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Carbon Form ı Solid Oxide Fuel Cells (SOFCs) Using H_2S

by

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Abstract

Solid oxide fuel cells (SOFCs) are promising devices for power generation due to their high efficiency and clean operation. Another prominent feature of SOFCs is their ability to operate with not only H_2 fuel but also hydrocarbons and syngas. Unlike many other fuel cells, SOFCs also are capable of utilizing CO as fuel. This flexibility with respect to fuel lessens the dependency on pure H_2 and complex fuel processing and has increased the interest in SOFCs as an alternative power source. However, their widespread commercialization is still hindered by high cost and poor long term stability associated with high temperature operation and carbon deposition at the anode when fuelled with hydrocarbons.

The main objective of the research described in this thesis was to introduce and investigate a method to mitigate the effects of carbon formation in Ni-based anodes operating at intermediate temperatures with hydrocarbon fuels (e.g., CH_4). Ni-samaria-doped-ceria (Ni-SDC) anode-supported cells were fabricated and their performance and susceptibility toward carbon deposition were studied when operating galvanostatically with various fuels including CH_4 and CO-CO_2 mixture at intermediate temperatures (550-700°C). Ni-SDC anode-supported cells operating with CH_4 and CO-CO_2 were strongly affected by the temperature when the cell performance with CH_4 was found to be more stable during operation at 700°C than at 600°C. The maximum power density of the cell with CH_4 as fuel was found to be higher than that achieved with H_2 as fuel at 700°C. Meanwhile, the cell voltage during operation with CO-CO_2 fuel was more stable at 600°C than at 700°C. Degradation of the performance of the Ni-SDC cells with CH_4 and CO-CO_2 fuels under conditions where carbon formation is thermodynamically favored was found to be relatively small despite the fact that significant amounts of carbon accumulated in the anode. This may due to the fact that carbon deposited predominantly at the surface of the anode closest to the fuel entry point.

Sulphur in the form of H_2S was introduced into the SOFC at ppm level concentrations to evaluate its effect as a potential carbon inhibitor in a cell operating under dry CH_4 at 700°C. Two methods for exposing the anode to H_2S were investigated: i) continuous introduction throughout

cell operation as part of the gas feed stream and ii) introduction as part of a mixture with H_2 only for a short period of time as a pre-treatment before regular operation with dry CH_4 alone. These studies showed that continuous feeding of H_2S within the dry CH_4 fuel at the level of only a few ppm (10 and 2 ppm) was enough to cause catastrophic failure of the cell within ~20 hrs due to the poisoning effect of H_2S. On the other hand, the introduction of H_2S at a level of 2 ppm in dry H_2 into the cell for 30 minutes as an anode pre-treatment before switching to dry CH_4 was very successful and enabled the SOFC to maintain stable performance for over 100 hours of operation under dry CH_4, with a lower degradation rate than that observed when a cell was not pre-treated with H_2S. This pre-treatment did not affect the methane conversion significantly during the subsequent galvanostatic operation with dry CH_4. The presence of H_2S influenced the type of carbon formed depending on the manner in which the H_2S was introduced into the SOFC. Carbon deposits that formed during operation with dry CH_4 alone after the 30-minute pre-treatment with H_2S were more easily removed than those produced when the fuel contained dry CH_4 alone or H_2S-containing fuel was introduced continuously over the entire run. The introduction of H_2S for a short duration prior to shifting to dry CH_4 suppressed the formation of graphitic carbon at the anode.

The amount of carbon formed on the cells during CH_4 operation was estimated by shifting the gas stream to humidified H_2 while maintaining the applied current unchanged and measuring the quantity of carbon-containing gases evolved. These measurements revealed that less carbon was deposited in a cell that had been pre-treated with H_2S prior to 100 hrs of operation with dry CH_4 compared to a cell that had not been exposed to H_2S. This analysis also showed that the procedure of flowing humidified H_2 into the cell after operation with dry CH_4 while maintaining the same current appeared to remove carbon from the anode and reduce the rate of degradation of the cell voltage.

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Nomenclature

Raman symbols

a_i	Activity of reactant or product *i*
Ce'_{ce}	Concentration of Ce^{3+} ions
E	Cell potential (V)
E_r	Equilibrium cell potential (V)
E^0	Cell potential at standard condition (V)
E_a	Activation energy
E_B	Binding energy
E_K	Kinetic energy
E_0, I_0	Amplitude of voltage and current
$\tilde{E}, \tilde{I}$	Oscillating voltage and current
F	Faraday's constant (96,487 C mol^{-1})
ΔG	Change in Gibbs free energy (J mol^{-1})
ΔG°	Standard change in Gibbs free energy (J mol^{-1})
$h\nu$	Photon energy
I	Current (A)
i	Current density (A cm^{-2})
i_L	Limiting current density (A cm^{-2})
i_0	Exchange current density (A cm^{-2})
j	Imaginary unit
k	Boltzmann constant (8.617 $\times 10^{-5}$ eV K^{-1})
K_{eq}	Equilibrium constant
ℓ	Thickness
n	Number of electrons
n_i	Mole flow rate of species *i* (mol min^{-1})
P	Power density (mW cm^{-2})
$p_{O_2,an}$	Partial pressures of oxygen at the anode (atm)
$p_{O_2,ca}$	Partial pressures of oxygen at the cathode (atm)
R	Gas constant (8.314 J $mol^{-1}K$)
R_s	Ohmic resistance (Ω cm^2)

R_p	Polarizarion resistance (Ω cm^2)
R_b	Bulk grain resistance (Ω cm^2)
R_{gb}	Grain boundary resistance (Ω cm^2)
R_{el}	Electrode resistance (Ω cm^2)
T	Temperature (K)
t	Time
$V_{\ddot{O}}$	Oxygen vacancy
W_{elec}	Work (J mol^{-1})
$W_{elec,max}$	Maximum work (J mol^{-1})
Z	Impedance (Ω cm^2)
$Re\ Z$	Real part of impedance (Ω cm^2)
$Im\ Z$	Imaginary part of impedance (Ω cm^2)

Greek Symbols

α	Activity of reactant or product
η	Overpotential (V)
η_{act}	Activation overpotential (V)
η_{ohm}	Ohmic overpotential (V)
η_{conc}	Concentration overpotential (V)
δS_s	Entropy change due to irreversible losses (J mol^{-1} K)
v_i	Stoichiometric coefficient of reactant or product *i*
ω	Angular frequency (radian s^{-1})
ϕ	Phase angle
$\mu_{O_2,an}$	Chemical potentials of oxygen at anode
$\mu_{O_2,ca}$	Chemical potentials of oxygen at cathode
σ_e	Electronic conductivity (S cm^{-1})
σ_i	Ionic conductivity (S cm^{-1})

Subscripts

ca	Cathode
el	Electrolyte
an	Anode

Abbreviation

AC	Alternating current
AFC	Alkaline fuel cell
APU	Auxiliary power unit
BSCF	$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$
BSE	Backscattered electron
CPE	Constant phase elements
CE	Counter electrode
CHP	Combined heat power
CTE	Coefficient of thermal expansion
DFT	Density functional theory
EDX	Energy Dispersive X-ray
EIS	Electrochemical impedance spectroscopy
GDC	Gadolinia-doped ceria
GNP	Glycine-nitrate process
IT-SOFC	Intermediate temperature SOFC
i-V	Current density-voltage
L	Inductor
LGSM	$La_{0.88}Sr_{0.12}Ga_{0.82}Mg_{0.18}O_{3-\delta}$
LSCM	Lanthanum strontium manganese chromite
LSM	Strontium-doped lanthanum manganite
LSCF	Strontium-doped lanthanum cobalt iron oxide
MCFC	Molten carbonate fuel cell
MIEC	Mixed ionic electronic conductor
MS	Mass spectrometry
Ni-SDC	Ni-samaria doped-ceria
Ni-YSZ	Ni-yttria-stabilized zirconia
NiO	Nickel oxide
OCV	Open-circuit voltage
OSC	Oxygen storage capacity
PAFC	Phosphoric acid fuel cell
PEMFC	Proton exchange membrane fuel cell

RE	Reference electrode
S/C	Steam-to-carbon ratio
SDC	Samaria-doped ceria
SE	Secondary electron
SEM	Scanning electron microscopy
SOFC	Solid oxide fuel cell
SMMO	Sr_2MgMoO_6
SSC	Strontium-doped samaria cobalt
TPB	Triple phase boundary
TPH	Temperature-programmed hydrogenation
TPO	Temperature-programmed oxidation
WE	Working electrode
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
YDC	Yttria-doped ceria
YST	Yittria-stabilized titania
YSZ	Yittria-stabilized zirconia

Chapter 1
Introduction

World-wide energy consumption has dramatically increased over the last two decades due to population and economic growth as well as changes in quality of life. This rapid growth in energy consumption in both industrialized and developing countries has led to an ever increasing dependence on fossil fuels, causing faster depletion of these resources and serious environmental problems (e.g., air pollution and greenhouse gas emissions). To overcome this problem, better use of these energy resources and the development of sustainable and cleaner energy sources are essential.

Fuel cells are efficient energy generation devices that enable clean conversion of chemical energy from fuels into electrical energy. Due to the direct one-step conversion of chemical energy into electrical energy, the efficiency of energy conversion in fuel cells is higher than in conventional combustion turbines. In addition, fuel cells do not generate harmful pollutants such as nitrogen oxides (NO_x), sulphur oxides (SO_x), carbon monoxide (CO) and particulates since combustion does not take place (Li, 2006).

Known as a high temperature fuel cell operating between 600-1000°C, solid oxide fuel cell (SOFC) can operate with electrical energy efficiencies above 50%. A very important feature of SOFC is that it can operate with many types of fuel including H_2, syngas and hydrocarbons. High temperature operation enables direct conversion of hydrocarbons to occur within the SOFC itself, thereby solving the problems associated with having to purify the fuels before introduction into the fuel cell. When H_2 only is used as fuel, SOFCs emit only water and heat with no pollutants (Stambouli and Traversa, 2002). With other fuels such as hydrocarbons (e.g., CH_4) or synthesis gas (syngas), the carbon dioxide (CO_2) content in the SOFC exhaust stream becomes high since it is not diluted with nitrogen. This may offer better efficiency for eventual CO_2 capture (Dijkstra and Jansen, 2002).

SOFC applications include essentially stationary power generation ranging from residential-scale power units (1 to 5 kW) to on-site power plants (100 kW to 1 MW) and larger-scale distributed power plants (2 to 10 MW). In multi-kW power generation, SOFCs are commonly incorporated with combined heat power (CHP) systems which utilize the generated heat to

produce steam and/or provide space heating or domestic hot water. In multi-MW systems, SOFCs can be integrated with gas turbines for further electricity generation using the unreacted portion of the feed stream to the fuel cell. SOFCs are also used for smaller applications such as automobile auxiliary power units (APUs) (5 kW) and portable devices (20-500 W) (Minh, 2004).

Although SOFCs have great potential, technical barriers must be resolved before their widespread commercialization becomes possible. The main challenges are associated with the high costs of the cell component materials and interconnects and the poor long-term performance and stability at the high operating temperatures (i.e., 800-1000°C for high temperature SOFC). Also, when hydrocarbon fuels are used, carbon deposition occurs on the anode and degrades SOFC performance. The accumulation of the carbon in the anode deteriorates performance by impeding the transport of fuel to the active anode sites and in the worst case, by destroying the anode structure.

1.1 Motivation

Intermediate-temperature-SOFCs (IT-SOFCs) which operate from 500 to 700°C have received considerable attention among researchers since they enable much less expensive materials to be used and are more stable due to less thermal degradation than at higher temperatures. However, a decrease in temperature increases the ohmic resistance of the cell operating with the state-of-the-art material (yttria-stabilized zirconia, YSZ). Therefore, the use of materials with better ionic conductivity and a SOFC design aimed at reducing the thickness of the electrolyte is desirable.

Doped ceria (doped-CeO_2) exhibits higher ionic conductivity than YSZ at low operating temperatures. In addition, it has been reported that the presence of ceria in the anode cermet enhances the electrochemical oxidation reaction (Murray *et al.*, 1999). Anode-supported cell design features a thin electrolyte with a thick anode which also serves as the cell support. The thick anode also offers a large number of catalyst sites for chemical and electrochemical reactions to take place when the SOFC is directly fuelled with hydrocarbons. In this work, Ni-samaria doped-ceria (Ni-SDC) anode-supported cells are used. Their performance and the tendency for carbon deposition to occur when hydrocarbon fuels (i.e., CH_4) and CO are used have been examined in this thesis.

Ni-based anodes are highly active for chemical and electrochemical reactions and have high electronic conductivity. However, Ni metal provides a good surface for the formation of carbon and so is prone to carbon deposition when hydrocarbons are fed directly to the anode. Consequently, researchers have made great efforts to improve the carbon tolerance of Ni-based anodes. Most of this work has involved modification of Ni-based anodes during cell fabrication by alloying or impregnating the Ni with metals, noble materials or alkaline earth oxides (Nikolla *et al.,* 2009a; Takeguchi *et al.,* 2003; Asamoto *et al.,* 2009). In this work, we examine the potential to minimize carbon formation by introducing a gas stream containing sulphur in the form of H_2S into the SOFC anode.

Sulphur compounds are well known to be able to poison catalysts and electrodes and thereby terminate electrochemical and chemical reactions. It has been shown that a few ppm of H_2S (e.g. 2-15 ppm at 800 °C) are sufficient to dramatically degrade the electrochemical performance (Matsuzaki and Yasuda, 2000) and methane reforming activity (Rasmussen and Hagen, 2010) in SOFCs. However, according to DFT calculations by Abild-Pedersen *et al.* (2005), the introduction of the appropriate sulphur-bearing species which has a strong affinity for Ni, can inhibit carbon formation by adsorption onto Ni sites that are active for carbon formation. In a work with methane steam reforming, Rostrup-Nielsen (1984) also reported that the used of 1 ppm H_2S for catalyst pretreatment has eliminated the carbon filaments, leaving only amorphous carbon on the Ni catalyst.

Since sulphur compounds can poison catalysts if present in excess amounts, it is important to determine the range of concentrations at which they can suppress carbon formation, but do not unduly poison the Ni-based anodes. Researchers have focused on the negative effects of sulphur on the reforming activity and electrochemical reactions on Ni-based anodes when SOFC is fuelled directly with CH_4. Yet, very little research so far has focused on the potential positive effect of sulphur to inhibit carbon deposition. For this reason, we focus on this topic in this work.

Briefly, the main objectives in this work were:

- To evaluate the performance of Ni-ceria-based (Ni-SDC) cells and their susceptibility towards carbon deposition when directly fed with hydrocarbons (i.e., CH_4) and CO.
- To investigate the effect of incorporating H_2S into the inlet gas stream on carbon deposition at the SOFC anode when operating Ni-SDC cell with CH_4 fuel.

1.2 Organization of the thesis

This thesis is organized into eight chapters.

Chapter 1 presents a general introduction of the research and discusses the research motivation and objectives of the research. This is followed in Chapter 2 with background on fuel cells and SOFC operation, a review of the types of electrolyte, anode and cathode materials used in SOFCs, discussion of the forms of carbon that deposit in SOFC anodes and describes the previous efforts to minimize carbon deposition in Ni-based anodes. Chapter 3 provides details on the procedures to synthesize the electrolyte and anode materials, fabricate the cell and cell set-up, carry out the electrochemical experiments, analyze gas composition and characterize the anode constituents and morphology. The results of experiments carried out to evaluate the performance and stability of anode-supported Ni-SDC cells operating with different fuels (H_2, CH_4 and CO) at temperatures ranging from 600 to 700°C are presented in Chapter 4. Chapter 5 focuses on carbon deposition in Ni-SDC cells when operating with CH_4 and CO fuels. Chapter 6 describes the results of applying different strategies for introducing H_2S into the Ni-SDC cells operating with dry CH_4 fuel to mitigate the deleterious effects of carbon formation. Based on the results obtained in Chapter 6, a procedure to reduce the extent of carbon deposition during SOFC operation with dry CH_4 fuel that involves pre-treating the anode with a gas stream containing low concentrations of H_2S is explored further in Chapter 7. In particular, the effects of this approach on SOFC performance, outlet gas composition, CH_4 conversion and the amount of carbon deposited are determined. Finally, the thesis closes with conclusions and recommendations for future work in Chapter 8.

Chapter 2
Literature Review

This chapter is divided into three main parts. The first part begins with a background discussion on fuel cells and thermodynamics with specific focus on SOFC operation. As this research is aimed at operating SOFCs at intermediate temperatures, an overview of suitable materials for fuel cell components and cell design are also given. The second part of the chapter covers the topics of internal reforming, direct utilization of hydrocarbon fuels in SOFCs and problems associated with the use of hydrocarbon fuels such as carbon deposition. Included is a review of the forms of carbon that deposit in SOFC anodes. Finally, in the third part of the chapter, efforts to minimize carbon deposition in Ni-based anodes and use H_2S to inhibit carbon formation are discussed.

2.1 Introduction to fuel cells

Fuel cells are very promising devices for energy transfer and power generation. Using the principle of electrochemical conversion, fuel cells produce electricity directly from chemical energy available in their reactants (fuel and oxidant) (O'Hayre *et al.,* 2006). Fuel cells are theoretically more efficient than heat engines and batteries. A heat engine converts the chemical energy into thermal energy and then into mechanical energy before transforming it into electrical energy. This multistep energy conversion tends to lower the overall energy efficiency. Compared to heat engines, fuel cells have potentially higher energy efficiency and are not restricted by Carnot efficiency.

Batteries share the same operational principles as fuel cells where electrical energy is generated directly from reactants through electrochemical reactions. Batteries operate as both energy conversion and energy storage devices. A primary battery undergoes only one discharge cycle in which its chemical reactants are consumed and no attempt is made to recharge it. The maximum amount of energy available depends entirely on the amount of chemical reactants stored within the device. Meanwhile, a secondary battery operates through repeated charge/discharge cycles and requires an external electric power source to regenerate its chemical reactants and thereby recharge its electrical energy. Fuel cells, on the other hand, act solely as

energy conversion units by producing electrical energy as a fuel and oxidant are continuously supplied (Li, 2006).

The conventional pathway of generating electricity involves the thermal combustion of fuel. In a heat engine when hydrogen is used as its fuel, hydrogen reacts with oxygen to produce water and heat:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + heat \qquad 2.1$$

The cleavage of the bonds within H_2 and O_2 and the formation of water involve the transfer of electrons between atoms. The resulting energy change associated with these bonds is released as heat which can be converted into intermediate forms of energy and finally into electricity (O'Hayre *et al.,* 2006). In fuel cells, electrons that move from high-energy reactants to low-energy product are directly harvested as electrical energy. This is made possible since the fuel and oxidant reactants and the sites for oxidation and reduction are spatially separated so that the electrons necessary to complete the overall reaction must flow through an external circuit. The electrons produced by the half-cell reaction at the fuel electrode are transferred to the oxidant electrode via the external circuit to complete the reaction. The net reaction in a fuel cell is exactly the same as in a heat engine when the fuel is combusted (O'Hayre *et al.,* 2006). A significant amount of energy in the form of heat is also generated within fuel cells. Thus, the simultaneous utilization of this exhaust heat and electrical energy in a fuel cell-gas turbine can potentially improve the overall efficiency of power generation.

A fuel cell consists of three main components: i) fuel electrode (anode) and ii) oxidant electrode (cathode) separated by iii) an electrolyte. The anode and cathode are connected to an external circuit to provide a pathway for the electrons generated/consumed by the electrochemical reactions. The half-cell reactions at the anode and cathode involve ions and electrons. The ions migrate through the electrolyte, while the electrons are transported between the electrodes through the external circuit in the form of electricity. To achieve a high reaction rate and a large power output, the electrodes are porous to maximize the surface area in contact with the reactants, while the electrolyte is thin to minimize its ionic resistance (Varga, 2007). The electrodes provide sites for the electrochemical reactions and the conductivity required to transport electrons. Meanwhile, the electrolyte acts as an ionic conductor, electronic insulator

and a barrier to separate the reactants. Ions can also flow through the electrodes because the electrodes are composite porous materials containing ionically conducting materials (Li, 2006). During fuel cell operation, gaseous fuel (e.g., hydrogen) is delivered to the anode and gaseous oxidant (i.e., oxygen from air) is supplied to the cathode. By-products can also be formed at the electrodes depending on the fuel. These by-products are also transported out of the electrode into the gas stream (Haile, 2003).

Fuel cells are primarily classified into five major types: alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), proton exchange membrane fuel cells (PEMFCs), molten carbonate fuel cell (MCFCs) and solid oxide fuel cells (SOFCs). These five major fuel cells operate via different half-cell reactions depending upon the characteristics of the electrolyte. The principal half-cell reactions operating in each fuel cell are given in Table 2-1.

Table 2-1 Half-cell reactions of five major types of fuel cells

Fuel Cells	Anode Reaction	Cathode Reaction
AFC	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
PAFC	$H_2 \rightarrow 2H^+ + 2e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
PEMFC	$H_2 \rightarrow 2H^+ + 2e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
MCFC	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ $CO + CO_3^{2-} \rightarrow 2CO_2 + 2e^-$	$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$
SOFC	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$ $CO + O^{2-} \rightarrow CO_2 + 2e^-$	$O_2 + 4e^- \rightarrow 2O^{2-}$

Among these fuel cells, AFCs were the first developed and successfully operated in space shuttle missions. Attempts to use AFCs for terrestrial applications, however, have been restricted due to the requirement that pure H_2 and O_2 be used. Acid-based PAFCs are available in commercial units that can generate up to 200 kW power. Nevertheless, this type of fuel cell is not yet considered to be commercially mature. PEMFCs and SOFCs have received the most attention in recent years. With membrane electrolyte and low-temperature operations, PEMFCs are ideal for transportation and have been employed in most prototypes for fuel-cell-powered vehicles. The demand for alternative power generation has drawn considerable interest in developing SOFCs. Due to their high operating temperatures, SOFCs are able to utilize

hydrocarbon fuels, making them more flexible with respect to fuel options than the other types. MCFCs which are the other high temperature cells are still in the early stages of development and pre-commercial demonstration (Li, 2006). The operating characteristics of the five types of fuel cells are summarized in Table 2-2.

Table 2-2 Major types of fuel cells (Li, 2006; Demirbas, 2009; Shah, 2007)

Features	Type of fuel cells				
	AFC	PAFC	PEMFC	MCFC	SOFC
Electrolyte	KOH aqueous (immobilized)	H_3PO_4 solution (immobilized)	Polymer membrane	Molten carbonate salt	Ion-conducting ceramic
Electrodes	Pt (Anode/ Cathode)	Pt (Anode/ Cathode)	Pt (Anode/ Cathode)	Ni (Anode/ Cathode)	Ni-YSZ (Anode) $La_{0.8}Sr_{0.2}MnO_3$ (Cathode)
Charge carrier	OH^-	H^+	H^+	CO_3^{2-}	O^{2-}
Operating temperature (^oC)	60-80	160-220	50-80	600-700	600-1000
Fuels	H_2	H_2	H_2, CH_3OH, C_2H_4OH	H_2, CO, CH_4	H_2, CO, CH_4
Efficiency (%)	60-70	40-45	45-60	60-65	55-65
Applications	Transportation, space travel	Stationary power generation, CPH	Transportation, portable equipment, space travel	Stationary power generation, CPH	Stationary power generation, CPH

CHP: Combined heat and power