium [483].

Degradation of Ni/YSZ cermet anodes exposed to trace amounts of H₂S in H₂ fuel usually manifests itself in two distinct stages [484,485]. Immediately after exposure to H₂S, there is often a precipitous drop in cell performance followed by a second stage of degradation behavior that generally shows two types of behavior, one where the cell power density eventually attains a steady-state behavior over time, and the other where the cell power monotonically decreases with time and does not seem to approach steady-state. This is illustrated schematically in Figure 33. In general, the extent of cell degradation due to poisoning increases with increasing H₂S content of the fuel, decreasing overpotential, decreasing temperature and decreasing current density. Also, the extent of the performance loss due to sulfur poisoning is considerably higher in anode-supported SOFCs than for electrolyte-supported SOFCs, where the overall cell

impedance in the latter is significantly higher such that the anode polarization loss contributes to a smaller fraction of the overall loss mechanisms, while in anode-supported cells the overall cell resistance is much smaller so that anode deactivation has a more profound impact on the overall cell resistance [485]. Sulfur poisoning studies particularly on Ni/YSZ anodes as well as insights for the development of sulfur-tolerant anode materials have been discussed extensively in recent review articles [486,487].

There is reason to believe that sulfur poisoning of SOFC cermet anodes may involve not just the metal component of the cermet, but also the ceramic component, which is usually made of the same electrolyte material used in the cell structure to match thermal stresses during the cycling of the cell operating temperature. Indeed, there is experimental evidence [484,488], for example, that Ni/ScSZ anodes provide better sulfur tolerance than Ni/YSZ cermets, suggesting that Ni may be a major but not the only contributor to poisoning. Although better understanding of the mechanistic roots of sulfur poisoning is still evolving, a recent DFT study [489] of sulfur adsorption at the *tpb* of the Ni/XSZ cermet anode, where X denotes the X^{+3} dopant cation in the stabilized zirconia electrolyte, provided some clues to the important role of the electrolyte, and reported a strong correlation between the adsorption energy of sulfur and the ionic size of the dopant cation X, such that stabilized zirconia doped with smaller ionic size dopants (e.g., Sc^{+3}) is indeed expected to provide better tolerance to sulfur. It was calculated that the binding energy of sulfur to Ni-YSZ is about 0.1 eV stronger than it is for Ni-ScSZ. The higher tolerance of Ni-ScSZ is attributed to the lowering of the ScSZ surface energy and the weakened binding of sulfur on to this surface.

Figure 33. Illustration of sulfur poisoning effect on Ni/YSZ cermet anode upon exposure to H_2S . The sudden drop in the cell power output (solid line) upon exposure is followed by two types of 2nd stage behavior: a) cell power reaches steady-state after initial rapid drop (dotted line), and b) cell power shows steady and continuous decline over long periods of time without reaching steady-state (dashed line). “Reprinted with permission from ref. [486] Cheng Z, Wang JH, Choi YM, Yang Li, Lin MC, Liu M, Energy Environ. Sci. 2011; 4, 4380-4409. Copyright (2011) Royal Society of Chemistry”

Sulfurous species interact with the Ni catalyst anode surface in at least two major ways. One is by dissociative adsorption or chemisorption on the active sites on the catalyst surface and blocking them from participating in further reaction. This process, which is generally associated with rapid deactivation immediately upon exposure of the Ni surface to H_2S , can be represented by the

reaction,

Thus the reduced active site density naturally reduces the flux of rate processes at the anode surface, including adsorption, dissociation, oxidation and surface diffusion that lead to lower turnover frequencies for chemical and electrochemical reactions. The other interaction mode is by direct chemical reaction between the catalyst and the sulfurous species to form a new phase or reaction product with loss in catalytic activity and stability. In addition, other forms of interactions have also been proposed to account for anode deactivation and those are discussed further below in the context of second stage degradation processes.

It is known that the dissociative adsorption of H_2S on Ni surfaces occurs rapidly and strongly with an enthalpy of adsorption that decreases rapidly as surface coverage increases (-125 to -165 kJ/mol for high coverage of 0.5-0.9, and estimated to be -250 kJ/mol when extrapolated to 0 coverage), such that the surface S-Ni bonds are over a factor of three times more stable than the bulk Ni-S bonds at low surface coverage [478]. Similar chemisorption studies on Ni surfaces using H_2 mixtures containing 0.1-30 ppm H_2S indicated dissociative adsorption at low surface coverage, and non-dissociative, i.e., molecular, adsorption at high surface coverage with a heat of adsorption values ranging from -125 to -167 kJ/mol at 450°C at high surface coverage of 50-90%. [490]. Accordingly for the Ni-S system, the equilibrium is strongly shifted towards a sulfur-covered Ni surface, i.e., adsorption, instead of the formation of the sulfide phase. Moreover, only 1-10 ppb of H_2S concentration in the feed is sufficient to achieve 50% surface site coverage on Ni at $T > 450^\circ\text{C}$, which is a demanding quantity even to identify and control for analytical detection. Almost complete coverage of Ni surface can be achieved with 0.1-1 ppm H_2S , which are below the concentrations typically achieved after desulfurization of the feed gas prior to undergoing catalytic processes. In other words, desulfurization alone is incapable of total eradication of sulfur poisoning of Ni-based catalysts. By the same token, use of Ni-based anodes for methane conversion may not be the best option even if natural gas were to undergo desulfurization. This accentuates the great need for developing sulfur-tolerant anode materials.

5.2.1.1. Stage I poisoning of Ni-based catalytic anodes with H_2S

As noted in reaction (42), the dissociative adsorption of sulfur on the Ni surface blocks the active sites and reduces the site density of *tpb* that leads to an increase in the anodic polarization resistance. This mechanism is proposed to account for the sudden loss of cell performance immediately following exposure of the anode to ppm level of H_2S in the fuel feed. Interaction of Ni surfaces with H_2S studied by *in situ* Raman spectroscopy [491-493] and thermodynamic studies [494], as well as DFT calculations [495] independently indicate that under the typical operating conditions of SOFCs and at H_2S concentrations in the low ppm level, bulk sulfides of nickel such Ni_3S_2 do not form, instead the Ni surface is covered with adsorbed sulfur. Therefore, bulk sulfides of Ni are not likely responsible for the sudden drop in performance. Moreover, the rapid degradation that may happen within the first minutes after exposure to H_2S also supports the conclusion that surface adsorption is primarily responsible for the initial rapid cell degradation due to anode deactivation [496-497]. Additional support for surface sulfur is

provided by other studies that investigated the effect of different sulfurous species, namely, H_2S , COS and CH_3SH in humidified (3% H_2O) H_2 and CH_4 fuels on Ni/YSZ cermet anodes and found the same deactivation rate at constant current regardless of the type of the sulfurous contaminant [498]. Upon removal of H_2S from the fuel, the cell performance generally recovers fully or partially under H_2 flow from the initial sudden drop, where the extent of recovery depends on the initial H_2S content of the fuel, cell temperature, and exposure time [484,496,497,499]. The pace of the cell recovery process seems to improve greatly with increasing temperature as well as the cell current density [500]. This suggests that lattice oxygen through the YSZ electrolyte may play a role in oxidizing the adsorbed sulfurous species and cleansing the anode surface.

The critical sulfur content required for the onset of significant poisoning and deactivation of the catalytic anode shows a strong temperature dependence, and decreases rapidly with decreasing temperature. In a systematic study that investigated the impact of 1, 2, 4, 6, 8, 10, and 15 ppm H_2S addition to a gas mixture of 79% H_2 + 21% H_2O , it was reported that for H_2S concentrations exceeding 0.05, 0.5, and 2 ppm at 750, 900 and 1000°C, respectively, a dramatic increase in the Ni/YSZ anode overvoltage was observed

Figure 34. Calculated gas phase S-O-C-H equilibrium mole numbers of sulfurous species in 1 mole CH_4 at 800°C, assuming an initial concentration of 10 ppm of sulfur. The vertical (blue) dotted lines indicate the typical operating voltage regime of the SOFC, namely, between OCV and 0.7 V vs air.

Thermodynamic calculations indicate that H_2S is the dominant species in CH_4 environments with COS not far behind. “Adapted with permission from ref. [501] Kishimoto H, Horita T, Yamaji K, Brito ME, Xiong Y-P, Yokokawa H, J. Electrochem. Soc. 2010; 157: B802-B813. Copyright (2010) The Electrochemical Society”

to be 10 ppm [501]. Even with such low H_2S content initially in the fuel, the equilibrium distribution of the gaseous species shown in Figure 34 indicate that H_2S and COS are the

upon exposure to H_2S for 12, 9, and 4 ks at 750, 900 and 1000°C, respectively [497]. However, the poisoning effect was reversible and the cell performance recovered when H_2S -free H_2 was supplied to the cell. This study also reported that under open circuit conditions the anode resistance, when exposed to 2 ppm H_2S , increased by 72% and 18 % at 900 and 1000°C, respectively, while at 750°C the increase in the anode resistance was significantly higher (up to 105%) after exposure to only 0.05 ppm H_2S . To achieve such extremely low H_2S threshold values in the feed gas is demanding and costly, but critically important to avoid the onset of sulfur poisoning. It also highlights the importance of developing catalytic anodes that possess sufficient tolerance to sulfur.

In a recent thermodynamic study, the gas phase equilibrium species in the C-H-O-S system has been reported for the case, where the initial sulfur content is assumed

two dominant species in the gas phase at 800°C over a wide range of oxygen partial pressures. The lightly shaded area in Figure 34 bounded by the vertical dotted lines marks the typical operating regime of SOFCs between OCV and 0.7 V versus air. This operating regime corresponds to $P_{O_2} \sim 10^{-20}$ atm and $P_{O_2} \sim 10^{-15}$ atm at the anode for OCV and 0.7 V cell voltage, respectively, where H_2S and COS are the more stable species in highly reducing conditions, while SO_2 is the more stable gaseous species under relatively more oxidizing conditions. It is clear that in the dry methane environment at the anode, the dominant form of sulfur in the gas phase is H_2S , and whose interactions with the catalyst surface need to be taken into consideration for the development of advanced anode materials with sufficient sulfur tolerance.

At intermediate temperatures lower than 650°C, sulfur-induced cell degradation

Figure 35. Electron microscopy images of the same region in the Ni/YSZ cermet anode after (left top) and before (left bottom) exposure to 100 ppm H_2S at 440°C for 12 hours. The images on the left panel show the formation of the Ni_3S_2 phase, while the corresponding Raman spectra are shown on the right panel. “Reprinted with permission from ref. [493] Cheng Z, Abernathy H, Liu M, J. Phys. Chem. C, 2007; 111: 17997-18000. Copyright (2007) American Chemical Society”

Figure 35, where the formation of bulk Ni_3S_2 phase and the corresponding Raman spectra are presented [493].

5.2.1.2. Stage II poisoning of Ni-based catalytic anodes with H_2S

Mechanistic underpinnings of the long-term deactivation and degradation process are yet to be understood. Upon exposure to H_2S , an immediate and precipitous increase in the polarization resistance of Ni-based anodes may soon be followed by either a steady-state behavior or a monotonic increase over prolonged times that may or may not approach steady state even after hundreds or thousands of hours (see Figure 33). There have been various attempts made to explain and account for the observed degradation behavior under prolonged operation, albeit without unified agreement among the studies.

Life time studies on sulfur tolerance of SOFC anodes ran at 1000°C in gaseous fuels containing 1000 ppm H₂S reported that cell performance quickly attained a steady state behavior soon after the initial sudden drop upon exposure to H₂S, and remained practically unchanged for the following 800 hours of continuous operation [502]. Similar results of a swift steady state behavior were reported more recently on Ni/YSZ cermet anodes exposed to 1 and 10 ppm H₂S-containing H₂ at 750°C under current carrying conditions for over 3000 hours [485]. In other studies, lifetime test results showed performance degradation continued in a monotonic manner up to several thousand hours [488,496]. Long term sulfur stability in humidified H₂ fuel was demonstrated by modifying the Ni/YSZ cermet anode with ceria nanoparticles infiltrated into the porous anode cermet structure, where the cell voltage at an applied current of 400 mA/cm² dropped from the initial value of 0.78 V to 0.6 V upon the introduction of 40 ppm H₂S but then maintained its stability for nearly 500 hours of testing time producing 220-240 mW/cm² of power at 700°C, while the power density for the benchmarked cell featuring the uncoated traditional Ni/YSZ cermet anode precipitously dropped to ~ 0 mW/cm² in about 13 minutes upon the addition of 40 ppm H₂S [503].

The prolonged degradation in these cells suggests that the dominant rate process responsible for this behavior most likely proceeds at a slow rate, although its nature or origin is still unresolved. Several notable accounts of long-term deactivation have been linked to disparate phenomena including surface reconstruction [496], sulfur-electrolyte interactions and Ni oxidation [484], *tpb* site blocking by the sulfur trapped in oxygen vacancies [504]. Even factors extraneous and non-specific to Ni-based anodes have been proposed to account for the prolonged cell degradation process including impurity or defect segregation to the Ni surface, contamination by impurity cross-over from the glass sealant used in the SOFC, sulfur poisoning of the cathode [505] by H₂S leakage through cracks from the anode compartment or by the sulfurous impurities present in the air [485,486]. So the mechanistic nature of the 2nd stage degradation is not understood yet, although one study ruled out the loss of Ni percolation and microstructural changes in the Ni-based cermet on the basis of observations that the cell fully recovers its initial performance upon removal of H₂S from the feed gas [499]. Also, *ab initio* thermodynamic studies of the Ni-S system indicated that regeneration of the Ni surface and removal of sulfur can be effectively achieved by O₂, or preferably H₂O, treatment, and mapped out the temperature and partial pressure regimes for O₂, H₂O, H₂S, and SO₂ to achieve desulfurization of the Ni surface without oxidizing it to NiO during the process [506].

Sulfur induced reconstruction of the Ni(111) [507] and Ni(100) [508] surface has been known for a long time. As adsorption involves both electronic and geometric site interactions between the adsorbate and the surface, the charge redistribution induced by the strong adsorbate-Ni bond removes charge from Ni-Ni bonds at the surface. The weakening of the surface Ni bonds gives rise to surface stresses due to imbalance in the repulsive interactions of the weakly screened surface Ni. Eventually, this can lead to reconstruction of the surface. As this involves rearrangement of surface atoms via diffusion, it has been proposed as a possible explanation to account for the prolonged deactivation behavior of Ni-based anodes [496]. Indeed, the high S/Ni* site ratio observed during desorption experiments were attributed to reconstruction of the Ni surface to a surface sulfide, consistent with the NiS stoichiometry [490].

DFT calculations of the Ni/YSZ interface predicted that adsorbed sulfur does not favor the stoichiometric Ni/YSZ interface because of the coulombic repulsion between the adsorbed sulfur S^{-1} species and lattice oxygen O^{2-} , but so long as there happens to be an oxygen vacancy present at this interface, the adsorbed S^{-1} readily diffuses over a negligibly small (0.03 eV) barrier towards the interface and trapped deeply inside the oxygen vacancy with a considerable barrier height of 1.3 eV [504]. Consequently, the sulfur-trapped oxygen vacancy can no longer participate in oxide ion transport and hinders the charge transfer process at the *tpb*, which leads to reduction in cell performance.

5.2.1.3. Towards Ni-free catalytic anodes for sulfur tolerance

There have been intensive efforts towards better understanding of sulfur-tolerance of catalytic anodes, but no viable materials solution or hypothesis has been developed yet. Although a vast variety of materials have been investigated for this purpose, a large fraction of the work reported to date has been focused on Ni-based catalytic anodes, despite the fact that Ni is known to be susceptible to sulfur poisoning even at sub ppm level as discussed in detail above. Moreover, methane oxidation over Ni-based anodes often leads to coking problems too. On the other hand, studies on Ni-free anodes cover such a broad range of materials that, without a central hypothesis, it is difficult to judge their catalytic merits and stability in the context of sulfur-tolerant applications.

To improve sulfur tolerance, Ni-containing bimetallic or non-Ni based cermet anodes as well as oxides have been investigated. Exploring the impact of metal dispersion and passivation of Ni surfaces, one study investigated Ni/YSZ cermet anodes exposed to Sb and Sn vapors in order to passivate the active surface sites and suppress nickel-sulfur interactions [509]. It was estimated that exposure of the Ni/YSZ cermet anode to 1 ppm Sb vapor resulted in about 2 monolayers (ML), while exposure to 10 ppm Sn vapor gave about 20 ML of surface coverage, discounted for limited solubility of Sb and Sn in Ni particles. Sulfur stability tests conducted at 0.7 V and 800°C with H_2S concentrations of 1 ppm and 5 ppm added to humidified H_2 fuel, respectively, indicated significant improvement in tolerance for both Sb and Sn passivated Ni compared to benchmarked Ni/YSZ anode, especially with Sn, where no change in cell performance was observed in 1 ppm H_2S for nearly 90 hours. However, higher surface coverage of Sb and Sn not only reduced the catalytic activity and cell performance even in pure H_2 possibly by blocking the active sites, but also the performance drop upon exposure to 1 ppm H_2S due to sulfur poisoning became irreversible. Although about 1 ML of surface passivation with Sb or Sn seems to eliminate the catastrophic effect of sulfur poisoning of Ni in 1 ppm H_2S , it should be noted that at high cell polarization, i.e., high current densities, it is very likely that both Sb and Sn are oxidized, and their oxides may offer better sulfur tolerance but at the expense of significant reduction in cell performance due to their blocking effect.

Many transition metals were considered as viable alternatives to Ni from the catalytic point of view, but most of them share similar affinity for sulfur and carbon, and hence the susceptibility for deactivation by both species. Accordingly, decreasing the activity of Ni by alloying with a non-coking metal such as Cu was proposed to mitigate deactivation of the catalytic cermet [378], which eventually lead to full replacement of the Ni/YSZ cermet anode with Cu/YSZ [380,510] and Cu/ceria [312,314,511] cermets.

The advantages of Cu are that it is an inexpensive metal with excellent electrical conductivity, and unlike Ni, does not promote carbon deposition. Also, its sulfides are less stable than the sulfides of Ni. Indeed, Cu/CeO₂/YSZ composite cermet anodes exposed to increasing H₂S levels up to 450 ppm in humidified H₂ fuel (10% H₂O+90% H₂) indicated stable cell performance at 800°C over several hundred hours, while concentrations above 900 ppm H₂ resulted in catastrophic cell degradation, which is attributed to the reaction of ceria with H₂S to form the Ce₂O₂S phase at these high concentrations [512].

Many different families of metal oxides with sufficient transport and catalytic properties are being explored as candidates for Ni-free anode structures. The sulfur tolerance of the pyrochlore structure Gd₂Ti₂O₇ doped with molybdenum to form the mixed ionic electronic conducting (MIEC) anode composition Gd₂Ti_{1.4}Mo_{0.6}O₇ was tested for stability in 10% H₂S + 90% H₂ mixture at 0.7 V constant cell voltage and at 950°C for 114 hours, and showed no observable degradation in cell performance as well as no new phase formation other than the pyrochlore Gd₂Ti_{1.4}Mo_{0.6}O₇ as determined by x-ray diffraction [513]. The modified pyrochlore Gd₂Ti_{1.4}Mo_{0.6}O₇ anode also had considerably high catalytic activity and produced a peak power density of 342 mW/cm² at 950°C in 10% H₂S + 90% H₂ mixture.

Perovskite-based MIEC/electrolyte composite anode structures were also investigated for sulfur tolerant anodes.

Figure 36. Performance of SOFC cells with Ni-BZCYYb anodes on BZCYYb and SDC electrolytes at 750°C operating in dry propane and in humidified H₂ with and without 20 ppm H₂S. The latter demonstrates the sulfur stability of the Ni-BZCYYb anode. “Reprinted with permission from ref. [462] Yang L, Wang SZ, Blinn K, Liu ML, Liu Z, Cheng Z, Liu ML, Science, 2009; 326: 126-129. Copyright (2009) The American Association for the Advancement of Science”

A porous ceramic composite of yttrium-doped SrTiO₃ (YST) and YSZ was impregnated with Ru nanoparticles and CeO₂ displayed a high tolerance up to 40 ppm H₂S containing H₂ fuel, and high catalytic activity with a decent performance of 470 mW/cm² in 10 ppm H₂S containing H₂ at 800°C. Addition of 10 ppm H₂S at a current density of 0.5 A/cm² dropped the cell voltage only slightly from 0.79 V to 0.78 upon exposure to H₂S [514]. Stability studies of La_{0.75}Sr_{0.25}Cr_{1-x}Mn_xO₃ (LSCM) for x= 0.4, 0.5, and 0.6 conducted in 10% H₂S-containing humidified H₂ at 950°C for 5 days, indicated the formation of new phases such as MnS, La₂O₂S and MnOS, suggesting that this catalytically active anode material does not possess sufficient stability against high concentrations of sulfur [321]. Nevertheless, these results suggest the possibility of employing MIEC-based catalytic anode compositions for sulfur tolerance in moderately low sulfur content fuels.

A significant deviation from the MIEC perovskites that conduct oxide ion and electron hole species concurrently, is a new class of potential anode materials based on the mixed ionically (i.e., oxide ions and protons) conducting perovskites of the doped-BaZrO₃ and BaCeO₃ families and their solid solutions that were proposed for mitigating coking and sulfur tolerance in SOFCs [462]. Using yttrium and ytterbium co-doped compositions BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} (BZCYYb) and BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} (BZCY), cells featuring Ni/BZCYYb cermet anodes showed higher and more stable OCV and performance in humidified H₂ than Ni/BZCY, possible due to the cooperative effect of these B-site cations to improve both ionic conductivity as well as catalytic activity. Indeed, cells with Ni/BZCYYb anodes achieved impressively high peak power densities of 1.13, 0.63, and 0.53 W/cm² at 750, 650, and 600°C, respectively, in humidified hydrogen [463,515]. When 20 ppm H₂S was added to wet hydrogen, the cell performance remained practically unchanged with peak power densities of ~1.1 and ~0.66 W/cm² at 750 and 650°C, respectively [462]. The stability of the Ni-BZCYYb anode, especially with the SDC electrolyte under 700 mA/cm² of constant current at 750°C in humidified H₂ containing up to 50 ppm H₂S was exceptional even after more than 50 hours of operation. It was suggested that the dissociatively adsorbed water near *tpb* on the BZCYYb surface facilitates the oxidation of H₂S or elemental sulfur to SO₂, which desorbs readily. The performance of the cells with Ni/BZCYYb anode and either BZCYYb or SDC electrolytes in dry propane and humidified H₂ with and without 20 ppm H₂S is shown in Figure 36. The cell with Ni-BZCYYb anode on BZCYYb electrolyte showed the onset of only minimal degradation for H₂S contents 30 ppm or higher. These values are in general agreement with theoretical predictions by DFT of phase equilibrium studies between the Y-doped Ba(Zr,Ce)O₃ phase and sulfurous environments containing up to 100 ppm H₂S between 600 and 850°C, where only the Zr-containing composition BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} is shown to provide sufficient tolerance to sulfur up to about 60 ppm at 750°C, while the BaCeO₃ and BaCe_{0.8}Y_{0.2}O_{3-δ} phases both decompose into BaS and individual oxides even at few ppm of H₂S [486]. The Ni/BZCYYb was also found to be stable against coking when operated in dry propane, and mass spectrometry of the effluent gas stream confirmed the production of C₂H₄, CH₄, H₂, H₂O, CO₂ and CO species, indicating that this anode composition also possessed good catalytic activity for both the reforming and oxidation reactions of C₃H₈. Unfortunately, no sulfur studies in connection with hydrocarbon oxidation were conducted by the authors on these catalytically active anodes, but their high cell performance in conjunction with high sulfur tolerance up to 20 ppm H₂S as well as their chemical and structural stability against electrochemical cycling for nearly 1000 cycles with no appreciable change [462] makes them quite attractive for further work towards the development of highly tolerant catalytic anodes for sour fuel utilization in SOFCs.

5.2.2. Metal sulfide-based anodes

Some metal sulfides, such as MoS₂, are well known as effective dehydrosulfurization catalysts and have been employed commercially in industrial processes. Accordingly, sulfur and chemical stability as well as catalytic activity of metal sulfide-based materials and others were investigated for SOFC applications. An extensive study using both experimental techniques and thermodynamic analyses screened a large class of materials including metal carbides, borides, nitrides, sulfides, silicides and perovskite-type oxides,

and analyzed their stability against hydrolysis, carbonation, and sulfidation or decomposition in H_2S , CO_2 and H_2O environments, as well as possible interactions and reactions of these materials with other cell components under the conditions relevant to SOFC operation [494]. Due to their chemical instability under SOFC conditions in these environments, the study ruled out most of the metal carbides, nitrides, borides and silicides as potential candidates for sulfur tolerant anodes. The thermodynamic analyses predicted that SrTiO_3 would be stable against 10% H_2S at 950°C , while LaTiO_3 and SrVO_3 , and most likely LaVO_3 too, are all prone to sulfidation reactions, and hence, do not exhibit sufficient tolerance to sulfur. It also predicted that most transition metal sulfides would not be suitable candidate anodes if the fuel contains only ppm level of H_2S , as most would decompose to their metals under these low sulfur activities and may not be suitable for SOFC applications. However, at sufficiently high H_2S levels exceeding 1000 ppm or more, some of the sulfides such as WS_2 or MoS_2 , may have sufficient stability. For example, the thermochemical equilibrium sulfur activity for WS_2 at 1000K corresponds to 9.4×10^{-4} or ~ 1000 ppm H_2S .

On the other hand, the stability of these metal sulfides in high sulfur activities was exploited for removal of H_2S from highly concentrated streams or for the electrochemical oxidation of H_2S for power generation. Indeed, electrochemical removal of H_2S from hot coal gas streams using a Ni_xS -based cathode [516], as well as its electrochemical oxidation on CuFeS_4 catalytic anode [517] in SOFCs has been proposed several decades ago. Experimental results for electrochemical utilization of H_2S on Pt in SOFCs at H_2S levels of 1-25% (balance nitrogen) and SOFC operating temperatures of 600 - 850°C indicated that the favored reaction pathway was the complete oxidation of H_2S to SO_2 and H_2O [518], while another study using 0.37% H_2S (balance He) in a Pt/YSZ/Pt cell demonstrated the NEMCA effect for the decomposition of H_2S to H_2 and S_2 at 600 - 750°C with a rate enhancement factor of 11 achieved at 600°C beyond the Faradaic rate [519]. The underlying reason for the stability of the Pt electrodes in these H_2S environments was revealed by a study that used H_2S as fuel in a Pt/YSZ/Pt cell for co-generation of SO_2 and electrical power between 650 and 800°C [520]. It was reported that the stability and product selectivity of the Pt anode was dependent on the ratio between the O^{2-} ion flux through the YSZ and the rate of arrival of H_2S on to the Pt surface. Poor selectivity for SO_2 was observed when this ratio is less than 0.33, where elemental sulfur is the major reaction product, and the Pt anode has undergone significant sintering and its surface severely deactivated. For higher ratios, there was complete selectivity for the production of SO_2 , and as high as 99% H_2S conversion was achieved.

Several metal sulfides, namely, $\text{CoS}_{1.035}$, WS_2 , and $\text{Li}_2\text{S}/\text{CoS}_{1.035}$ were investigated as possible anode materials for the oxidation of 25% H_2S (balance inert) in SOFCs, where a remarkably high power density of $412 \text{ mW}/\text{cm}^2$ at a cell voltage of 0.317 V and up to 75% conversion of H_2S was achieved with the $\text{Li}_2\text{S}/\text{CoS}_{1.035}$ composite anode at 770°C [521]. The cell performance of the cell with the WS_2 anode was considerably lower, and gave a low power density of $16 \text{ mW}/\text{cm}^2$ for 25% H_2S at 820°C .

MoS_2 is an inexpensive and active catalyst tolerant to sulfur, but it also tends to sublime above 450°C at atmospheric pressure, which limits its use in the high operating temperature regime of SOFCs. To overcome this drawback, bimetallic sulfides of M- MoS_2 (M=Fe, Co, Ni) were investigated as sulfur tolerant anode candidates in pure H_2S /air SOFCs between 650 and 830°C [522]. Although the composite metal sulfide

anode structures practically eliminated volatilization losses of MoS₂, the performance of the cells were modest at best but still comparatively better than for the benchmarked Pt catalyst, which was severely deactivated by the 100% H₂S fuel. IR-compensated maximum power density of 115 mW/cm² was achieved with the cell employing Co-Mo-S composite anode at 850°C. The sulfur and performance stability of this cell was greatly improved by adding Ag power to the Co-Mo-S composition, and stable operation without any degradation was achieved in pure H₂S at 450 mA/cm² constant current density at 850°C for over 6 days of continuous testing [522].

5.2.3. Sulfur tolerance in CH₄ environments

Much of the preceding discussion on sulfur poisoning is related mostly to H₂S containing H₂ fuel environments at the catalytically active Ni-based SOFC anodes. As indicated in the equilibrium gas phase composition of Figure 34, inclusion of the carbon chemistry to hydrogen, as is the case for methane, introduces new sulfurous species, especially COS, which also interact with the anode surface, and hence must be accounted for in the development towards sulfur-tolerant catalytic anode materials.

Accordingly, anode deactivation processes during methane oxidation are more complicated than for the case of H₂S-contaminated H₂ oxidation. Aside from the interactions of sulfur with the anode surface, oxidation of sulfur-containing hydrocarbons proceed somewhat differently from H₂ due to the prevalence of reformation and water gas shift reactions taking place concurrently, and being affected by sulfur and potentially by carbon deposition also.

5.2.3.1. Sulfur-poisoning of Ni-based anodes in CH₄ environment

As an excellent reforming catalyst, Ni has been employed in many SOFC studies for hydrocarbon conversion. An EIS study of the Ni/ScYSZ cermet anode (zirconia co-doped with 10 mol% Sc₂O₃ and 1 mol% Y₂O₃) in dry CH₄ fuel containing 0-100 ppm H₂S at 850°C and under various current densities ranging from 0 to 1 A/cm² indicated several interesting results [523]. EIS results indicated that the presence of H₂S affected two major processes, namely, the chemical kinetics of the internal reforming reaction and the electrochemical charge transfer reaction at the *tpb*. Contrary to the behavior in H₂ fuel, increasing the current density for the CH₄-fueled cell did not seem to mitigate the poisoning effect of the electrochemical charge transfer reaction. However, the poisoning effect was found to be reversible upon removal of H₂S from the methane fuel, but the initial loss in performance was higher at higher current densities, which is in contrast to some of the earlier studies that reported the drop in the anode polarization resistance due to poisoning in H₂S-containing H₂ fuel was smaller at high current densities [500]. A study comparing the behavior of Ni/YSZ and Ni/ScYSZ cermet anodes reported that the latter anode composition greatly improved the sulfur tolerance of CH₄-containing fuels with sulfur contents of 10-20 ppm H₂S over hundreds of hours, yet the cell behavior indicated both anodes suffered severe poisoning even at 2 ppm H₂S that greatly reduced the reforming activity and degraded cell operation [488]. In a separate study using Ni/YSZ anodes, nearly 60% of the methane reforming activity was lost after introducing 4 ppm of H₂S at OCV, but at 1 A/cm² of current density a reasonably stable cell operation was possible below 7-9 ppm H₂S [483]. Also, the impact of sulfur poisoning on the

charge transfer reaction at the *tpb* was significantly more pronounced than for internal reforming. This finding is supported by theoretical predictions of increased charge transfer resistance due to sulfur trapping in oxygen vacancies at the Ni/YSZ *tpb*, blocking the pathway for oxide ion transfer [504]. Similar studies on direct internal reforming of methane on Ni/YSZ at 750°C indicated that addition of 1 ppm H₂S significantly degrades both the reforming activity and cell voltage, while the extent of degradation was found to be only partially reversible due to residual adsorbed sulfur detected by depth profiling on the surface of Ni particles down to ~40 nm below surface [524]. Addition of 2 ppm H₂S into simulated coal-syngas containing methane was also reported to inhibit the reforming activity of the Ni/YSZ anode at 750°C [525]. Doubly doped ceria-based cermet anodes of the composition Ni/Ce_{0.8}Y_{0.1}Yb_{0.1}O_{1.9} were reported to show resistance to coking as well as display excellent sulfur tolerance to 5 ppm H₂S-containing dry CH₄ at 750°C for 120 hours of stable cell operation at a current density of 200 mA/cm² [526]. The cooperative effects of the two rare earth cation dopants combined with the catalytic activity of ceria were proposed to account for the enhanced tolerance and stable cell operation.

Nevertheless, the rapid deactivation due to strong binding of sulfur to Ni even at sub-ppm concentrations makes it very difficult to effectively employ Ni as the catalytic anode for CH₄ oxidation in the presence of sulfur-containing contaminants, as is the case for natural gas. In recognition, there is major interest in the SOFC community to develop catalytically active sulfur-tolerant anodes for natural gas conversion.

5.2.3.2. Sulfur-tolerance on transition metal-based anodes in CH₄ environment

Cu/ceria-based cermet anodes were developed and investigated for direct oxidation of dry hydrocarbons in sulfurous environments. A comparative study of coking and sulfur tolerance properties as well as cell performance at 800°C between the Cu/YSZ cermet anode and Cu/CeO₂/YSZ composite cermet anode reported better cell performance for the composite cermet than with Cu/YSZ in both H₂ and dry CH₄ fuels resulting in full oxidation of methane to CO₂ as confirmed by current measurements and product gas analysis [527]. Although Cu exhibited no catalytic contribution, the addition of ceria to the cermet greatly improved cell performance and indicated that ceria is a good oxidation catalyst transferring the lattice oxygen to the *tpb* site for the oxidation reaction. Interestingly, however, the sulfur tolerance of the Cu/YSZ was significantly better than the ceria-containing cermet, where cells operating in n-decane fuel containing 5000 ppm sulfur in the form of thiophene operated without degradation for 24 hours, while Cu/ceria/YSZ anode showed severe deactivation when exposed to 5000 ppm sulfur due to the formation of the Ce₂O₂S phase [512]. Sulfur tolerance of Cu is possibly due to the fact that Cu does not play a significant role in catalyzing the methane oxidation reaction and so its surface sulfur does not affect its catalytic behavior. Moreover, sulfides of copper are less stable than nickel sulfides. This presents a challenging choice between the catalytically active ceria-based cermets prone to sulfur deactivation versus sulfur tolerant but catalytically inactive YSZ-based cermets. Many of the salient electrical and catalytic properties of Cu-based cermet anodes for methane oxidation, their fabrication processes and microstructural features are discussed in detail elsewhere [312,314,380].

Other transition metal or alloy cermet compositions such as Fe-Ni alloy/ScSZ cermet [528] and Fe/YSZ cermet [373] anodes have been investigated for oxidation of

hydrocarbon fuels in SOFCs, but with the expected outcome of carbon deposition, while sulfur tolerance of these anodes was not examined. A density functional theory (DFT) study investigated M/Ni alloys (M= Bi, Mo, Fe, Co, Cu) for methane activity, and sulfur and carbon tolerance and the results indicated that surface carbon and sulfur can be inhibited by surface alloying of Ni with Mo while preserving the catalytic activity, but the best catalytic activity was obtained with Cu/Ni, Fe/Ni, and Co/Ni alloys [529].

Aside from perovskite-type oxides, other structures were also explored. A more notable and promising development is the cermet anode matrix of the composition $\text{Pr}_{0.8}\text{Sr}_{1.2}(\text{Co,Fe})_{0.8}\text{Nb}_{0.2}\text{O}_{4+\delta}$ having the K_2NiF_4 -type crystal structure and containing dispersed Co-Fe alloy nanoparticles. This material was investigated for methane oxidation activity and sulfur resistance in a SOFC, and the composite anode containing the Co-Fe alloy nanoparticles showed excellent catalytic activity of 960 mW/cm^2 of power density in H_2 at 850°C and 860 and 920 mW/cm^2 of power density when exposed to 50 and 100 ppm H_2S -containing H_2 fuel, respectively, at the same temperature and showing stable operation for nearly 100 hours under constant current conditions of 600 mA/cm^2 at 800°C in 50 ppm H_2S containing H_2 [530]. Moreover, this redox stable composite anode also performed well in CH_4 and C_3H_8 fuels giving power densities of 600 mW/cm^2 and 940 mW/cm^2 , respectively, at 850°C with no indication of coking. The presence of the Co-Fe alloy was ascribed to the high performance of this anode material that compares well with Ni-based cermets, but with better tolerance to coking and sulfur poisoning.

5.2.3.3. Sulfur-tolerance studies on oxide anodes in CH_4 environment

Much of the attention towards the development of sulfur-tolerant anodes is focused on doped perovskites. A redox stable perovskite composition $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) was proposed as a potential anode material for oxidation of H_2 as well as for complete oxidation of CH_4 to CO_2 [181,197,531-533] with catalytic activity comparable to Ni/YSZ without the carbon deposition problem, but found to display low activity for CH_4 reforming either with H_2O or CO_2 [415]. This composition undergoes a phase transformation from hexagonal structure in air to orthorhombic in H_2 , which is accompanied by a negligible ($\sim 1\%$) volume change. Accordingly, its conductivity increases about an order of magnitude in the 10% H_2S containing H_2 environments [321]. Exposed to 10% H_2S -containing humidified H_2 , the SOFC exhibits the typical catastrophic deactivation behavior due to sulfur poisoning of this anode material, where the current density at 0.7 V dropped from about 220 mA/cm^2 to 120 mA/cm^2 within 1 hour. Also, the formation of secondary impurity phases such as the electronically conducting MnS and α -MnOS and the insulating $\text{La}_2\text{O}_2\text{S}$ were detected by x-ray diffraction analysis upon exposure for 5 days at 950°C [321], or even 2 hours of exposure to 5% H_2S containing H_2 at 800°C [194]. These results suggest that the LSCM anode composition may not possess sufficient sulfur tolerance and stability at such high H_2S concentrations as originally proposed. Moreover, catalytic studies of methane oxidation over LSCM in pulse reactors, although reported 100% total oxidation at high oxygen stoichiometries, also observed insufficient catalytic activity short of what may be desirable for practical applications [181]. MgO-promoted chromite-based oxides with the general formula $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_{3-y}\text{MgO}$ ($x = 0, 0.25$, and $y = 0, 17$) were investigated

in a fixed bed reactor for catalytic combustion of methane in 200 ppm SO₂-containing 2% CH₄+18% O₂ (balance He) reaction mixture at 800°C, and indicated several interesting results, namely, the presence of MgO improves catalytic activity and sulfur tolerance by providing preferential adsorption sites for SO₂, while the catalytic activity scales with the Cr content in the structure [534]. The study suggested LaCr_{0.5}Mg_{0.5}O₃ representing the optimal composition for reasonable catalytic activity as well as sufficient sulfur tolerance.

Sulfur tolerance studies for the La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ}/Gd_{0.2}Ce_{0.8}O_{1.9} composite anode structure were conducted in 0.2% and 0.5% H₂S containing humidified CH₄ between 750 and 900°C under anodic polarization conditions [535]. Stability tests in humidified 0.5% H₂S + 99.5% CH₄ mixture at 850°C under a constant anodic potential of -0.5 V indicated the typical initial drop in current density from 0.233 A/cm² to 0.2 A/cm² in the first 10 hours representing a degradation rate of 1.4%/h was followed by the 2nd stage slow decline at a rate of 0.017%/h for the next 110 hours of operation. Electron microscopic and energy dispersive x-ray analysis of the anode indicated the absence of carbon or sulfur, and the 2nd stage slow degradation was ascribed to coarsening effects in the anode microstructure. With such limited sulfur tolerance and moderate cell performance for methane oxidation, the practical prospects for the LSCM catalytic anodes remain questionable.

Sulfur poisoning and catalytic activity for methane combustion of the Ce-doped lanthanum manganite cobaltite of the composition La_{1-x}Ce_xMn_{1-y}Co_yO₃ was investigated in 20 ppm SO₂-containing 1% CH₄ in air at 700°C and full combustion of CH₄ to CO₂ was reported for all compositions of x and y. However, all compositions also displayed poor tolerance to sulfur due to the formation of sulfate groups around the surface La³⁺ ions forming La₂(SO₄)₃ [536].

Alternatively, the vanadate-family of doped perovskites is also investigated as potential candidates for sulfur-tolerant SOFC anodes. La_xSr_{1-x}VO_{3-δ} was reported to be stable over the range of oxygen partial pressures from 10⁻¹⁴ to 10⁻²⁰ atm, with high n-type electronic conductivity up to 120 S/cm measured at 800°C and oxygen pressure of 10⁻²⁰ atm for the composition La_{0.7}Sr_{0.3}VO_{3-δ}, but did not seem to possess sufficient redox stability with the irreversible formation of Sr₃V₂O₈ phase in oxidizing conditions with poor electrical conductivity [537]. Another study reported much higher electrical conductivities of 800 S/cm for La_{0.3}Sr_{0.7}VO_{3-δ} in humidified H₂ and 149 S/cm for La_{0.7}Sr_{0.3}VO_{3-δ} at 800°C, and found La_xSr_{1-x}VO_{3-δ} is stable in reducing (4% H₂+96% Ar) atmosphere as well as when exposed to high H₂S content (10% H₂S+3% H₂O+ 87% H₂) mixture at 950°C for 5 days for the stoichiometries x=0.3, 0.5, 0.7, where no changes in the x-ray diffraction patterns were observed [538]. Despite decent electrochemical activity, however, the x-ray diffraction results also indicated large volume changes during re-oxidation of LSV that makes it difficult to employ LSV as the lone anode material. The La_{0.7}Sr_{0.3}VO_{3-δ} composition was tested for stability and performance in 5% H₂S (balance N₂) and 5% H₂S (balance H₂) mixtures at 1000°C, and showed modest cell performance of 90 mW/cm² and 135 mW/cm², respectively, as well as good stability against 5% H₂S with no significant deterioration over 48 hours [539]. Based on these encouraging results, LSV anodes with the nominal composition La_{0.7}Sr_{0.3}VO_{3-δ} were tested for sulfur tolerance in 5% H₂S + 95% CH₄ mixture at 950°C with decent power density of 280 mW/cm², and stable cell

performance for 4 hours before cell degradation commenced [540]. Interestingly and unexpectedly, the same anode composition run in pure H_2 gave nearly a factor of 2 less performance of only 155 mW/cm^2 at the same temperature, and the higher performance of the LSV anode in the 5% H_2S + 95% CH_4 fuel mixture was attributed to the formation of a catalytically active surface sulfide at these high H_2S concentrations. Moreover, the cell degradation after 4 hours was ascribed to slow delamination of the anode layer from the YSZ electrolyte, and not to sulfur poisoning.

$La_{0.7}Sr_{0.3}VO_{3-\delta}$ catalyst infiltrated into porous YSZ to make a LSV/YSZ composite anode with ~10% LSV loading did not possess sufficient activity but the addition of Pd catalyst and CeO_2 to the anode improved the cell performance at 700°C from 90 mW/cm^2 to 470 mW/cm^2 in humidified H_2 fuel, while cell performance at 800°C was 960 mW/cm^2 in H_2 fuel and 510 mW/cm^2 in CH_4 [419]. However, the composite anode with Pd/ CeO_2 active catalyst and LSV/YSZ, when heated in air, indicated strong degradation in the cell performance that decreased to 280 mW/cm^2 at 700°C in humidified H_2 fuel suggesting an adverse interaction of the active catalyst with LSV. Despite their tolerance to sulfur, their poor fuel cell performance in the absence of an active catalyst does not qualify LSV-based anodes as promising candidates for methane oxidation due to their inherently insufficient catalytic activity.

Rare earth metal doped- $SrTiO_3$ perovskites are investigated for potential sulfur tolerant catalytic anodes for SOFCs that utilize sulfur-containing fuels. An all-ceramic composite anode made by mixing a 50:50 mass ratio of $La_{0.4}Sr_{0.6}TiO_3$ (LST) with YSZ indicated high catalytic activity, high stability, and excellent sulfur tolerance when tested at 850°C in CH_4 containing up to 20% H_2S , where the power density was measured to be 450 mW/cm^2 compared to the case in pure CH_4 , which only yielded 2 mW/cm^2 on the same composite anode [541]. This intriguing result of such dramatic improvement of more than 2 orders of magnitude in cell performance from 2 to 450 mW/cm^2 merely by the addition of 20% H_2S into methane was attributed to the strong promoting effect of H_2S in CH_4 activation, where the formation of the surface intermediate methyl thiolate (CH_3SH) was proposed to participate in the oxidation reaction to form CS_2 , which was confirmed by gas analysis. XPS analysis of the anode surface indicated the presence of elemental sulfur, but no trace of metal sulfides. Furthermore, x-ray diffraction analysis indicated no new phases after this 50:50 composite anode was exposed to 5000 ppm H_2S at 1200°C for one week, confirming its superior chemical and sulfur stability in high sulfur environments. A slightly modified composition $La_{0.4}Sr_{0.5}Ba_{0.1}TiO_3$ (LSBT) of the catalytically active LST was impregnated into porous YSZ to make a composite anode, where the presence of 5000 ppm H_2S in CH_4 made it more difficult to remove carbon deposits [542], but the cell performance in dry CH_4 containing 5000 ppm H_2S was again significantly higher than in pure CH_4 , with similar trends for H_2 - H_2S mixtures, at temperatures 800 - 900°C [543,544]. As in the case of LST/YSZ and LSBT/YSZ composite anodes, it is interesting to note that the YSZ/YST composite anodes made by impregnating porous YSZ with $Sr_{0.86}Y_{0.08}TiO_3$ also indicated dramatic improvement in cell performance by a factor of 35 when 5000 ppm H_2S was added to humidified CH_4 fuel, such that the maximum power densities obtained with and without H_2S addition to CH_4 were, respectively, 37 and 1.1 mW/cm^2 at 850°C [545]. The origin of this enhancement is not understood. It is suspected that the adsorption of H_2S on oxygen

vacancies may lead to sulfur groups on the surface that may be playing a critical role in activation of the catalyst for methane oxidation.

6. Opportunities and Outlook for Methane Conversion in SOFCs

Largely driven by the focus of federal research programs in hydrogen, most of the prior work on SOFCs has been based on the use of H₂ as the preferred fuel, although hydrogen, unlike natural gas, is not a naturally occurring energy source. With the distribution infrastructure already in place, natural gas conversion to electrical power in SOFCs is a promising technology, but it poses major technical difficulties also. Natural gas typically contains 85-95 vol% CH₄ with the remaining made up by CO₂, N₂, other hydrocarbons and sulfurous contaminants. The presence of sulfur and its detrimental impact on anode activity has been one of the big impediments to effectively use natural gas in SOFCs without major pretreatment. Additional demands are placed on the catalytic anode, as the methane molecule is difficult to activate and oxidize electrochemically. Hence, the logical progression to natural gas conversion has to be built on fundamental understanding of methane oxidation as the first step towards natural gas utilization in SOFCs.

6.1. Role of theoretical tools in catalyst design

Although much progress has been made in the fundamental understanding of catalysis and how it relates to materials properties, much of the prior work for catalyst development has traditionally been done by an *ad hoc* approach based mostly on trial-and-error. However, the advent of massive computational tools and development of effective theoretical descriptors have made it possible to increasingly utilize rational design of catalysts and gain mechanistic understanding of surface reactions [411,546-551]. Effective methodologies and computational tools are becoming increasingly predictive for designing catalysts for a wide range of diverse reactions, including methane activation [408], steam reforming of methane [409,457,552], the oxygen evolution reaction (OER) [553,554], NH₃ synthesis [555], photoelectrochemical water-splitting reactions [556], and the oxygen reduction reaction (ORR) [557].

6.1.1. Computational tools and activity descriptors

As in most catalytic reactions, methane oxidation involves multiple elementary steps, and individual identification and determination of these steps usually pose major difficulties experimentally. Spectroscopic *in situ* probing and determination of surface intermediates participating in the catalytic reaction is also quite challenging and not always possible *in operando*. In this regard, computational methods can play an important role in gaining better insights in understanding the energy barriers associated with reaction steps and participating intermediates along the reaction coordinate, as well as rationalizing how and why catalytic activity changes from one catalyst to the next [546,549]. Reactivity trends of metal surfaces can be studied by *ab initio* calculations of activation barriers for transition states and surface intermediates, from which one can construct potential energy surfaces for various reaction pathways and identify the kinetically significant steps in the reaction pathway to gain mechanistic insights for the reaction. It has long been recognized that electronic factors play a major role in catalytic

surface, and hence interact more strongly with the adsorbed intermediates at these sites than the highly coordinated metal atoms on closed packed surfaces. The stronger binding energy shifts the electronic effect along the BEP line as shown in Figure 19.

The universality of the linear BEP rule was demonstrated to hold more broadly for numerous reaction systems [563] as shown in Figure 37. The linear fit to these reactions can then be expressed universally in terms of the scaling parameters γ and ζ that represent the slope and the intercept of the linear plot in Figure 37, respectively.

$$E_a = \gamma \Delta E + \zeta \quad (43)$$

When the change in ζ is much smaller than ΔE , then the reaction mechanism on that metal surface is governed largely by electronic effects, as is the case for methane hydrogenation,

Figure 38. Volcano plot for the oxygen evolution reaction (OER) showing calculated values of theoretical overpotentials as a function of the adsorption energies of the surface intermediates HOO* and HO* for the OER on doped surfaces of M-Ti₁₅O₃₂ (where M= V, Nb, Ta, Cr, Mo, W, Mn, Fe, Ru, Ir, Ni, colored points) Green circles denote configurations where the dopant cation resides in a 5-fold coordinated site, while the triangles denote dopants residing in 6-fold coordinated sites on TiO₂. Undoped TiO₂ and RuO₂ are shown in boxes, where the latter is still the best OER catalyst. “Reprinted with permission from ref. [553] García-Mota M, Vojvodic A, Metiu H, Man I C, Su HY, Rossmeisl J, Nørskov JK, Chem. Catal. Chem. 2011; 3: 1607–1611. Copyright (2011) John Wiley and Sons”

while geometrical effects become dominant if the change in ζ is significantly larger than ΔE on the BEP plot. In recent years, density functional theory (DFT) calculations have successfully been employed to show that this linear relation indeed holds for a wide range of reactions, including NH₃ synthesis, CO hydrogenation, and many others involving hydrocarbons [561,564]. The scaling parameters γ and ζ for the CH_x-O coupling reaction were calculated to be in the range of 0.77-0.87 and 1.59-2.32, respectively [563]. Note that the calculated best-fit BEP slope of 0.77-0.87 for the methane oxidation reaction is close to but slightly lower than unity. Nevertheless, the BEP relation is a useful tool in estimating the activation barrier for a given reaction and establishing catalytic trends among the expected

behavior of prospective catalysts.

Likewise, effective descriptors such as d -band center (ϵ_d) and binding energy have been identified to construct ‘volcano plots’ that describe the trends in catalytic activity of metal surfaces, which provide immense insights into materials screening, selection, and mechanistic understanding [411]. The d -band center is a good measure and descriptor of the d -states, as the interaction of the surface adsorbate valence states with the metal d -states largely governs the interaction energy (i.e., surface binding energy). The sp bands of the metals are usually broad and structureless while the d -bands are narrow such that small changes induced by the adsorbate lead to significant changes in the d -band states. A similar theoretical approach was employed to examine doped perovskite-based catalytic anodes for the oxygen evolution reaction (OER), which showed good correlation between the catalytic activity and the occupation of the d -states [554,557].

It is well known that catalytic and transport properties of materials can effectively be altered or improved through appropriate doping, but experimental testing and verification of the prospective materials is tedious and time consuming. Density functional theory (DFT) calculations can provide helpful guidance to establish trends and devise synthetic strategies towards developing effective catalysts. For example, RuO_2 is the best catalyst for the oxygen evolution reaction (OER) but it is expensive, while TiO_2 is a poor catalyst with a high overpotential for OER, but it is cheap and abundant. DFT studies have suggested that proper doping of TiO_2 with transition metal oxides may significantly enhance its catalytic activity approaching to that of RuO_2 . This is shown in Figure 38, where the activities of the Cr-, Mo- and Mn-doped TiO_2 catalysts approach the best OER catalyst [553]. In a similar manner, it should be possible to search for low-cost and abundant catalytic materials that can effectively and selectively oxidize methane, while providing significant tolerance against coking and sulfur poisoning. Progress in this promising area of predictive computational design of catalysts will have huge practical implications and benefits for energy research [565].

6.1.1.1. Catalyst screening and selection

Density functional theory approach represents a trade off between speed and accuracy of studying systems of a few hundred atoms to understand the physical and chemical behavior of materials. For this purpose, a computational materials repository has recently been developed at the Technical University of Denmark and is available for the use of the scientific community [566,567]. Such major advances in DFT and other theoretical methodologies enable the study and understanding of surface rate processes and the energetics of reaction mechanisms and hence, create the possibility for theory-guided catalyst design. There have been useful developments in this direction. For example, a web-based application program dubbed CatApp is now available online [547] and stores energetic information for transition states and intermediates in elementary reactions on transition metal surfaces. To make rapid advances in methane catalysis, there is a need to devise high throughput computational screening of the materials space for prospective catalysts specifically targeting methane oxidation.

There have been numerous DFT studies of methane transformation reactions on individual catalysts. However, many of the DFT calculations for catalysis reported for methane adsorption [568], activation [98,408,569], dehydrogenation [570], and steam

reforming [457,552] reactions have focused only on a single metal catalyst or at best, on a handful of potential catalysts [409]. With such a small and specific sampling, it is difficult to draw generalized conclusions about the best candidates predicted for methane oxidation.

There are only a few examples of first principles studies in methane catalysis in search of a novel methane steam reforming catalyst. One DFT study screened several transition metals and alloys, including precious metals, considered different surfaces for catalyst-adsorbate interactions, ruled out all precious metals after filtering the candidates through cost considerations, and finally recommended a short list of several Ni and Co alloys as potentially active reforming catalysts [409]. Among the recommended were Co_3Ni and Ni_3Fe , which are already known to be effective catalysts, but interestingly, the list also included several potential candidates such as Ni_3Ge , Ni_3Sb and Co_3Ge , which have yet to be investigated and tested experimentally. A similar study of methane steam reforming catalysis combined DFT calculations with experimental work at 500°C and 1 bar pressure and 10% conversion, and evaluated the catalytic activity for different combinations of supported catalyst systems that considered the metal catalysts Ru, Rh, Ir, Pt, Pd, Fe, Co, Ni, Cu, Ag, Au, and W supported on three oxides, namely ZrO_2 , Al_2O_3 , and MgAl_2O_4 [552]. After eliminating thermodynamically unstable, or catalytically inactive or easily deactivated metals, and assuming that the metal-support interactions are negligibly small, good agreement between theoretical and experimental results was

Figure 39. Predicted stability-band gap diagram of various perovskites that may be candidates for photoactive for photoelectrochemical splitting of water using visible light. The redox potentials for water, and the direct and indirect band gaps are also indicated. Several of the oxynitride compositions look promising, but have not been investigated yet. Adapted with permission “Reprinted with permission from ref. [572] Castelli EI, Olsen T, Datta S, Landis DD, Dahl S, Thygesen KS, Jacobsen KW, Energy Environ Sci. 2012; 5: 5814-5819. Copyright (2012) Royal Society of Chemistry”

reported for the rank ordering of catalytic activities. While experimental results ranked the reforming activities as $\text{Ru} \sim \text{Rh} > \text{Ni} \sim \text{Ir} \sim \text{Pt} \sim \text{Pd}$, the theoretical predictions followed a similar trend, namely, $\text{Ru} > \text{Rh} > \text{Ni} > \text{Ir} > \text{Pt} > \text{Pd}$. Such insights into catalytic trends gained through computational studies promise important advances in better understanding and discovery of new catalytically active materials for methane activation.

An excellent example of high throughput quantum calculations for massive materials screening and discovery methodologies relates to the recent computational study in search of identifying new photoactive electrodes in the perovskite family of oxides for the photoelectrochemical (PEC) splitting of water using sunlight [551] [556]. Although this particular example lies outside the topical area of this article, it is nevertheless presented here

in order to demonstrate the exceptional power and potential benefits of such

computational screening methodologies for rapid materials discovery. This study included a matrix of 52 elements of the periodic table for the A and B cations in the ABO_3 perovskite-structure materials space with 7 different anions and their combinations such as oxynitrides, oxysulfides, oxyfluorides, resulting in a materials space of 19,000 different possible compositions. The massive materials selection process in these electronic-structure calculations used chemical stability, Goldschmidt's tolerance factor for structural stability, and band gap as the key criteria to qualify prospective candidates for potential photoelectrodes. Out of the 19,000 compositions that were investigated, only about 20 perovskite compositions possessed the required light harvesting and stability properties for a one-photon PEC process for water splitting [571,572]. This is shown in Figure 39, which also indicates the corresponding positions of the redox potentials for water with respect to the band gaps of the candidate materials. For PEC activity, the band gap needs to straddle the redox potential of water for an effective and efficient photoelectrode. Furthermore, the overvoltage losses associated with the hydrogen reduction reaction (HRR) at the cathode and the oxygen evolution reactions (OER) at the anode with respect to the positions of the band gap place additional constraints on the materials screening process and bring the numbers of candidate materials further down to only a handful, some of which, such as the oxynitrides, have not been investigated yet for photoelectrode applications.

Equally important is the ability to predict relative stability of the candidate materials in the working cell environments. For this purpose, DFT calculations were successfully employed to construct surface Pourbaix (i.e., potential-pH) diagrams for various oxides and perovskites considered as candidate photoelectrodes to evaluate their relative stabilities against corrosion in the aqueous photoelectrochemical cell environment [573]. Although this particular system, especially the concept of pH, may not be directly relevant to high temperature methane conversion in SOFCs, but this theoretical approach points to invaluable opportunities to use DFT calculations to construct surface Pourbaix diagrams to predict materials stability under SOFC operating conditions. As surface acidity plays a major role in the activation of the C-H bond for methane catalysis (see sections 3.1.1. Catalyst-support interactions, and 3.3. Role of lattice oxygen), the concept of surface acidity may be employed in place of pH to provide meaningful guidance to materials screening and selection processes for the design and development of advanced catalytic anodes for methane oxidation.

It is clear that these massive screening methodologies afforded by theoretical computations are becoming invaluable tools to establish trends, predict semiquantitative information about expected properties, provide guidance to experimental research and verification, and greatly expedite development time for novel catalytic materials. This holds particularly true for the rapid development of sulfur-tolerant catalytic anodes for direct oxidation and conversion of natural gas for power generation in SOFCs.

6.1.2. Mechanistic understanding of reaction pathways

A detailed mechanistic understanding of how catalysis occurs at the atomic scale and how to effectively design and control matter for catalyzed transformations has been identified as one of the grand challenges for basic energy research needs by the U.S. Department of Energy [565]. Major breakthroughs in the understanding of catalysis and

design of advanced catalysts are expected to result from advances in theoretical and computational methods [574]. Such in-depth understanding is essential to design and modify catalytic behavior of matter at the atomic scale in order to accomplish selective catalysis of the desired reaction product(s) with sufficient rates. This in turn requires accurate prediction and understanding of the energetics of intermediate species, especially transition states, along the reaction pathways at the level of elementary steps that may lead to the identification of the minimum energy pathways. Indeed, the DFT approach can effectively be used to estimate the interaction energies of atomic or molecular species with metal surfaces and to establish catalytic trends in activity and selectivity [575]. Use of these computational tools to screen materials properties and map out the possible candidates to be synthesized and tested experimentally in the laboratory is an effective, fast and low cost way of developing new catalysts. In other words, electronic structure calculations for materials screening combined with quantum

Pd-ceria Mixed Oxide Most Active for Methane Oxidation

Figure 40. (Top) Calculated activation barrier heights for methane oxidation on catalytic $\text{Pd}(111)$, $\text{PdO}(100)$ and $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2(111)$ surfaces in the Pd/ceria system, indicating the lowest barrier for $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2(111)$. (Bottom) Reaction free energy diagram for methane oxidation via reaction $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) = \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ over the $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2(111)$ catalytic surface at 25°C, and partial pressures of 0.01 atm and 0.04 atm for $\text{CH}_4(\text{g})$ and $\text{O}_2(\text{g})$, respectively. The stable intermediate H^*-OH^* on the (111) surface is depicted in the inset, where Ce atoms are in tan color, O in red, Pd in blue, and H in white. “Reprinted with permission from ref. [98] Mayernick AD, Janik MJ, J. Catal. 2011; 287: 16-25. Copyright (2011) Elsevier”

calculations of the energy landscape along the reaction pathways offer invaluable information to guide catalyst design and development.

Despite the large number of DFT studies on chemical transformations of methane, only a handful has been for the catalytic oxidation of methane, while others investigated catalytic routes to higher value chemicals or syngas. A DFT study of steam reforming methane on $\text{Ni}(111)$ under realistic reaction conditions of 800°C and 10 bar pressure with an initial $\text{H}_2\text{O}/\text{CH}_4$ ratio of 2.5:1

employed a statistical mechanical treatment to account for entropic effects and identified the primary reaction pathway, which involved the dissociative adsorption of $\text{CH}_{4(g)}$ to CH^* in addition to dissociative adsorption of $\text{H}_2\text{O}_{(g)}$ into 2H^* and O^* [576]. The rate determining steps were found to be the adsorption of $\text{CH}_{4(g)}$, and the surface reaction between adsorbed species CH^* and O^* to form CHOH^* . A more relevant DFT study involved methane oxidation over $\text{Pd}(111)$, $\text{PdO}(100)$, $\text{CeO}_2(111)$, and $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2(111)$ catalytic surfaces for CH_4 and O_2 gas mixtures with partial pressures of 0.01 atm and 0.04 atm, respectively [98]. This computational study examined the relative stabilities of the intermediate species and evaluated the energy barriers for methane activation on the Pd/CeO₂ catalytic system. It was found that the $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2(111)$ surface offered the most favorable energy profile and the lowest activation barrier for the methane oxidation reaction. This is presented in Figure 40, which shows the reaction free energy profile for the catalytic oxidation of methane over $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2(111)$ catalyst. Again, the reaction pathway for methane adsorption is initiated by the activation of the first C-H bond and abstraction of the resulting H by the surface oxygen to form CH_3^* .

Unfortunately, literature on first principles calculations specifically looking at anodic oxidation of dry methane in SOFCs is quite scarce. Among the few studies, two of them specifically address methane oxidation on the Ni/YSZ anode. A DFT study examined methane adsorption and oxidation on bare YSZ surface [577] to establish a baseline for a similar subsequent study that investigated methane oxidation at the Ni/YSZ interface of the SOFC anode [578]. DFT studies of methane on YSZ(111) and $\text{ZrO}_2(111)$ surfaces

Figure 41. Energy profiles of the intermediate species calculated by DFT for the reaction pathways for the dissociation (blue lines) and oxygenation (red lines) of methane on the Ni surface of the Ni/YSZ cermet (a) and on pure Ni surface (b). “Reprinted with permission from ref. [578] Shishkin M, Ziegler T, J. Phys. Chem C, 2009; 113: 21667-21678. Copyright (2009)

indicated that subsequent filling of the vacant sites by externally supplied oxygen was a mandatory energetic condition to achieve adsorption and oxidation. This is because the dissociative adsorption of methane on YSZ(111) and $\text{ZrO}_2(111)$ was found to be highly endothermic, and rendered these surfaces practically inactive unless oxygen is supplied through the YSZ electrolyte from the cathode side. By contrast, dissociative adsorption of methane on oxygen-enriched YSZ(111) surface was found to be exothermic and this surface was highly reactive to methane oxidation. As the oxygen vacancy content of YSZ is fixed primarily by the degree of extrinsic doping, the results suggest that a better anode support material may be ceria, which can tolerate some degree of

nonstoichiometry in the oxygen sublattice to supply the much needed lattice oxygen for methane oxidation.

In a subsequent study of methane oxidation at the Ni/YSZ *tpb*, the DFT findings indicated that not only the YSZ surface of the Ni/YSZ system was chemically inert, but more surprisingly, the oxygen-enriched YSZ surface of the Ni/YSZ anode was also found to be inactive for methane adsorption due to a high endothermic kinetic barrier [578]. The Ni surface of the Ni/YSZ cermet, however, was catalytically active and the energetics of the reaction pathways were qualitatively very similar to that of pure bulk Ni without the YSZ support. This is presented in Figure 41, which shows the comparative energy profiles of the surface intermediates along the reaction pathways for the dissociative adsorption and oxygenation of methane on Ni/YSZ as well as on pure Ni surfaces. The similarity of the profiles between the two catalyst systems is quite obvious, suggesting that YSZ in the Ni-based cermet does not play an active role in the electrocatalytic reaction other than transferring of oxygen.

It should be noted that although DFT has emerged as the preferred method to simulate catalysis, it has several drawbacks and inherent limitations that need to be taken into account in the interpretation of results and relative comparisons to establish trends, especially in simulating electrocatalysis in fuel cells, which in reality involves electrified interfaces between the electrode and the solid or liquid electrolyte. In most *ab initio* calculations, the canonical form keeps the number of electrons constant, whereas simulation of electrochemical systems often requires constant potential. The DFT functionals also fail to properly account for weak interactions such as hydrogen or van de Waals bonding. Although DFT works well for metals, the same is not necessarily true for metal oxide systems. The critical issue for the latter is the density functionals that can behave differently for the different transition metals in the oxide structure. Moreover, convergence of the band gap from the cluster to the bulk is also important. These require new advances to make the necessary improvements in these useful and powerful computational methods. Recognizing these limitations and uncertainties, theoretical computational methodologies should be employed with caution and not as quantitative tools but for establishing qualitative trends, scaling relationships, and design rules guidelines.

6.2. Lattice strain effects in catalysis

Strain effects between lattice-mismatched overlayers may provide exciting new opportunities and an effective lever to tune catalytic properties of materials. Elastic strain can be induced in several different ways into materials including lattice mismatch at interfaces in multilayers, by applied stress, or by chemical expansion as observed in nonstoichiometric and doped oxides, and particularly in MIEC oxides.

The mismatch in the lattice constants across an interface between layers induces strain in the overlayer, which may alter the catalytic properties of the strained surface. Inspired partly by epitaxial film studies, DFT calculations have predicted long ago that the chemisorption properties of the strained Ru(0001) surface can be quite different from the unstrained Ru(0001) surface, and reported significantly lower binding energies and activation barriers for CO and O chemisorption on the strained Ru(0001) surface [579]. Experimental verification of the theoretical predictions was immediately provided by a

scanning tunneling microscopy (STM) study of oxygen and CO adsorption on Ru(0001) surface, which indeed indicated that preferential adsorption of oxygen and formation of surface superstructures occurs where the substrate lattice is stretched, while regions of the Ru(0001) substrate that is under compressive strain are the least favorable for adsorption [580]. Further studies by DFT also reported lower barrier for N₂ dissociation on strained fcc-Fe(111) surface and the Ru(0001) surface covered with a monolayer of Fe [581], while no correlation or general trend was found for dissociative adsorption of H₂ on Cu(111), (100), and (110) surfaces as a function of lattice strain [582].

Exceptionally large lattice strains in ultrathin epitaxial metal films that can reach values as high as 6.5% had been reported before [583]. More recently, an eight orders of magnitude increase in electrical conductivity was reported [584] for epitaxial heterostructures made of 1 nm thick YSZ films sandwiched between 1-10 nm thick SrTiO₃ layers. Although the ionic nature of the observed increase in conductivity in this superlattice structure is still in debate [585], this work sparked renewed interest in the role of elastic strain in the surface kinetics and transport properties in oxide structures [586]. In fact, scanning tunnel microscopy studies of O₂ and CO adsorption on strained Ru(0001) surface locally induced by the formation of subsurface gas bubbles have shown that adsorption is weaker in regions of lateral dilatation of the lattice and stronger in regions under compressive strain around the rim of the bubble [580]. In other words, tensile strained lattice exhibit preferential adsorption, and hence higher catalytic activity. It is clear that strain can alter the energy barrier profile of surface adsorbates along the reaction coordinate and modify catalytic activity.

As a strategic tool to affect and enhance catalysis, it has been shown that near-surface alloying alters the surface electronic structure of the host material and provides an effective methodology to design catalysts that possess high activity and selectivity [550].

Figure 42. Effect of lattice strain on the surface vacancy formation energy, E_{vac}^s (circles), oxygen adsorption energy, E_{ad} (squares), and magnetization (triangles) on the LaCoO₃ surface. “Reprinted with permission from ref. [589] Kushima A, Yip S, Yildiz, B, Phys. Rev. B. 2010; 82: 115435 1-6. Copyright (2010) American Physical Society”

Indeed, it was shown that the binding energies of hydrogen and oxygen of Pt can be altered significantly by subsurface alloying [587]. A strained metal overlayer on top of another metal substrate exhibits significantly different catalytic activity, compared with the metal overlayer itself [579]. In the case of doped-perovskites, the chemical expansion [588] that is due to the large oxygen non-stoichiometry sustained by these materials, help provides an additional lever to tune strain and modify surface kinetics and catalysis on these oxides. In general, the reaction energies for various surface rate processes are expected to decrease with increasing lattice strain, which is generally expected to lower the oxygen vacancy formation energy by weakening the metal-oxygen bonds. For example, DFT studies have shown that vacancy formation energy on the perovskite

LaCoO₃(100) surface decreases with increasing elastic strain, which leads to increased concentration of oxygen vacancies with more active sites for oxygen exchange that in turn leads to lowering of the binding energy for oxygen [589]. This is illustrated in Figure 42, where the upturn in the trends in the two energies was attributed to the abrupt increase in the magnetic moment seen at ~3% strain.

For similar reasons, strain effects may also be important for ionic transport. For example, DFT studies including kinetic Monte Carlo simulations for oxide ion transport in biaxially strained YSZ lattice indicated that with increasing lattice strain, the oxide ion diffusivity increases exponentially up to a factor of 6.8×10^3 until a critical strain value is reached, after which the diffusivity decreases possibly due to relaxation processes beyond the elastic bond strain limit [585]. This effect is especially more pronounced at lower temperatures than at high.

This author is not aware of experimental or theoretical studies reported to date that have specifically investigated the role of strain on the activation of the C-H bond for the catalytic oxidation of methane. Nevertheless, the examples provided above on how surface binding energies and barrier heights can be altered or modified by inducing lattice strain opens up new opportunities for developing advanced catalysts for C-H bond activation and incorporating strained layers on to SOFC anode structures for enhanced oxidation of methane.

6.3. Lowering the SOFC operating temperature

The high operating temperature is considered a major stumbling block for the rapid commercialization and mass deployment of SOFC technology. Most SOFC research and development efforts still employ high operating temperatures above 800°C, which pose major challenges for the cost and stability of SOFC components. This necessitates the use of primarily ceramic components and specialized high temperature metal alloys for the SOFC stack and the balance of plant (BOP) for the system. The resulting high costs associated with both fabrication and materials render this temperature regime undesirable and expensive for SOFC, especially for small size combined heat and power (CHP) systems. Furthermore, high temperature operation promotes undesirable thermal cracking of the hydrocarbon fuel inside the SOFC and subsequent deactivation of the anode and/or clogging of the system due to carbon deposition.

It was recognized nearly two decades ago that lowering the operating temperature of SOFCs also help lower an important barrier to their commercialization [590]. Low manufacturing and operating temperatures minimize issues related to materials stability and compatibility while improving microstructural and morphological stability under prolonged use. Moreover, this opens up opportunities for inexpensive materials for cell components that otherwise could not be considered. Hence, there is clear advantage in lowering the manufacturing and operating temperatures of SOFCs to below 500°C [273].

Earlier efforts to reduce the SOFC operating temperature to intermediate regime of 600-800°C [268,591,592] have focused on thick film ceramic processing techniques to reduce the thickness of the YSZ electrolyte membrane down to about 10 μm . Development of such intermediate temperature solid oxide fuel cells, dubbed IT-SOFCs, has gained much interest and was largely made possible by adopting thinner or alternative electrolytes such as doped ceria-, bismuth oxide-, or lanthanum gallate-based

oxide ion conductors, and superior catalytic electrodes [261,273,288,311,590,593,594]. Others have attempted fabrication of thin film SOFC electrolyte membranes around 1 μm thick using thin film deposition or MEMS techniques [595,596].

Efforts for lowering the cell operating temperature involved primarily two major strategies, namely, reducing the thickness of the electrolyte, and improving the electrode kinetics. The ohmic loss across the solid electrolyte is a significant fraction of the total cell losses especially at low temperatures. Hence, fabrication of thin electrolyte membranes significantly reduces ohmic losses. Advances in fabrication techniques allowed the manufacturing of cathode-supported or anode-supported SOFC architectures, where the solid electrolyte component of the cell is typically around 10 μm thick.

Figure 43. SEM images of the self-standing 3-dimensional conformally nanostructured MEA supported on the open window of the Si substrate (top schematic) with a base opening of 585x585 μm . The MEA features a pinhole-free 50 nm thick ALD film of YSZ electrolyte membrane with 10 nm thin PLD film of YDC catalytic interlayer at the cathode interface, and sputtered porous Pt electrodes each about 30 nm thick, for a total MEA thickness of ~ 120 nm producing a record power density of 1.3 W/cm^2 at 450°C in H_2 . Adapted with permission “Reprinted with permission from ref. [604] An J, Kim YB, Park JS, Gür TM, Prinz FB, Nano Lett. 2013; 13: 4551-4555. Copyright (2013) American Chemical Society”

thin film materials for the electronic, optical, and other industries. Indeed, ultra-thin self-standing YSZ and GDC electrolyte membrane layers with nominal thicknesses around 100 nm have been successfully deposited by sputtering [597-599], PLD [600,601], and ALD methods [231,602,603].

These efforts helped lower the SOFC operating temperature to below 500°C without sacrificing on cell performance. For example, an exceptionally high power density of

As most SOFC work employed H_2 as the fuel whose oxidation kinetics is relatively fast, most of the attention to minimize the cell activation losses was focused on the oxygen reduction reaction (ORR) at the cathode. As reaction rates generally exhibit Arrhenius-type behavior, low temperature operation also requires catalytically superior electrodes. In other words, developing catalytic materials as well as thin film pinhole-free electrolyte membranes are critically important in order to achieve practically high cell performance and efficiency at low operating temperatures.

Although relatively inexpensive and pinhole-free fabrication of thin electrolyte membranes by conventional ceramic processing (e.g., tape casting) is limited to thicknesses around 10 μm in general, advances in chemical and physical vapor deposition methods such as atomic layer deposition (ALD), sputtering, and pulsed laser deposition (PLD) offer major advantages in pushing the membrane thickness further below the 1 μm level. These deposition techniques have already been employed commercially for mass fabrication of a wide variety of large area

1.34 W/cm² was achieved with H₂ fuel at 450°C for a 43x43 μm size self-standing MEA supported on silicon wafer and featuring 60 nm thick pinhole-free composite YSZ/YDC electrolyte [604]. This self-standing 3-dimensional conformally nanostructured MEA fabricated on a Si-substrate is illustrated in Figure 43. Similarly, planar or 3-dimensional ultra thin film (~100 nm) functional MEA architectures based either on YSZ oxide ion membranes [604,605], or BYZ-based proton conducting solid oxide electrolytes [606] have demonstrated high power densities of practical importance.

It should be noted, however, that the long-term stability as well as cost limitations with such ultra thin film SOFC architectures have not been fully tested and validated yet. Moreover, undesirable rate processes such as interdiffusion, demixing, and defect segregation due to reduced diffusional distances in these thin films may compromise performance and long-term stability. Likewise, the cost of metalorganic specialty precursors used for deposition may not particularly be suitable for fabrication of wide area, large power output SOFCs. Nevertheless, this thin film approach opens up a window for new opportunities to seek and develop better and cheaper methodologies for further reduction of the SOFC operating temperature for direct utilization and conversion of hydrocarbons.

Figure 44. Oxidation of methane and natural gas over Ru catalytic anode in thin film SOFC. (a) OCV and power density for dry methane and natural gas oxidation as a function of temperature, (b) cell performance for the oxidation of humidified natural gas at 500°C. “Reprinted with permission from ref. [424] Takagi Y, Kerman K, Ko C, Ramanathan S, J. Power Sources, 2013; 243: 1-9. Copyright (2013) Elsevier”

For hydrocarbon conversion, however, low temperature SOFC operation is still a debatable issue with a long list of pros and cons. Aside from significantly slowed rate processes and surface kinetics, lowering the operating temperature is expected to have two additional adverse effects on the SOFC performance. As discussed in detail above, it is expected that both carbon deposition (see section 5.1) and sulfur poisoning (see section 5.2) problems may pose more difficult challenges at lower temperatures due primarily to thermochemical considerations. Not only the binding of sulfurous species to Ni and other transition metal surfaces is stronger at lower temperatures and may lead to irreversible deactivation, but also the carbon deposition boundary of the C-H-O ternary system expands with decreasing temperature (see C-H-O phase diagram in Figure 25), and thus favoring coking. In this regard, development of advanced catalytic anodes will be as critical as optimization of cell fabrication and operation parameters to avoid or minimize these adverse effects.

On the positive side, low operating temperatures offer many benefits. Low temperatures are expected to avoid the thermodynamically-driven gas-phase cracking of the hydrocarbon fuels employed in SOFCs, reduce solubility of carbon in Ni and other transition metal catalytic anodes and slow down the kinetics of coking, help improve the conversion efficiency by thermodynamically favoring the formation of CO₂ as opposed to CO, and in this context also favor the full oxidation and water gas shift reactions, slows down cell degradation processes due to microstructural changes or interactions and interdiffusion across interfaces between cell components, expand the materials space for SOFC components into cost-effective alternatives, minimize adverse solid state reactions and segregation effects resulting from high temperature processes during SOFC manufacturing, and lead to lower materials and fabrication costs.

So in the context of hydrocarbon conversion in SOFCs, it may be premature to predict or judge at this time whether the advantages of lowering the operating temperature will clearly outweigh the major risks and disadvantages it will bring along, especially for natural gas utilization, where the presence of sulfur may ultimately be the Achilles' heel. It is likely that advances in both catalyst research and SOFC materials development will bear on this choice.

As hydrogen has typically been the preferred fuel, studies of methane utilization in thin film SOFCs have been quite scarce. One notable example among them is the report of a peak power density of 450 mW/cm² achieved at 500°C using humidified methane as fuel in a Si-supported thin film SOFC architecture with a total MEA thickness of ~180 nm that featured a 30 nm Ru anode deposited on a 80 nm thick YSZ electrolyte [422]. The most notable accomplishment shown in Figure 44, achieved a remarkable cell performance in a similar thin film SOFC architecture, where peak power densities of 410 and 800 mW/cm² were obtained at 500°C using dry and 3% humidified natural gas, respectively, on porous Ru anode [424]. These few but encouraging examples of methane conversion in thin film SOFCs with remarkably high power densities obtained at such low temperatures may pave the way for renewed interest and advancements in this direction.

7. Prospects for Natural Gas Conversion in SOFCs

Natural gas is a naturally occurring primary energy source that is also widely available through a vast transportation and distribution infrastructure already in place and is made of networks of gas pipelines, compression and liquefaction facilities and stations, and specialized transportation vehicles, trains and ships. However, the composition of natural gas is not fixed but varies widely with the geographic location of the gas field as well as the geologic formation and reservoir it is extracted from. A typical composition [607] is provided in Table 6. Natural gas may also contain other contaminants, such as mercaptans (R-SH), carbonyl sulfide (COS), and carbon disulfide (CS₂) in trace quantities. Mercury (Hg) may also be present in the vapor phase. When natural gas is primarily made of methane after all hydrocarbons are removed, it is considered “dry”. Otherwise it is “wet”, when other hydrocarbons are present. Such variation places additional constraints in utilizing natural gas directly without pretreatment as the higher hydrocarbons are unstable at typical SOFC operating temperatures and tend to crack, deactivating and degrading cell performance. Natural gas also takes on different names

depending on the nature and origin, including: sour (sulfur containing) or sweet (desulfurized) gas; non-associated gas or well-gas, which does not contain hydrocarbons higher than methane; associated gas, which is associated with crude oil production; coal bed methane, which is held in coal beds; and shale gas, which is extracted by hydraulic fracturing from shale formations. Such variability in both hydrocarbon composition and sulfur content place significant challenges and demands on SOFC components, but especially more so on the catalytic anode. Furthermore, also note that sulfur-based odorants are purposefully injected into natural gas for ease of detection by smell. In other words, flexibility and sufficient tolerance for sulfur must be built into the design and development of the catalytic anodes. This is a critical requirement to accommodate and convert such variant compositions of natural gas in SOFCs without the need for extensive pretreatment.

It is clear that conversion of natural gas in SOFCs as opposed to combustion offers significant environmental benefits. Gas-phase combustion of natural gas in air proceeds within the flammability limits (i.e., 4 to 15 vol% in air) with flame temperatures that can be as high as 1600°C, which promotes the formation of an unwanted pollutant and potent greenhouse gas NO_x (see Table 4) from the reaction of N₂ with O₂ at these elevated temperatures. Furthermore, the CO₂ content of the flue gases is typically around 5% with the balance primarily N₂, which requires costly post-separation operations to capture CO₂. By contrast, the typical SOFC operating temperature (~ 800°C) is significantly lower and not N₂ from the air can enter the process stream. Hence, formation of undesirable NO_x is discouraged under these conditions and eliminated for all practical purposes. Also, as N₂ is completely kept out of the conversion process, the flue stream from the SOFC does not contain any N₂, but is made of concentrated CO₂ that eliminates the need for post separation.

Significant improvements on the cost-effective and environmentally responsible utilization of natural gas can be achieved by conversion in SOFCs as discussed above in this article. With an extensive distribution infrastructure in place, SOFCs are ideally

Table 6. Typical composition of natural gas [607].

Name [?]	Formula [?]	Volume [?] (%) [?]
Methane	CH ₄	> 85
Ethane	C ₂ H ₆	3-8
Propane	C ₃ H ₈	1-2
Butane	C ₄ H ₁₀	< 1
Pentane	C ₅ H ₁₂	< 1
Carbon dioxide	CO ₂	1-2
Hydrogen sulfide	H ₂ S	< 1
Nitrogen	N ₂	1-5
Helium	He	< 0.5

sued to run on natural gas and can readily provide environmentally friendly and efficient production of electrical power in a distributed fashion. However, commercial realization of this goal without pretreatment operations will require advancements in the current SOFC materials and technology to accommodate acceptable levels of sulfur and carbon tolerance while maintaining high power densities for practically meaningful performance.

As known for a long time in the catalysis and chemical industries, sulfur poisoning is clearly a persistent and difficult challenge for SOFC catalytic anodes also. From published results, the acceptable levels for Ni-based

SOFC anodes seem to be close to 1 ppm, which is a threshold that is difficult to meet and maintain cost effectively. On the other hand, the variance in sulfur tolerance for alloyed-Ni, non-Ni, or oxide-based catalytic anodes covers a significantly wider range. There is an obvious need for establishing selection criteria that encompasses and optimizes sulfur and carbon tolerance with respect to catalytic activity, as all are critically important for high efficiency, and cell performance and stability. An added complication is introduced by the large variation in the concentrations of sulfurous species (ppm level up to 1%) and other contaminants in natural gas, which in return would demand more robust flexibility for the sulfur tolerance level of the catalytic anode, as well as other SOFC components such as current collectors. Wide flexibility and high tolerance will be critically important in order to accept natural gas feeds from different origins without significant reduction in SOFC performance, and long service life.

However, the key to realizing this goal is the development of superior catalytic electrodes for SOFCs. The materials, operational and stability challenges for SOFC anodes are discussed in detail in the preceding sections above, but there are also major challenges to do the same for the development of catalytic materials for the cathode in order to lower the large activation losses due to the sluggish oxygen reduction reaction (ORR) on this electrode. Similarly, one can argue that there is need for superior solid electrolytes with higher ionic conductivity and lower activation barrier for ionic transport than the ones currently available, and with sufficiently wide stability window so that the next generation SOFCs can operate in the low temperature regime below 500°C with high efficiency and high power density. Certainly making the electrolyte membranes thinner is helpful to lower the temperature, but what is really needed is a major breakthrough in the inherent properties of materials. Nanostructuring with rational design may offer new

opportunities in this direction for the development of the next generation SOFC electrolytes and catalytic electrodes.

Figure 45. The “new” materials octahedron that depicts advanced tools for rational design and development of superior SOFC materials. “Reprinted with permission from ref. [609] Gür TM, Bent SF, Prinz FB, J. Phys. Chem. C, 2014; 118: 21301-21315. Copyright (2014) American Chemical Society”

In this regard, a comprehensive approach that draws from the basic principles depicted by the “new” materials octahedron shown in Figure 45, provides the basis for rational design and development of advanced materials for SOFC functional components with superior properties and performance. Recent additions of theoretical and computational tools as well as the ability to control matter at the nanoscale, i.e., nanostructuring, allow new directions for bottom-up design and development of novel catalytic and functional materials for next generation SOFCs. Use of theoretical simulations for qualitative prediction of comparative trends in materials properties has proved effective and useful, but for rational design of novel and practical

materials, such predictive tools need to extend into the multi-scale domain to bridge the

gap from quantum to continuum, and complemented by experimental validation and *in situ* and *in operando* characterization. Similarly, the newly gained ability to nanostructure materials at the nanoscale expands the domain of materials space immensely with the possibility to alter, modify or fabricate new materials structures with exceptional properties for advanced components for SOFCs. Controlling matter at the atomic scale and fabricating functional materials with nanoscale precision offer unprecedented opportunities for developing, for example, 3-dimensional catalytic electrodes architectures with optimized *tpb* site density, mass transport, mechanical robustness and thermal properties for electrocatalytically superior next generation SOFC electrodes. The strategic pathway and the tools to achieve such rapid progress have been presented thoughtfully in a recent article [608].

Nanostructuring allows tuning and sometimes even altering the fundamental properties of materials [609]. For example, the recent development of CuO nanowire (NW) catalytic structures illustrated in Figure 46 were grown by thermal annealing of Cu mesh and showed significant enhancement in the catalytic rates for methane oxidation, up to 40% above the rates measured over CuO nanoparticles and bulk CuO powder [610]. Moreover, CuO NWs treated under H₂ plasma and partially reduced to Cu⁺ has shown even higher activity for methane oxidation than untreated NWs, indicating that Cu⁺ is a more effective catalyst than Cu⁺⁺. Also, Cu NWs with 1-dimensional structures expose higher density of active crystal planes to the reaction environment, which of course lead to increased catalytic activity. This work also showed that CuO NWs are good oxidation catalysts for methane while Cu⁺ NWs may even be better, whereas metallic Cu is not an effective catalyst for this reaction [378,380]. Similarly, modification of catalytic SDC anode surfaces by nanostructured decorations of La_{0.6}Ca_{0.4}Fe_{0.8}Ni_{0.2}O₃ has shown improved catalytic activity for methane oxidation, achieving a maximum power density of 350 mW/cm² at 800°C [611]. It should be pointed out, however, that nanostructures generally suffer from poor thermal and microstructural stability and may not maintain

Figure 46. Fine (rolled) Cu mesh of 110 μm wire diameter (a) before, and (b) after annealing for 2 days at 520°C. (c) SEM, and (d) TEM images of as-grown Cu NWs, with average length of 50 μm and NW diameter of 100 nm. “Reprinted with permission from ref. [610] Y, Rao PM, Kim DR, Zheng X, *Proceed. Combust. Inst.* 2011; 33: 3169-3175. Copyright (2011) Elsevier”

their geometric size, shape, or architecture at elevated temperatures after prolonged use. Hence, it is important to lower the operating temperatures of SOFCs to below 500°C to be able to implement the benefits offered by nanostructured materials into SOFC cell design and architecture.

It is clear that strain effects also play an important role in the catalytic properties of surfaces. By fine-tuning the interfacial geometry and the associated strain, it may be possible to optimize the adsorption properties of reaction intermediates and dramatically enhance the catalytic rates of heterogeneous reactions. These strategies naturally open up new opportunities in further tuning of

catalytic properties particularly for direct utilization and oxidation of natural gas on SOFC anodes.

To gain better mechanistic insights for methane catalysis, another opportunity is offered by the use of sophisticated analytical tools that probe in unprecedented detail into the crystal and electronic structures of materials as well as in the identification of surface intermediates and active sites, or changes in oxidation states in the catalysts during catalytic reactions. These tools are becoming increasingly accessible particularly through the advancements made in synchrotron based x-ray techniques that offer both *in situ* and *in operando* measurements of materials behavior, properties, and even 3-dimensional microstructural imaging for a wide range of energy conversion processes and systems [247,612-614]. These advanced tools and techniques also offer opportunities to conduct *in situ* study of electrocatalysis at gas pressures as high as 100 Torr at room temperature [615], or in a total pressure of 300 mTorr and between 550 and 750°C [333]. In addition, low energy ion scattering spectroscopy (LEIS) provides atomic scale precision in identifying elemental surface species at the very top atomic layer of catalyst surfaces, and provides a rare glimpse at surface species and processes including catalysis, defect segregation, and nucleation and growth [616,617]. The newly developed X-ray laser capability (Linac Coherent Light Source (LCLS)) at DOE's SLAC National Accelerator Laboratory in California provides high intensity pulses in the $10\text{-}100 \times 10^{-15}$ s (femtosecond) time-scale, which is commensurate with typical lifetimes of surface intermediates. This unique capability offers unprecedented opportunities to monitor and follow catalytic reactions in real time. Such a battery of powerful analytical tools will help advance our understanding of catalytic processes and materials properties *in situ* and in real time.

There have been several successful attempts that demonstrated natural gas conversion in SOFCs at low temperatures with significant power densities. An anode-supported SOFC with 25 μm thick film YSZ electrolyte membrane and Ni/YSZ porous cermet anode achieved close to 1 W/cm^2 at 800°C using humidified natural gas [433]. However, the long-term stability of the Ni/YSZ anode in the sulfurous environment of natural gas is questionable. Recent progress in thin film micro-SOFCs have improved the cell performance by achieving low temperature oxidation of natural gas on nanoporous Ru anode with considerable power density of 410 W/cm^2 and 440 W/cm^2 at 500°C with dry natural gas and methane, respectively, while a remarkably high power density of 800 mW/cm^2 was achieved at 50°C using slightly humidified natural gas (see Figure 44 above) [424]. The scalability of micro-SOFCs to even 1 kW scale, however, is a debatable issue. So the projection of these promising results into large-scale practical SOFC systems remains an open question. Nevertheless, the results are important in guiding future SOFC research into achieving higher performance values with cost effective and durable electrode materials.

Certainly, SOFCs are ideally suited for distributed power generation. Numerous studies developed models to optimize operating parameters and predict system level performance of SOFCs using methane or natural gas with direct or indirect reforming combined either with a bottoming power cycle or micro gas turbine, or simply utilize the SOFC waste heat [618]. A model study considering a combined cycle natural gas conversion in SOFCs that also utilizes the high grade waste heat of the SOFC exhaust gases in a Rankine or Brayton cycle, or use it for heating purposes, has predicted

remarkable efficiencies up to 90% for the combined system depending on its configuration [619]. Such high efficiencies naturally translate into reduced CO₂ emissions during power generation. A comparative study of combining the SOFC either with steam or dry internal reforming reported that conversion efficiencies up to 65% is possible, and that the dry reforming pathway offers a significant reduction in CO₂ emissions per unit of electricity generated. The emission factor predicted by this study is about 299 kg of CO₂ per MWh of electricity generated, which represents a major reduction in emissions compared to 367 kg of CO₂/MWh for natural gas combined cycle (NGCC) and 762 kg of CO₂/MWh for pulverized coal (PC) power generation plants [620].

The potential of reducing CO₂ emissions by efficient conversion of methane in

SOFCs is also important for mitigating global climate change.

However, this represents only part of the problem.

The other aspect of the problem relates to methane emissions into the environment.

The high potency of methane as a greenhouse gas with a global warming potential of 21 times that of CO₂ (see Table 4) requires large scale mitigation efforts to contain and reduce methane emissions.

Unfortunately, the energy sector is the largest contributor to methane emissions with nearly 1774 Mton CO₂ equivalent released annually into the environment, which makes up nearly 29% of total global CH₄ emissions. Of this amount, nearly 62% of the emitted methane originates from natural gas and oil production and transportation systems, followed in

Figure 47. U.S. DOE estimates of system level conversion efficiencies and cost of electricity produced by natural gas and coal-fired power generation technologies compared with natural gas-based SOFCs (i.e., NGFC). (from ref. [622] by courtesy of SD Vora of DOE-NETL).

smaller quantities by coal mining, biomass combustion, etc. [621]. It is not clear if these numbers also include or account for flared natural gas at the gas or production sites and plants, which would add a significant fraction that is energy-wise wasted and emitted into the atmosphere as CO₂. Regardless, efficient utilization and conversion of methane on-site by SOFCs will help reduce emissions and produce distributed power for use in local communities.

However, there are techno-economic barriers for large-scale adoption of SOFC technology by industry, particularly by power generators. This is partly because reliability and cost are two of the several most critical tenets upon which the power production business is built. In this regard, SOFCs will have to prove themselves for cost-effective utility scale power generation. As renewable technologies such as wind and solar are increasingly being deployed, the price structure, reliability, grid compatibility, and percent availability of different power generation systems become even more competitive, especially if CO₂ capture and sequestration requirements, if implemented and enforced, are taken into account. Understandably by the competitive nature of their business, conventional power production companies prefer to remain risk-averse and conservative before they may make major commitments to adopt new technologies.

Such reluctance may be mitigated by placing a realistic price on the carbon released into the environment, as well as with federal programs and subsidies to encourage the discovery and development of advanced technologies for power generation. Indeed, federal subsidies from the U.S. government have certainly been helpful to SOFC developers such as Bloom Energy of California, arguably the biggest commercial developer and manufacturer of SOFCs based on methane conversion (via reforming), to remain competitive on the energy marketplace. However, it is difficult to predict the long-term market prospects of SOFCs beyond such subsidies from the U.S. government. Elsewhere in the world, similar financial incentives and programs from federal and local governments are needed to encourage both the public and industries to gradually adopt this technology for rapid deployment. Mass production is expected to help bring down materials and fabrication costs, but long-term stability of SOFCs is still a concern that needs to be overcome to comfort and assure the early adopters and risk takers. This author also believes that the implementation of a price on carbon is required to accelerate the commercial development and adoption of advanced power generation technologies that offer significantly higher efficiencies and reduced emissions.

As elaborated in this article, methane conversion in SOFCs offers many attractive advantages including conversion efficiency. Comparative study of system level conversion efficiencies and cost-of-electricity (COE) estimates by the U.S. Department of Energy [622] clearly highlight the advantages of methane conversion in SOFC as presented in Figure 47, which also takes into account the cost and energy burden for carbon capture and sequestration (CCS). Not only SOFC-based natural gas (NGFC) conversion offers the highest possible conversion efficiency at the power systems level, but it is also predicted to be the most cost-effective technology offering the lowest COE among the other coal- and natural gas-based power generation systems.

To realize these goals, the SOFC federal program of the U.S. Department of Energy (DOE) has been providing support for research and development projects that run on externally reformed natural gas in SOFC stacks, and aims to develop power systems capable of producing 250 kW in FY2018 and 1 MW by FY 2020 from natural gas. This

federal program requires stringent cost (\$225/kW for stack and \$900/kW for power system) and performance criteria of 40,000 hours of service lifetime with less than 0.2% degradation (currently 1-1.5%) in SOFC system output power per 1000 hours of continuous operation [622]. Significant progress made in this long running DOE program (formerly called SECA for “Strategic Energy Conversion Alliance”) that has already invested a total of \$600M provides optimism to achieve these targets.

In summary, natural gas conversion in SOFCs promise major advantages in more efficient utilization of energy sources with a significantly smaller carbon-footprint, albeit with technical and economic challenges yet to be overcome.

8. Summary and Conclusions

This article presents a comprehensive review of methane oxidation catalysis towards the ultimate goal of effective utilization and efficient conversion of natural gas in SOFCs. In this context, it covers a vast materials space from metals to complex oxides for heterogeneous catalysis, and predominantly ionic as well as mixed ionically and electronically conducting (MIEC) oxides for ionic and electronic charge transport, and also for electrocatalytic electrodes for SOFCs. Again in the context of methane oxidation, it discusses fundamental concepts and phenomena underlying electrochemical conversion, SOFC materials and performance loss mechanisms, electronic and geometrical effects in catalysis, catalyst-support interactions, mechanistic insights in methane activation, spillover and NEMCA effects, fundamentals of sulfur poisoning and anode degradation mechanisms, and thermodynamic and kinetic driving forces for carbon deposition and cell deactivation. It further discusses opportunities offered by recent advances and exciting developments in heterogeneous catalysis, such as theoretical and computational tools for materials screening and reaction pathways, doping and nanostructuring to modify surface properties, exploiting strain effects for enhancing catalytic activity, as well as lowering the SOFC operating temperature for methane conversion to overcome some of the materials challenges.

As the first logical step towards realizing natural gas conversion in SOFCs, understanding the mechanistic details of the electrocatalytic oxidation reaction of methane is important, as SOFCs offer many significant advantages including high conversion efficiencies nearly two times that of current combustion-based power generation technologies, capture-ready CO₂ emission produced at nearly one half the amount of current technologies, environmentally friendly and quiet operation with no moving parts except in the balance of plant. Furthermore, the cost-of-electricity (COE) estimates by the U.S. DOE also indicate that natural gas conversion in SOFCs economically offers the most competitive option compared with existing power generation technologies.

Experimental and theoretical studies on the catalysis of methane oxidation indicate general agreement that activation of the first C-H bond presents the highest barrier step followed by sequential abstraction of hydrogen. Ni and several precious metals are among the best catalysts for methane activation to full oxidation. Pd supported on ceria with the general composition Pd_xCe_{1-x}O₂ emerges to be one of the most active catalysts for methane oxidation, but the cost of Pd is an economic concern for practical applications.

Partly for economic reasons, abundance, and high catalytic activity, Ni has traditionally been the most preferred and commonly used electrocatalyst for SOFC anodes, albeit primarily for hydrogen oxidation. In methane environment, however, the propensity of Ni to deactivate rapidly due both to sulfur poisoning and carbon deposition present serious challenges to employ it as an inexpensive and highly effective electrocatalyst material for methane or natural gas conversion on SOFC anodes.

The literature reports collectively suggest a critical sulfur content that may be tolerable by a given electrocatalytic anode material. The critical level also depends on the current density as well as operating temperature, where poisoning effect is aggravated at reduced temperatures. Strategies have been devised to modify the catalytic behavior of Ni and to improve its stability and tolerance against sulfur and carbon. There has been much progress made in materials development for mitigating the adverse impact of sulfur and carbon, but most with limited success. The daunting task of maximizing catalytic activity along with sufficient tolerance for sulfur and carbon have led to attempts to compartmentalize these problems in order to devise appropriate solutions. For example, external reforming followed by gas cleanup, or internal reforming of desulfurized natural gas have been pursued as alternative chemical steps to supply sulfur-free syngas in place of methane to the Ni-based anode surface. Alloying of Ni has been beneficial and provided better tolerance, but still proved insufficient in most cases due to the stringently low tolerance of Ni to sulfur, which seems to approach 1 ppm H₂S. This level is much below the typical levels of sulfurous odorants such as mercaptans added to natural gas for ease of detection by smell. Hence, there is great need for the development of sulfur (and carbon) tolerant anode materials with catalytic activities comparable to or better than Ni.

For possible replacement of Ni, much attention has turned to MIEC oxides as potential candidates. Indeed, many oxides particularly in the doped-perovskite family have demonstrated greatly improved stability and tolerance for sulfur and carbon, but they lack sufficient catalytic activity for methane oxidation, and high electronic conductivity or stability. Again, diverse and multi-prong strategies have been employed for improving SOFC anode performance and stability towards utilization and conversion of natural gas, which inherently contains varying amounts of sulfurous species. These wide ranging strategies include alloying and coating (e.g., core-shell) of Ni, exploiting metal-support interactions as well as lattice oxygen, extrinsic doping of the host oxides especially the B-site of perovskites for enhancing catalytic activity and stability, and exploring modern design tools of nanostructuring and theoretical simulations for the discovery and development of novel compositions or combinations of materials structures. Many of these attempts have shown limited success in bringing about significant mitigation of the two primary difficulties posed by sulfur and carbon deactivation during methane activation in SOFCs. Despite such limited success, several notable examples with significant promise and successful results include the use of Ni/BZCYYb cermet anodes in sulfurous environments up to 10% H₂S, enhanced catalytic activity of ceria-based anode materials, and improved tolerance by alloying and doping.

Recent advances in achieving direct electro-oxidation of methane in SOFCs have demonstrated that pursuit of this approach has great potential. It offers inherently higher efficiencies and reduced balance of plant than reforming-based utilization of natural gas, and also does not need a fuel processor. With the advent of advanced anodes with high sulfur tolerance, the need for gas cleanup and desulfurization may also be eliminated

entirely. Although the current state-of-the-art has not fully demonstrated practically applicable and long lasting success stories yet, direct conversion still holds a great potential for attractive and high-return benefits.

It is clear that SOFCs offer many important advantages for natural gas conversion to electrical power. There are, however, serious scientific challenges still remain to be overcome that require innovative materials solutions before this promising technology can be considered for practical applications. This article presents an in-depth discussion of these challenges and points to emerging opportunities to expand the materials discovery space to develop novel and superior electrocatalysts.

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