A mechanistic investigation of fuel oxidation reactions on the solid oxide fuel cell electrodes by using palladium catalyst nanoparticles

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NANYANG
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UNIVERSITY

**A MECHANISTIC INVESTIGATION OF FUEL OXIDATION
REACTIONS ON THE SOLID OXIDE FUEL CELL
ELECTRODES BY USING PALLADIUM CATALYST
NANOPARTICLES**

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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NANOPARTICLES**

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Publications

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2. Babaei, A.; Zhang, L.; Tan, S. L.; and Jiang, S. P.; 2010, "Pd-Promoted (La,Ca)(Cr,Mn)O₃/GDC anode for hydrogen and methane oxidation reactions of solid oxide fuel cells," *Solid State Ionics*, 181(25-26), pp. 1221-1228
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List of symbols and abbreviations

AFC	Alkaline Fuel Cell
ASR	Area Specific Resistance
CH ₃ OH	Methanol
C ₂ H ₅ OH	Ethanol
DMFC	Direct Methanol Fuel Cell
EDS	Energy Dispersive Spectrometer
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
GDC	Gadolinium doped Ceria
GNP	Glycine Nitrate Process
LCCM	La _{0.7} Ca _{0.3} Cr _{0.5} Mn _{0.5} O ₃
LSC	La _{0.8} Sr _{0.2} CrO ₃
LSCF	La _{0.6} Sr _{0.4} Fe _{0.2} Co _{0.8} O ₃
LSCM	La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃
LSCT	La _{0.7} Sr _{0.3} Cr _{0.8} Ti _{0.2} O ₃
LSGM	La _{0.9} Sr _{0.1} Ga _{0.8} Mg _{0.2} O _{2.85}
LSM	La _{0.8} Sr _{0.2} MnO ₃
MIEC	Mixed Ionic / Electronic Conductor
MCFC	Molten Carbonate Fuel Cell
OCP	Open Circuit Potential
PAFC	Phosphoric Acid Fuel Cell
PEM	Polymer Electrolyte Membrane
SDC	Samaria-doped Ceria
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell
SSZ	Scandia stabilized Zirconia
TEC	Thermal Expansion Coefficient
TEM	Transmission Electron Microscopy
TPB	Triple Phase Boundaries
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
YSZ	Yttria stabilized Zirconia
η	Overpotential

Abstract

A solid oxide fuel cell (SOFC) is a solid device for electrochemically converting the chemical energy of a fuel into electrical energy without conventional combustion of the fuel. SOFCs have several advantages over other types of fuel cells, including high conversion efficiency, low sensitivity to impurities in fuels and fuel flexibility. The high operating temperature (600-1000°C) of SOFCs enables the use of not only hydrogen but also hydrocarbons as fuels. Direct utilization of hydrocarbon fuels without pre-reforming greatly reduces the complexity and cost of fuel cell systems. The imperative for direct use of hydrocarbons is the anode materials that should have high catalytic activity for hydrocarbon oxidation reactions and, at the same time, high resistance and tolerance towards the formation of coke and sulfur poisoning on the electrode surfaces. The performance of a SOFC can be improved significantly by addition of a catalyst to the electrodes.

The objective of this PhD research is to investigate the mechanisms and kinetics of chemical and electrochemical reactions occurring over SOFC electrodes catalyzed by palladium (Pd) nano particles with the emphasis on the hydrocarbon oxidation reactions. For this purpose the Pd nano particles were introduced into the microstructures of the Ni/GDC and LCCM/GDC anode and LSM cathode electrodes of the SOFCs. The loading of the Pd nano particles was incrementally increased in the microstructures of the electrodes by using a wet impregnation technique. The effects of the presence of Pd nano particles on the oxidation reactions of hydrogen, methane, methanol and ethanol over the anodes and the oxygen reduction reactions over the cathodes were investigated by means of various analytical techniques including electrochemical methods over a temperature

range of 650-900°C. The electrochemical measurements were performed at both open circuit and applied potentials to investigate the chemical or electrochemical nature of the reactions. When hydrogen was used as the fuel at the anode electrodes, the presence of the Pd nano particles significantly reduced the electrode polarization resistance of the anodes. The results indicated that the Pd nano particles mainly affected the adsorption/dissociation/diffusion processes of the hydrogen oxidation reactions over the both Ni/GDC and LCCM/GDC anodes. The activation energies for the gas adsorption, dissociation and diffusion processes dramatically decreased with the increase in loading of the Pd nano particles, revealing a specific electro-catalytic property of the Pd for the hydrogen oxidation reactions. The electrode impedances for the methane, methanol and ethanol oxidation reactions over the nickel/gadolinium-doped ceria (Ni/GDC) anodes also considerably decreased in the presence of the Pd nano particles. However, the impregnation of the Pd nano particles could not completely suppress the carbon deposition/cracking. On the other hand, the (La,Ca)(Cr,Mn)O₃ (LCCM)/GDC anode electrodes showed a quite stable performance in the methane fuel. The study of the Pd-impregnated La_{0.8}Sr_{0.2}MnO₃ (LSM) catalysts showed that a higher catalyst loading was detrimental to the performance stability of the electrodes. The co-impregnation of Pd with Ag and Co significantly improved the stability of the nano-structured catalyst phases at the operating conditions of the SOFCs.

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CHAPTER ONE

1. Introduction

1.1. Introduction

Fuel cells are defined as electrochemical devices which convert the chemical energy stored in the fuels directly to the electrical energy without conventional combustion of the fuels. In 1838 the Swiss scientist Christian Friedrich Schönbein discovered the underpinning principle behind the fuel cell operation and after him the concept was further developed and the first real fuel cell was invented by Sir William Robert Grove in 1845. Sir W. R. Grove is widely regarded as the father of the fuel cell. For several decades there were scattered research works on the fuel cells until 1960s that more attention was drawn to this electrochemical device mainly by General Electric Company [1]. In the recent years with the rising cost of fuels and increased impacts of pollution and global warming, specific attention has been paid to the fuel cell technology as it is considered as a highly efficient and green technology for the future hydrogen economy [2, 3].

There are several types of fuel cells working in different temperature ranges, using different types of materials for electrolytes and electrodes [4-7]. Each type of fuel cells has its own advantages, limitations, and potential applications [8, 9]. A common

classification method for fuel cells is based on the kind of electrolyte materials employed in the devices. According to this classification some of the most conventional types of fuel cells are listed as follows:

- Polymer Electrolyte Membrane or Proton Exchange Membrane fuel cell (PEMFC); this type of fuel cell normally operates at relatively low temperatures around 80°C, and the membranes are made of polymeric materials [10-14].
- Phosphoric Acid Fuel Cell (PAFC); this group of fuel cells uses liquid phosphoric acid as the electrolyte and operates at about 230°C [9].
- Molten Carbonate Fuel Cell (MCFC) which uses an electrolyte that is made of a porous and chemically inert matrix filled with a molten carbonate salt mixture. The operating temperature is relatively high around 650°C [2, 3, 15].
- Alkaline Fuel Cell (AFC) which uses potassium hydroxide as the electrolyte and operates in the temperature range of 65-220°C [16-18].
- Direct Methanol Fuel Cell (DMFC) which is similar to PEMFC as they both use a polymer membrane for the electrolyte. However, in a DMFC, instead of hydrogen, liquid methanol is used as the fuel and operates at a relatively low temperature between 50-90°C [19, 20].
- Solid Oxide Fuel Cell (SOFC) which uses a hard, rigid, non-porous ceramic compound as the electrolyte, and operates at elevated temperatures between 800-1000°C [2, 21-29]. As a result, SOFCs offer many advantages over the above mentioned fuel cell systems in term of higher fuel utilization rate (higher efficiency), reliability, fuel flexibility, modularity, higher tolerance to impurities in the fuel and environmental friendliness [30]. In addition, SOFCs offer the possibility of working in combined heat

and power systems which enable full exploitation of both electricity and heat. Using SOFCs in a combined heat and power system enhances the efficiency of the system to approximately 70% [31].

Fuel flexibility is also a very important factor in commercialization of the fuel cell technology. One of the biggest limitations of current fuel cell technology is the requirement that the fuel must be hydrogen. Although hydrogen is generally referred to as the ideal fuel for the future, there are still a number of problems related to production and storage of hydrogen that must be solved before it can be implemented on a large scale. The main problem is that the majority of hydrogen that is available in the industry is produced by reforming of hydrocarbons. Even in highly optimized large scale production plants about 20-30% of the fuel value of the hydrocarbons is lost during the reforming process. For portable applications there exists another limitation that storage of hydrogen is very expensive and the energy density is relatively low as compared with hydrocarbon fuels. SOFCs that can directly use hydrocarbon fuels such as natural gas, without initial reforming of those hydrocarbons to hydrogen, have great advantages compare to conventional hydrogen based fuel cells.

The technical issues related to direct utilization of hydrocarbons in SOFCs have been widely addressed in the literature [32-36]. The most critical issue for SOFCs based on the hydrocarbon fuels without pre-reforming is the need for the anodes that do not catalyze the formation of carbon at operating temperatures of SOFCs. Fundamental understanding of the mechanisms of chemical and electrochemical reactions taking place in the anode compartment in both hydrogen and hydrocarbon environments is very important for the development of SOFC technology [9, 10].

1.2. Objective

The main objective of this PhD research work is to fundamentally study the mechanisms and kinetics of various chemical and electrochemical reactions taking place over the electrodes, especially the SOFC anode promoted by metallic catalysts such as palladium. A mechanistic study is required for both hydrogen and hydrocarbon fuels. Because the presence of nano-sized metallic catalysts in the microstructure of the electrodes has significant effect on the electrode reactions, it is possible to make use of catalysts to explore the ways to effectively lower the electrode resistances for the reactions and to enhance the electrode tolerance towards carbon deposits. A fundamental and deep understanding of the oxidation reactions and promoting mechanisms of metallic catalysts would enable us to tailor the materials and microstructure of the electrodes in such a way that a higher performance can be achieved with lower cost and less complexity. For this purpose, two categories of anode materials are selected, namely, Ni/GDC and Ni-free LCCM/GDC composite materials. Furthermore, the performance enhancement of Pd catalyst on the LSM cathode electrode of SOFC will be investigated to some extent.

1.3. Scope

The scope of this work will cover the synthesis, fabrication and characterization of catalyst promoted Ni-containing and Ni-free anode materials and their reaction mechanisms. Catalysts will be introduced into the anode structure by wet impregnation or

infiltration. The stability of the impregnated catalyst phases on the cathode will also be studied. The reaction mechanisms are studied for a wide range of fuels including hydrogen, methane, methanol and ethanol. The catalyst effects on the performance of LSM cathode electrodes will be studied in some extent.

1.4. Report arrangement

A literature survey of SOFC anode and cathode materials with the emphasis on the role of externally added metallic catalysts on the performance and reaction mechanisms of electrode reactions is presented in Chapter 2.

Chapter 3 presents the applied experimental procedures and characterization techniques.

Chapter 4 addresses the results and discussion for hydrogen oxidation on Pd-promoted Ni/GDC anode.

In Chapter 5, hydrocarbon oxidation reaction on Pd-promoted Ni/GDC anode is presented and discussed.

Chapter 6 includes the results and discussion for hydrogen and hydrocarbon oxidation reactions on Pd-promoted LCCM/GDC anode.

Chapter 7 discusses the performance and stability of LSM cathode promoted with palladium based catalysts.

Finally, conclusions are drawn and future work is recommended in Chapter 8.

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CHAPTER TWO

2. Literature review

2.1. Fundamentals of fuel cell

As an electrochemical device, a solid oxide fuel cell (SOFC) consists of one electrolyte and two electrodes one of which is negatively charged called cathode and another positively charged called anode. Figure 2.1 shows a schematic diagram of a SOFC. The electrolyte in a SOFC is a solid, non porous ceramic material with high oxygen ion conductivity but negligible electrical conductivity. The electrodes are made of ceramic or cermet materials with a relatively high porosity. The electrodes must be sintered to the electrolyte with a good interface to provide a proper passage for transferring of oxygen ions from the electrode to the electrolyte or vice verse.

The main function of the electrolyte is to isolate the fuel and oxidant compartments of the fuel cell and to provide a high oxygen ionic conductivity. The chemical reactions that produce electricity take place at the electrode/electrolyte interfaces. The electrolyte material must be dense enough to separate the fuel and air compartments of the cell and retain its negligible electrical conductivity and high ionic conductivity under working condition. At the same time the coefficient of thermal expansion for the electrolyte material should match with those of anode and cathode.

Figure 2.1 A schematic diagram of a solid oxide fuel cell [37]

Cathode is where molecular oxygen is reduced to oxygen ions using electrons supplied from the external circuit under operating condition of SOFCs, according to the reaction (2.1):

The cathode materials must have the ability to adsorb and dissociate oxygen molecules to oxygen ions in order to transfer them to the electrolyte. The electrons supplied from the external circuit must reach to the cathode/electrolyte interface for the O_2 reduction reaction, thus the cathode material must possess good electrical conductivity. Sr doped LaMnO_3 (LSM) is the most investigated cathode material for SOFCs. Some alternative types of cathode material are also developed [38] and several new materials are under investigation [13].

Analogous to the cathode, the anode must be catalytically active for the fuel oxidation reaction and must retain sufficient ionic and electronic conductivity under

operating condition. Usually, the presence of a catalyst in the electrode structure will speed up the electrode reaction. The following sections will be concentrated on the basic requirements and properties of the anode and cathode electrodes and electrolyte materials with special emphasis on the catalytic properties of the electrode materials and the role of catalysts on the performance and reaction mechanism of the electrodes.

2.2. Electrolyte

The main concern for selecting an appropriate fuel cell electrolyte material is high ionic conductivity, while the other parameters like low cost, abundance, stability at processing and operating temperature in both oxidizing and reducing environment, easy fabrication process with dense and non porous final structure, compatibility with other cell components, low electrical conductivity and high mechanical strength are also important.

Pure zirconia (ZrO_2) has a monoclinic lattice arrangement at room temperature and at $\sim 1170^\circ\text{C}$ it transforms to a tetragonal structure. Adding yttria (Y_2O_3) to zirconia stabilizes its structure in the cubic fluorite structure form, and the ionic conductivity of the resultant Y_2O_3 doped ZrO_2 (YSZ) is considerably higher than that of pure zirconia. Other doping elements like Sc_2O_3 , CaO and MgO show similar effect on the stability and ionic conductivity of the zirconia [28]. Overall, doped zirconia fulfills the basic requirements for an ideal high temperature fuel cell electrolyte at operating temperature of 850°C and above; however, for the applications in lower temperature range, YSZ shows a relatively poor ionic conductivity. Two strategies are normally taken to overcome the problem of low ionic conductivity of YSZ [39, 40]. One of them is to

fabricate a thin electrolyte layer of around 10-15 micrometer [41, 42] and the second one is to substitute the YSZ electrolyte with alternative electrolyte materials with high conductivity at intermediate temperatures like doped ceria [43] and doped lanthanum gallate family such as $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ (LSGM) [44]. The above mentioned strategies can also be applied together at the same time [45, 46]. Conductivity data for some conventional SOFC electrolyte materials are presented in Figure 2.2 [4]. Although doped ceria has shown a very promising ionic conductivity, in a reducing atmosphere, partial reduction of Ce^{4+} to Ce^{3+} occurs which leads to a higher level of electronic conductivity. The induced electrical conductivity decreases the fuel cell efficiency and is detrimental for SOFC electrolyte applications. The ionic conductivity of lanthanum gallate family is very similar to that of doped ceria and lanthanum gallate is significantly more stable as compared to doped ceria under reducing environment. However some phase instabilities and formation of different impurity phases at grain boundaries are reported [47].

Figure 2.2 Conductivities of selected high temperature conducting electrolyte materials [4]

2.3. Anode

The functions of a porous anode are to provide electrochemical reaction sites for oxidation of the fuel, allow the fuel and byproducts to be delivered and removed from the reaction sites, and to provide a path for electrons to be transported from the electrolyte/anode reaction sites to the interconnects in SOFC stacks [48]. Thus, the anode material must be stable in the fuel environment and have sufficiently high electronic and ionic conductivities and catalytic activity for the fuel gas oxidation reaction at the operating temperature of the SOFC and possessing good porosities that allow the reactants to diffuse from the fuel compartment to the reaction sites inside the anode. The oxygen ions, which are electrochemically transported through the electrolyte toward the anode, oxidize hydrogen, carbon monoxide or hydrocarbons at the anode reaction sites.

The reaction that takes place at the anode/electrolyte interface, depending on the fuel used, might be one of the following [49]:

Since a SOFC operates at high temperatures, the anode must also be chemically and thermally compatible with the other fuel cell components at fabricating and operating temperatures of the SOFC. The compatibility is particularly important with electrolyte material which provides oxygen ions for the reactions at the anode. A traditional type of SOFC anode which is still widely in use is a composite of yttria stabilized zirconia (YSZ) and nickel, which hereafter is referred to as Ni/YSZ [50-56]. This cermet has excellent properties as an anode due to its high electrical conductivity, good thermal compatibility with YSZ electrolyte and high electrochemical activity for hydrogen oxidation reaction, but suffers from two drawbacks. One of them is deposition of carbon on the anode surface when hydrocarbon is used as the fuel [57-61] and the other problem is poisoning of the active sites of the anode by sulfur, which is normally exist in the natural gas pipe lines. Presence of a small amount of carbon in the electrode microstructure is usually beneficial, because it increases the electrical conductivity of the cermet structure [62], but the larger amount is detrimental as it blocks the active catalytic sites on the nickel surface and also causes deterioration of the cermet structure by the so called Ni dusting phenomenon. One approach to overcome the carbon deposition problem is to replace Ni with alternative materials, however among the metallic and ceramic material that have

been investigated yet, none of them show similar excellent electrical and catalytic properties as nickel for anode material applications [63-70].

The mechanism of the oxidation reactions of fuels such as hydrogen and methane on the SOFC anode is an area of intensive research for several decades but has not been completely clarified yet [71]. For Ni based cermet anodes, it is widely accepted that Ni dissociates hydrogen molecule and subsequent hydrogen atoms are transported to the electrode/electrolyte interface either through bulk or surface diffusion. Finally, H^+ ions combine with the oxygen ions forming water as the final product at the triple phase boundaries. It has been suggested that oxygen ions are transferred from the electrolyte to the nickel phase where it reacts with hydrogen [72].

In principle, there are six important requirements that an ideal anode material must possess:

(1) Ionic Conductivity

An ideal anode material must have sufficient ionic conductivity in order to transfer oxygen ions from electrolyte to triple phase boundaries (TPB), where ionic conducting phase, electronic conducting phase and fuel molecules meet (Figure 2.3). For this purpose metal/ceramic cermets, perovskite structure oxides family and fluorite structure materials are the proper choices [73].

The perovskite family oxides have the general formula of ABO_3 , in which A and B are cations. The valence of the cations A and B are indicated by n and m in the Figure 2.4. The cations with lower valence A (like La, Sr, Ca and Pb, etc.) are large and reside on the larger spaces in the 12-fold oxygen coordination, and B cations (like Ti, Cr, Ni, Fe, Co and Zr, etc.) occupy the octahedral positions (six fold coordination). Partial or full

substitution of A or B cations with other cations of different valence is feasible. Some example of this group of materials include; $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM), $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ (LSGM), $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.8}\text{Ti}_{0.2}\text{O}_3$ (LSCT), etc. Figure 2.4 shows typical structure of a cubic perovskite ABO_3 . These anode materials are stable in both air and reductive fuel environment, and show stable electrode performance in methane [73, 74].

Figure 2.3 Schematic diagram of three-phase boundaries on a Ni/YSZ anode [36]

In the family of fluorite structure materials, zirconia based oxides and ceria based oxides are the most famous candidates. Zirconia is generally doped with yttria, or titania, or a combination of them to form yttrium/titanium- zirconium oxides (YTZ). Ceria is generally doped with gadolinium oxide (for example $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$) [75-80]. In the ceria based family, reduction of Ce^{4+} to Ce^{3+} leads to better electronic conduction [77]. Ceria based oxide is one of the best oxidation catalysts among oxides especially when it is employed in conjunction with precious metals[81].

Figure 2.4 A unit cell of a typical “ABO₃” perovskite structure. The valences of cations A and B are indicated by n and m, respectively [73]

Mixed ionic and electronic conducting oxides such as gadolinium or samarium doped ceria have also been investigated as potential anode materials for intermediate temperature SOFC application [80, 82, 83]. The major attractiveness of such mixed ionic and electronic conductive oxides is the possibility of having much larger triple phase boundaries as a result of simultaneously having high ionic and electronic conductivity. For example, the oxygen ion conductivity of samaria doped ceria is 0.1 Scm^{-1} at 800°C which is about four times higher than that of YSZ, while at the same temperature, its electronic conductivity is 4 Scm^{-1} under hydrogen reducing environment [64]. There exist some other groups of material that can be employed for using as anode materials, such as tetragonal tungsten bronze structure anode material and pyrochlore anode materials which are under investigation [84, 85].

(2) Electronic Conductivity

Electrons that come out from the chemical reactions on the anode surface need to be transferred to the external circuit. Normally a metallic current collector is used to collect electrons. However, resistive losses within the anode need to be minimized by employing an anode material that has a good electronic conductivity. If the anode is used as a support for the thin layer electrolyte, the electrons must travel a relatively long distance in the anode to the current collector; in this case a higher electronic conductivity of the anode material is needed [37].

(3) Thermal Compatibility

Because a SOFC works at high temperatures, the thermal expansion of the anode needs to be matched to that of the electrolyte in order to maintain the structural stability. Otherwise the weaker side will be cracked as a result of the mismatch between the anode and electrolyte. Also the thermal expansion must be matched to that of the current collector with which it makes physical contact [37].

(4) Chemical Stability

The anode material must be chemically stable with the electrolyte at elevated temperature during processing steps and also in operating condition in reducing atmosphere. Interface phases that might block transport of electrons from the anode to the current collector or O^{2-} ions transport from the electrolyte to the anode must not be

formed over time under operating conditions. Also, if the anode is used to support the thin layer of ceramic electrolyte, it needs to be chemically stable relative to the electrolyte under the conditions of sintering of the electrolyte [37]. Stability of the microstructure and interface at electrode-electrolyte interface is an important issue in the development of SOFC. It should be noted that stability of an individual component in SOFC is not only related to that component itself, but also to the interaction between adjacent components of a SOFC stack [64].

(5) Microstructure and Porosity

Because the fuel gas must make contact with the triple phase boundaries of the anode, the anode needs to be fabricated in the form of a porous structure that retains its physical shape under operating conditions over time. Also the current collector must not cover the entire surface of the electrode [37]. Jiang et al. [24-26] explained that electrode performance of the Ni/YSZ cermet anodes is critically dependent on the microstructure of the cermet and the fabrication method. The final microstructure is affected by the original NiO and YSZ powder size, their particle size distribution, weight percentage of two constituents, manufacturing method, sintering time and temperature, volume of the pore former and the thickness of the electrode layer. Reduction of NiO to Ni metal brings about a considerable amount of porosity change in the microstructure. Usually the volume percent of porosity increases around 25% after reduction.

Sintering of the anode layer at high temperatures is essential to achieve high polarization performance and low electrode ohmic resistance. For example sintering of the Ni/YSZ and Ni/GDC cermet take place at 1400°C. Formation of the YSZ particles

connection within the cermet occurred at the sintering temperature of 1400°C. This corresponds to the smallest electrode ohmic and polarization resistance of the cermet anodes. High sintering temperature creates strong bonding between the YSZ phase in the cermet and interface with YSZ electrolyte, leading to the formation of a three dimensional and rigid YSZ structure to extend the reaction sites into the cermet [86].

On the other hand, microstructure stability of the anode cermet is a major concern. In Ni/YSZ cermets, stability of the microstructure and long term performance are critical issues. Degradation problems in long term operation of SOFCs are characterized by a considerable decrease in the surface area and consequently the TPB areas and finally the performance of the fuel cell system. In the case of Ni/YSZ cermet anodes, the most predominant micro-structural change is the coarsening and agglomeration of Ni phase. Poor wettability between metallic Ni and YSZ oxide phase in the Ni/YSZ system is the main reason for the agglomeration of Ni phase. Therefore, preventing agglomeration and sintering of metallic Ni particles in Ni/YSZ cermet electrodes mainly relies on micro-structural optimization of the Ni/YSZ cermets.

(6) Catalytic Activity

Oxidation of hydrogen or hydrocarbons on the anode surface commences with chemical adsorption and dissociation of the fuel molecules. The anode material must facilitate the reaction in anode electrode regardless of type of the fuel that is used. The dissociated and chemisorpted species of the fuel react with O^{2-} ions that have formed in the cathode side and transferred to anode through electrolyte and released electrons must be transported to the external circuit via current collector. Figure 2.5 shows the proposed

models for reaction mechanism on the H_2 / electrode/ electrolyte interface. However, if anode is a mixed ionic/electronic conductor (MIEC) material [48, 76, 77, 80], oxygen ions are transported to the anode surface from the electrolyte and fuel oxidation reaction steps such as chemical adsorption of the fuel molecule and the charge transfer, take place at the surface of the MIEC anode [87].

Figure 2.5 Schematic illustration of possible reaction processes for hydrogen oxidation around H_2 – H_2O /anode/electrolyte interfaces: (a) proposed by Holtappels and coworkers and (b) proposed by Badwal and Jiang [88]

An important requirement is that the catalytic activity of the anode should remain at a reasonable level over a long life. This imperative requires that if a hydrocarbon fuel is used, the anode must not be poisoned by carbonaceous residues or impurities in the feeding fuel gas; it also requires retention of the electronic pathways from the anodic reaction sites to the current collector. Sulfur is an impurity that usually exists in hydrocarbon fuels, and because sulfur poisons most catalysts, removal of this element is a

necessary requirement. Finally, the higher sulfur tolerant the anode materials, the less sulfur removal from the fuel gas would be required [37].

2.3.1. Catalyst promoted anodes

Proper addition of precious metal catalysts to the solid oxide fuel cell electrodes improves the electro-catalytic activity and consequently the performance of the system. In order to make the best use of the catalytic agent, which is generally a precious metal; the surface to volume ratio of the catalyst phase in the electrode microstructure should be maximized. To meet the above mentioned requirement, impregnation technique is the most preferred route to distribute the catalyst agent inside the electrode microstructure [89]. In this technique, aqueous solution of a salt of the catalyst metal is usually used for impregnation purpose. A droplet of the solution is placed on the porous electrode surface and the solution is soaked into the porous electrode by capillary force. By heating the impregnated electrode, the catalyst solution decomposes, forming catalyst deposits over the surface area of the porous structure in the form of metal oxide or pure metal. The finer the distribution of the catalyst particles, the higher is the surface area of the catalyst. For some of the deposited metal oxide phases like palladium or nickel oxides, reduction of the cell in a reducing atmosphere can convert an oxide phase to a metallic form. This conversion usually takes place by a considerable amount of shrinkage in the particle size and increase in pore volume. The loading of the catalyst element can be controlled by repeating the impregnation processes.

Until today, various precious metals are tested in different anode or cathode electrode systems by the researchers; however the effect of presence of catalytic phase on the anodic or cathodic reaction mechanism is not fully clarified. Uchida et al [90-96] proposed the new concept of catalyzed reaction layers in the electrode structure of SOFC with high performance and activity for intermediate temperature SOFCs. A schematic illustration of the proposed concept is shown in Figure 2.6. They investigated the electro-catalytic effects of some precious metal catalysts such as Ru, Rh, Pd, Ni, Ir and Pt on the electrode performance and reported that by loading a small amount (0.1 mg cm^{-2}) of Pt, Rh, Ir and Ru into the structure of samaria-doped ceria (SDC) mixed conducting oxide, the anode polarization resistance and its activation energy were greatly decreased in wet hydrogen atmospheres, while Ni and Pd showed lower activities. They obtained the best enhancement in the performance of LSM cathode material by addition of Pt [96].

(a) Ni-YSZ cermet anode (conventional type)

(b) Catalyzed anode layer (New concept)

Figure 2.6 Schematic illustrations of anode reactions in SOFCs using (a) conventional Ni/YSZ cermet anode and (b) catalyzed reaction layer [96]

Effect of Ru catalyst on the performance of SDC anode under a synthetic fuel gas environment was also investigated by Uchida et al. [93]. The results showed that at 800 and 900°C, the anodic overpotential was considerably decreased by loading a small amount of Ru catalyst. SDC anode without catalyst showed a good performance at 1000°C in the synthetic gas, however the performance dramatically decreased at the temperatures lower than 900°C. With addition of 0.1 mg cm^{-2} Ru catalyst, at 800°C, the current density was 2.5 times higher than that on the pure SDC and further increase of Ru catalyst to 0.5 mg cm^{-2} enhances the performance even more, while at 900°C the loading of 0.1 mg cm^{-2} is sufficient to activate the SDC anode (see Figure 2.7). Since SDC is a good n-type mixed conductor, decrease in P_{O_2} may result in a high electronic conductivity, which may contribute to the enhancement of the current densities due to increase of the active reaction sites. In another work they impregnated $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solution into a $\text{La}(\text{Sr})\text{CoO}_3$ (LSC) cathode and reported that addition of 0.1 mg cm^{-2} platinum nano particles increases the current density of the cell by about 1.7 times. They also concluded that the reduction of cathode overpotentials brought about by the Pt particles can be ascribed to the high catalytic or electro-catalytic action and not the improvement of electronic conductance [91].

Figure 2.7 Polarization properties of SDC anodes with and without Ru microcatalyst loading measured in SG ($H_2/CO_2=4$), ($\circ$) pure SDC without catalyst, (Δ) Ru/SDC (0.1 mg cm^{-2}), and ($\square$) Ru/SDC (0.5 mg cm^{-2}) [93]

Takeguchi et al [55] added different type of precious metals including Rh, Ru, Pt and Pd to the Ni/YSZ anode and studied the change in electrochemical properties of the anode as well as the change in carbon deposition rate and steam reforming of CH_4 over the cermet as a result of addition of the catalysts. Compare to pure Ni/YSZ anode, they observed lower carbon deposition rate in the anodes with addition of Ru, Pt and Pd, but higher carbon deposition in the presence of Rh. They reported that addition of the precious metals improved steam reforming of the methane. Impedance spectra for pure Ni/YSZ anode was reported to be consisted of two semicircles at high and low frequencies. As a result of addition of Ru and Pt catalysts the low frequency arc disappeared while the high frequency arc remained intact. This suggests that Ru and Pt

addition did not affect the impedance caused by reaction, but greatly reduced the impedance caused by gas diffusion process (Figure 2.8).

Figure 2.8 Impedance spectra for anode/electrolyte interface of SOFC using Ni/YSZ cermets modified with Ru and Pt at 1000°C. Steam/carbon = 3 at OCP [55]

Gorte and McIntosh [36, 62, 97] studied the effects of addition of dopant levels of precious metals (Pd, Pt or Rh) to a 10% Ceria- YSZ anode. They used two methods to increase electric conductivity of the anode material; depositing a carbonaceous phase onto the anode structure, and addition of an inert electrical conductor like copper. Addition of 1%Pd to the anode structure with carbonaceous layer deposition doubled the maximum power density in hydrogen fuel at 973K with an increase in open circuit voltage. As shown in Figure 2.9 the effect of Pd addition was even more considerable on the oxidation of methane. When ceria is the only catalyst, the cell performance in methane is much lower than that obtained with hydrogen, probably due to the difficulty

of breaking the strong C–H bonds. After addition of Pd, the performance in methane approaches that obtained from hydrogen, which is a clear indication that the reaction barrier has been reduced significantly. When copper phase was used to improve the electrical conductivity of the microstructure, they found that the performance of Pd impregnated samples is similar to that of pure samples probably due to the formation of a catalytically inactive alloy. In their experiments performance of the cell under n-butane fuel was much less affected by Pd addition as compared to that for methane fuel, probably due to the coverage of the surface of the Pd particles by carbon.

Figure 2.9 Potentials (open symbols) and power densities (filled symbols) as a function of current density at 700°C for (♦) H₂, (▲) n-butane, and (●) CH₄. In (A) the cell has a C-ceria-YSZ anode; and in (B) the anode contains 1 wt% Pd [97]

Nabae et al [98] performed a comprehensive study on the Pd promoted Ni anodes and claimed that simultaneous application of Ni and Pd leads to a synergetic catalytic effect of the catalysts for direct oxidation of methane. Aqueous solution of Ni and Pd salts were impregnated into the SDC anode microstructure to achieve a final loading of 5 wt% Ni and 9 wt% Pd, respectively. Over Pd-Ni composite anode, they achieved a maximum power density of 420 mW cm^{-2} for methane fuel at 900°C , which was comparable to the maximum power density for hydrogen fuel over the same anode at 800°C . They also investigated the effect of the cell voltage on the formation rate of the products for the CH_4 oxidation at 800°C . Interestingly, the conversion rate of CH_4 were almost constant or slightly increased with the decreasing cell voltage, even though the current density was increased. They concluded that because the conversion rate of CH_4 is independent of the cell voltage, a non-electrochemical reaction step may determine the conversion rate of the methane. The conversion rates of the products were also constant under polarization over the time, which indicates that the cell exhibits good stability under methane gas. The impedance studies of the cells with different catalyst materials show a spectrum consisted of two semicircles, which decreases in size with the order; bare > Ni > Pd > Ni-Pd (see Figure 2.10). The inset in the Figure 2.10 shows the impedance spectrum over the Pd-Ni composite anode in hydrogen. The synergetic catalytic activity between Ni and Pd is considered to be the reason for the very small impedance value for Ni-Pd containing samples. The impedance spectra for the Ni-Pd/composite anode with different loading of catalyst at 0.5 V and 800°C in CH_4 fuel revealed decreasing amount of low frequency arc as a result of increasing the loading. They concluded that the low frequency arc is reflecting the hydrogen production reaction

from CH_4 and suggested that the rate limiting process is the decomposition of methane, and Ni-Pd catalyst considerably promotes the cleavage of C-H bond of CH_4 .

Figure 2.10 Impedance spectra for methane oxidation reactions over bare SDC/LSCr and Ni, Pd and Pd-Ni promoted composite anodes at 0.5 V (dc) and 800°C. The inset shows the spectrum over the Pd-Ni composite anode in hydrogen [98]

Nabae et al [98-100] also studied the effect of the support material used for deposition of catalyst particles on the carbon formation rate and the reaction mechanism in direct utilization of dry methane [100]. They found that Pd-Ni alloy on the $\text{La}(\text{Sr})\text{CrO}_3\text{-Ce}(\text{Sm})\text{O}_2$ support has a significant catalytic activity for the activation of CH_4 but does not catalyze the carbon deposition. To clarify how the support material affects the formation of carbon species, decomposition of dry methane was performed with the Pd-Ni catalyst loaded on various supports including SiO_2 , carbon, YSZ, LSCr and SDC. Figure 2.11 shows the time function for the hydrogen formation rate during

methane decomposition with Pd-Ni catalyst on various supports at 800°C. Pd-Ni/SDC and Pd-Ni/LSCr composite anodes show negligible hydrogen formation capability, while Pd-Ni catalyst on YSZ, carbon and SiO₂ support shows considerable hydrogen formation rates.

Figure 2.11 Formation rates of hydrogen in methane decomposition over Pd-Ni catalyst supported on (a) SiO₂, (b) carbon, (c) YSZ, (d) SDC, and (e) LSCr at 800°C. The photographs show the volumes of catalysts before (left) and after (right) the reactions in each graph [100]

The photographs a, b, c, d and e show the catalyst volume before and after methane decomposition at 800°C. The remarkable difference in catalyst volume for SiO₂, carbon and YSZ supports reveal serious carbon deposition on these anodes, where Pd-Ni/LSCr and Pd-Ni/SDC electrodes show very low affinity to carbon deposition.

Specific enhancement of catalytic activity of Ni with addition of Pd is also reported in the methane decomposition reaction. Methane decomposition is an alternative way to produce pure hydrogen and is of much interest for development of hydrogen based energy system. In the methane decomposition process Ni catalyst is loaded on a support and methane gas is passed over the supported catalyst in a reactor at relatively high temperature and the methane is directly decomposed to carbon and hydrogen gas, however the main concern in this process is the deactivation of the catalyst over the time as a result of carbon formation and deposition on the Ni surface. Different support materials can be used as supported catalyst, among them SiO_2 , Al_2O_3 , TiO_2 and carbon nano-fiber show reasonable performance in conjunction with Ni. In order to investigate the possibility of increasing the catalytic performance and catalytic life of the supported catalysts, Takenake et al. [101] modified a SiO_2/Ni supported catalyst with different catalyst metals such as Rh, Cu, Ir, Pd and Pt and compared the hydrogen yield and catalytic life time of the modified catalysts with those of the conventional SiO_2/Ni catalyst. Figure 2.12 demonstrates the hydrogen yields in the process of methane decomposition over Ni/SiO_2 catalyst modified with different metal catalyst species.

Figure 2.12 Hydrogen yields in methane decomposition over Ni/SiO₂ modified with different metal species and Ni/SiO₂ [101]

Addition of Cu, Rh, Ir and Pt decreases the hydrogen yield as compared to that for pure Ni/SiO₂, but Pd addition almost doubled the hydrogen yield of the catalyst.

Figure 2.13 shows the percentage of methane conversion for the SiO₂/Ni catalyst modified with different catalysts over the time. As can be seen in the graph, except Pd modified catalyst, the rest of the modified catalysts as well as pure Ni catalyst lose their catalytic activity relatively quickly. Some of the additives like Ir, Rh and Pt even decrease the catalytic life of the catalyst, while Pd has a positive effect on the catalytic life. After a sharp decrease in around 4 to 6 h the conversion process find a relatively steady state and the deactivation is delayed to about 50h. It is noteworthy that pure Pd shows very poor conversion efficiency. The researchers proposed that the synergetic effect between Ni and Pd relates to the formation of binary Ni-Pd alloy considering that the XRD investigation proved formation of Pd-Ni alloy. The TEM studies of the microstructure show that presence of palladium cannot prevent formation of carbon.

Figure 2.13 Change of methane conversion as a function of time on stream of methane in methane decomposition over Ni/SiO₂ modified with different metal species as well as Ni/SiO₂ and Pd/SiO₂. T = 823 K; catalyst mass = 0.040 g; CH₄ = 101 kPa and 40 ml/min [101]

Steam reforming of hydrocarbons is another field that superior effect of Pd-Ni alloy is discussed. Zhang et al. [102, 103] compared the catalytic activity, hydrogen selectivity and long time stability of Ni/Alumina and Pd-Ni/Alumina catalysts for partial oxidation and steam reforming of hydrocarbon fuels and reported superiority of the Ni-Pd/Alumina catalyst compare to the Ni/Alumina catalyst. They performed their experiments in a range of Ni catalyst loading and temperature from 500 to 750°C. n-Octane was selected as the hydrocarbon fuel. With 5 wt% loading of Ni in Ni/Alumina catalyst, 85% methane conversion was achieved at 750°C, while at the similar condition Ni-Pd/Alumina catalyst yields about 100% of n-octane conversion. The selectivity for hydrogen was quite similar for both catalysts and increased slightly from 90% in Ni catalyst to 92% in Ni-Pd catalyst. A considerable difference was observed in the long time stability of two catalysts under working condition at 750°C. Performance of Ni/Alumina catalyst was stable in the first

40 h of the test and then decreased. The conversion was totally stopped after 60 h tested in n-octane. Contrary to the short life time of Ni/Alumina catalyst, Ni-Pd/Alumina catalyst demonstrates a high and stable conversion up to 500 h of working at similar condition. Comparison of the surface area of both catalyst before and after stability test show that after 54 h test, the surface area of the Ni/Alumina catalyst decreased by 15%, while after 500h test surface area decreased only 5%. They also tried to re-use the deactivated catalysts by combustion of the used catalyst in air at 600°C and reducing again in a stream of mixture of hydrogen and nitrogen gas. Figure 2.14 shows the conversion rate of n-octane on (a) Ni/Alumina and (b) Pd-Ni/Alumina catalyst for the fresh catalyst as well as for the regenerated one up to 3rd regeneration cycle.

Figure 2.14 Effect of time on stream on the catalytic activity of (a) Ni/Al₂O₃ and (b) Ni-Pd/Al₂O₃ ([O₂]/[C₈H₁₈]=1.0, [H₂O]/[C]=3.0, T=750°C) [103]

Figure 2.14 (a) clearly shows that after every regeneration cycle the conversion rate is decreased while in the case of Pd-Ni/Alumina catalyst, the 3rd regenerated catalyst showed that conversion rate remains high, almost in similar level with the fresh catalyst.

Wang et al. [104] investigated a series of Ceria added Pd-Ni/Alumina catalysts for partial oxidation and steam reforming of wet hydrocarbons. The selected hydrocarbon was a mixture of n-pentane, n-hexane, n-octane, isooctane and small amount of benzene and water. Water was vaporized before entering to the reactor. They prepared Pd-Ni/Alumina catalyst by impregnation of the alumina substrate with the solution of Ni nitrate and Pd chloride. Solutions containing different concentration of cerium nitrite were also prepared and finally the Pd-Ni catalysts with different loading of ceria. (0 to 1.5 wt%) were tested in the reforming reactor at the temperature of 700°C. The catalyst activity of Ni-Pd/ γ -Al₂O₃ and Ni-Pd-Ce/ γ -Al₂O₃ in the partial oxidation and steam reforming process as a function of the reaction time at 700°C is shown in Figure 2.15. In the case of Ni-Pd/Al₂O₃ catalyst, the conversion of hydrocarbon mixture was almost constant at about 93%. The activity for the Ni-Pd-Ce/Al₂O₃ catalyst was considerably higher than that of Ni-Pd/Al₂O₃ catalyst because of the presence of cerium in the microstructure. Moreover, Ni-Pd-Ce/Al₂O₃ catalyst activity was slightly increased with increasing content of cerium; the catalyst activities reached 99%, when the content of cerium on the catalyst was over 0.5 wt%.

Figure 2.15 Effect of Ce loading on Ni–Pd–Ce catalyst activity at 700°C [104]

Cerium content of 0.5 wt% was selected as the best loading and the stability of the catalyst was tested with and without presence of the cerium. The effect of time on stream reforming, up to 540 h, is presented in Figure 2.16 for the Ni-Pd/Al₂O₃ and Ni-Pd-Ce/Alumina catalysts. As shown in the Figure, the activity of the Ni-Pd/Al₂O₃ catalyst for the conversion of the mixture of hydrocarbons was slightly decreased with increasing reaction time in the first 300 h, however, the activity of Ni-Pd-Ce(0.5)/Al₂O₃ catalyst remained almost constant up to 540 h. These results indicated that cerium plays an important role for partial oxidation and steam reforming of hydrocarbons mixture, and the addition of cerium into Ni-Pd/Al₂O₃ catalyst not only improves Ni-Pd/Al₂O₃ catalyst activity but also its long time stability. At the end of their experiments, carbon deposition on the catalysts with and without ceria was measured and compared. Analysis of Pd-Ni-Ce/Alumina catalyst shows presence of 1.8 mg g⁻¹ carbon on the catalyst, while it was 2.9 mg g⁻¹ for the catalyst without Ce.

Figure 2.16 Effect of time on stream performance of Ni-Pd and Ni-Pd-Ce catalyst activity at 700°C [104]

Lu et al [30] studied the effects of Pd catalyst addition on the performance of LSCM/Cu composite anode for direct oxidation of methane and hydrogen. In the experiments the loading of Pd was adjusted at 1.5 wt. %. $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ (LSGM) was selected for electrolyte material. $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ was used as the cathode material. A La_2O_3 doped Ce_2O_3 interlayer was deposited on the LSGM electrolyte to reduce the detrimental reaction between LSCM and LSGM. Copper oxide was deposited into the porous anode first and after that palladium was loaded into the structure of LSCM/Cu composite. By introducing Pd catalyst, the maximum power density of the cell increased from 0.86 to 0.89 W/cm^2 in hydrogen and from 0.48 to 0.6 W/cm^2 in methane, respectively. Enhancement is mainly observed for the oxidation of methane. Also in impedance measurement test, considerable decrease in the electrode polarization resistance of the lower frequency arc was reported with the addition of Pd catalyst to the composite anode (see Figure 2.17). They also demonstrated that further increasing the Pd

amount above 1% did not increase the maximum current density. The sulfur tolerance of the LSCM anode was found to be very poor, and the power density of the cell tested at 850°C was dropped from 0.46 to 0.09 W/cm² after introducing 50 ppm H₂S to hydrogen feed gas stream after 2 h. The low sulfur tolerance of LSCM anode could be due to the formation of MnS, La₂O₂S and α -MnOS phase on the anode as reported by Zha et al [105].

Figure 2.17 Impedance spectra of single cells with LSCM + 20 wt% Cu composite anodes without and with 1.5 wt% Pd at 800°C in CH₄ under OCP [30]

Zhang et al synthesized a series of doped lanthanum manganese chromite based perovskite materials, La_{0.7}A_{0.3}Cr_{0.5}Mn_{0.5}O_{3- δ} (LACM; A=Ca, Sr, Ba), and compared the electrochemical activity of LACM/YSZ composite anode for hydrogen oxidation reaction.

Figure 2.18 shows the impedance spectra and polarization performance for the oxidation of wet hydrogen at 900°C. Electrode polarization resistance for LBCM/YSZ, LSCM/YSZ and LCCM/YSZ composite anode is 11.1, 2.1 and 1.4 $\Omega \text{ cm}^2$ respectively. The polarization test also shows better performance of LCCM/YSZ composite cathode as compared to LBCM/YSZ and LSCM/YSZ.

Figure 2.18 (a) Impedance spectra and (b) polarization curves of LCCM/YSZ, LSCM/YSZ and LBCM/YSZ composite anodes for hydrogen oxidation reaction in wet H_2 at 900°C. EIS spectra were measured under OCP [106]

Ye et al [107] investigated applicability of a Pd promoted LSCM/YSZ composite anode for direct utilization of methane in solid oxide fuel cells. LSCM based materials do not show appreciable catalytic activity for oxidation of methane, however when Pd is added to the anode microstructure it leads to considerable enhancement in catalytic

activity of the cell. They reported that the impedance responses for the oxidation reaction in wet hydrogen are not affected by presence of Pd catalysts. At 800°C, electrode polarization resistance for bare LSCM/YSZ anode was about $1.0 \Omega \text{ cm}^2$ and decreased slightly to $0.8 \Omega \text{ cm}^2$ after impregnation of palladium. For Pd loading more than 0.66 mg cm^2 the impedance starts to increase. In contrast to the negligible effect of Pd on the hydrogen oxidation reaction, the impedance arc for methane oxidation reaction decreased considerably by addition of Pd. For methane oxidation on a pure LSCM/YSZ anode, the R_E was $6.71 \Omega \text{ cm}^2$ at 800°C and decreased to $1.96 \Omega \text{ cm}^2$ with 0.1 mg cm^2 palladium loading, a 3 times reduction in electrode polarization resistance for the methane oxidation reaction. With further addition of palladium loading, the change in R_E was very small. As demonstrated in Figure 2.19, with the impregnation of Pd nano particles, the size of impedance arc is reduced significantly and the electrode impedance becomes separable with the increase of Pd loading. For the reaction on a 0.75 mg cm^{-2} Pd impregnated LSCM/YSZ composite anode, the impedance response were separated by three impedance arcs at low, medium and high frequencies, indicating that oxidation reaction in wet CH_4 is limited by at least three process. The reduction in the electrode impedance with Pd impregnation was found primarily on the low frequency arc.

Figure 2.19 Fitting results of impedance spectra measured under OCP at 800°C for the reaction in wet CH_4 on LSCM/YSZ composite anodes with respect to impregnated Pd loadings [107]

They concluded that the low frequency impedance arc is likely related to the non-charge and non-electrochemical reaction steps and suggest that wet methane oxidation reaction on the bare LSCM/YSZ anode is controlled by the oxygen surface exchange and diffusion process, which is limited by the high energetic process of oxygen vacancy diffusion in the perovskite structure LSCM. The high electrode polarization resistance for

the reaction in wet methane over the LSCM/YSZ composite anode might be related to the low concentration of hydrogen due to the relatively low catalytic activity of the anode for methane oxidation and steam reforming reactions. The results for polarization performance of wet hydrogen and methane on the composite LSCM/YSZ anode were consistent with the impedance result and showed that effect of Pd catalyst on hydrogen oxidation is relatively low as compared to significant promotion effect on the methane oxidation reaction. The cell was stable in methane fuel and no carbon deposition was detected on the anode surface.

Under solid oxide fuel cell operating condition, the possible reactions in wet methane can be considered as:

Because no carbon deposition was observed in their work, the reaction path in equation 2.5 cannot be the main reaction for methane oxidation. Oxidation of methane can be proceeding through one of the reactions 2.6, 2.7 and 2.8, followed by the electrochemical oxidation of H_2 and CO .

2.3.2. Anode materials for direct oxidation of hydrocarbons

2.3.2.1. Ni-containing cermets

Direct oxidation of hydrocarbons is strongly desired because of high efficiency in energy conversion and cost reduction in fuel transportation and storage [108, 109], however, the major problem for the direct oxidation of hydrocarbons over conventional Ni containing cermets is the carbon deposition [56, 110, 111]. Currently, there are remarkable interests in solid oxide fuel cells with non Ni-based anodes; on the other hand, because of unique catalytic activity and high electrical conductivity of Ni, it is desirable if the established solid oxide fuel cell technology based on Ni containing cermet anodes can be utilized. Operating the fuel cell at low operating temperature (below 700°C) or at high current density can reduce the carbon deposition problem. Scott Barnett et al [112] investigated the application of conventional Ni/YSZ anode for direct utilization of methane in solid oxide fuel cells. They prepared an anode supported fuel cell consisted of NiO/YSZ anode electrode support, a composite of LSCF/GDC cathode and a thin (10-20 μm) YSZ electrolyte layer. The results indicate that the cells at high current densities show a very stable performance. For each testing temperature, there exists a threshold current density above it the fuel cell operation is stable. This threshold increases as the operating temperature increase. Visual observation as well as SEM and EDS measurements showed no evidence of coke formation on the anode in the cases where the cell performance were stable. Carbon formation was detected either at high operating temperature or low current density. The thermodynamic prediction which supports the results and agrees with mass spectrometry results of the reaction products is shown in

Figure 2.20. The results were explained as follows: at low current densities, and hence low O₂-to-CH₄ ratio (χ) the reaction products are primarily solid carbon and hydrogen indicating methane cracking according to equation (2.9).

As χ increases up to 0.5, the main change is that the reaction product changes from solid carbon to carbon monoxide, which could be due to partial oxidation of methane (equation 2.10),

Finally, when χ increases above 0.5, CO and H₂ are increasingly replaced by CO₂ and H₂O until the reaction becomes complete oxidation at $\chi=2$ according to equation 2.11.

Comparing the above mentioned results at 800 and 700°C, the main difference is that the amounts of CO₂ and H₂O are generally larger at lower temperature. Mass spectrometer measurements of the reaction products showed a good agreement between thermodynamic analysis of the products.

Figure 2.20 Thermodynamic prediction of the equilibrium anode gas composition and fraction of CH_4 cracking to form C, assuming an input fuel composition of humidified (3% H_2O) CH_4 , versus the $\text{O}_2\text{:H}_2$ ratio, at (a) 700 and (b) 800°C [112]

2.3.2.2. Ni-free oxides

Some promising Ni-free anode materials such as doped ceria and lanthanum chromite based oxide materials were studied recently to solve the problems of carbon deposition in direct utilization of hydrocarbons [46-49]. These groups of anode materials exhibit high tolerance to carbon deposition [113-118]; however the electrochemical activity for hydrocarbon conversion is still low. CeO_2 based oxides exhibit mixed

electronic and ionic conductivity in a reducing atmosphere because of the reduction of Ce^{4+} to Ce^{3+} . In addition, it is believed that the good catalytic activity of cerium oxide based materials stemmed on the oxygen vacancy formation and migration associated with reversible $\text{CeO}_2 - \text{Ce}_2\text{O}_3$ transition. It has been reported that ceria based materials have a high resistance to carbon deposition, which permits direct exposure of dry hydrocarbon fuels to the anode, and the catalytic activity of the anode material for breaking the C-H bond of hydrocarbons can be enhanced by addition of Ni, Co or some noble metals such as Pt, Rh, Pd and Ru.

Ramirez et al [76] used the $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) material for the oxidation of methane. The activation energy for steam reforming over GDC was found approximately equal to that for reaction of GDC in dry methane and no carbon deposition was observed on GDC anode. Jiang and co workers [69] investigated the application of LSCM/YSZ composite anode as alternative anode for direct utilization of CH_4 in SOFCs. Electrochemical performance of pure LSCM composite anode was poor for methane oxidation and addition of YSZ phase considerably improved the adhesion and reduced the electrode polarization resistance of the anode. The composite anode showed relatively good performance for the wet methane oxidation reaction, and the best electrode performance was achieved for a weight ratio of 1:1 for LSCM and YSZ with polarization resistance of $2\text{--}3 \Omega \text{ cm}^2$ at 850°C . The activation energy for methane oxidation reaction was 160 kJ mol^{-1} . Chan et al [119] studied the performance of a 1:2 weight percent LSCM:GDC composite anode. Because GDC has a moderate reforming activity for the methane compare to YSZ, the LSCM/GDC composite anode showed higher OCV compare to LSCM/YSZ under methane fuel, although it is still much less than the

theoretical value and this shows that the LSCM/GDC composite anode has relatively poor activity toward methane oxidation. The anode performance in wet CH_4 at 850°C was quite stable under different current loading for an operating period of 50 h and no carbon deposition was found after exposure to methane for a long time. Barnett and Zhan reported that applying a catalyst layer of Ru-Ceria over the conventional anode increases the stability of the cell under iso-octane fuel without coking [120].

Wan et al [121] reported that performance of an $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ / Cu composite anode in methane fuel can be enhanced by sputtering a thin layer of Pt catalyst over the anode cermet surface. They compared the anode overpotential of an LSGM/LDC/LSCM+Cu composite anode without and with a thin sputtered layer of Pt on the surface of the anode at 800°C in hydrogen and methane environment. In dry methane, presence of Pt considerably decreased anode overpotential especially at higher range of current density as shown in Figure 2.21, while platinum sputtering had no effect on anode overpotential in hydrogen fuel.

Figure 2.21 Anode overpotentials of SCF/LSGM/LSCM based fuel cells without and with addition of Cu or Cu+Pt at 800°C using dry CH_4 as fuel [121]

2.4. Cathode

In order to facilitate the progress of the cathodic reaction (2-1), the cathode should possess some specific properties. Generally an ideal cathode material must have I) high electrochemical activity for oxygen reduction reaction, II) considerable electrical conductivity, III) appropriate thermal stability, IV) low mismatch and high compatibility with both electrolyte (YSZ, GDC, etc...) and interconnect materials and V) good micro-structural stability.

Among different candidates for cathode materials, platinum is one of the earliest choices which has moderate catalytic activity for oxygen reduction reaction. However platinum is a precious metal and is very expensive. Consequently, perovskite oxide-based materials are studied as a possible substitute for Pt electrode and among them Sr doped LaMnO_3 (LSM) shows the best performance for fuel cell applications. Good catalytic activity of LSM for oxygen reduction reaction as well as its relatively high electronic conductivity has made it the most attractive cathode material for SOFC. The electronic conductivity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ is reported to be between 40- 480 S cm^{-1} at 1000°C depending on the preparation methods, density and crystal structure [38]. It has been proved that the preparation history of the LSM powder has a significant effect on the properties of the cathode electrode. Ionic conductivity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ is $\sim 5.76 \times 10^{-6} \text{ S cm}^{-1}$ [122] and thermal expansion coefficient (TEC) is about $12.0 \times 10^{-6} \text{ K}^{-1}$ in the temperature range from 50 to 1000°C [123] which is close to that of YSZ in similar temperature range ($10.3 \times 10^{-6} \text{ K}^{-1}$) [124]. To achieve to an acceptable level of ionic conductivity in cathode electrode, the LSM phase is mixed with ionic conductive YSZ (or

GDC) powder. This helps better percolation of oxygen ions in cathode microstructure as well as lower mismatch between thermal expansion coefficient (TEC) of electrode and electrolyte. Altering the doping level of strontium can affect the TEC and also the electronic and ionic conductivity values.

There is a strong tendency for decreasing the working temperature of SOFCs from conventional temperature range of 800-1000°C to the intermediate temperature range of 600-800°C. Lowering the operating temperature reduces the cost of the SOFC stacks and accelerates commercialization of SOFC technologies. In the intermediate temperature range a wider range of materials can be used for the cell components, degradation of the components will be slower, the problem of Cr poisoning will be decreased sharply and the alternative interconnect materials can be employed as well. An inherent problem of the LSM material is that its overpotential increases dramatically with decreasing temperature [125]. The overpotential value for LSM electrode at 100 mA cm⁻² was reported equal to 41, 256 and 542 mV respectively at 900, 800 and 700°C by Jiang [126]. The sharp increase in overpotential indicates that pure LSM may not be the appropriate cathode material for intermediate temperature solid oxide fuel cells (IT-SOFCs). One of the reasons for such a dramatic increase in electrode polarization resistance is the low ionic activity of the LSM especially at low temperatures. To overcome this problem, mixing the LSM with an ionic conductive phase, like YSZ or GDC, is proven to be useful. Barnett et al. reported that addition of YSZ and GDC phase to LSM cathode decreases the interfacial resistance effectively at low operational temperatures. Figure 2.22 shows the interfacial resistance for pure and composite LSM/YSZ and LSM/GDC electrodes on

different electrolyte materials [127]. The data in the Figure reveal that mixing LSM with GDC causes 87% reductions in interfacial resistance from 51.03 to 0.49 $\Omega \text{ cm}^2$ at 600°C.

Figure 2.22 Summary of low-current polarization resistances of various LSM, LSM/YSZ and LSM-GDC cathodes at various temperatures. The numbers to the right of the respective bars are the resistance values given in $\Omega \text{ cm}^2$ [127]

Wet impregnation method is an alternative way for adding ionic conductive phase to the porous structure of SOFC electrodes. Jiang and Wang studied the structure and properties of the LSM cathode impregnated with different loading of $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_2$ [128] and reported significantly enhanced catalytic activity of the cathode electrode by introducing 5.8 mg cm^{-2} ionic conductive GDC nano particles. Lower loading of GDC causes reduction in interfacial resistance but the best results is achieved after GDC loading increased to 5.8 mg cm^{-2} as shown in Figure 2.23. Effect of cathodic current treatment is clearly mitigated by increasing GDC loading as can be seen in the Figure 2.23.

Figure 2.23 Impedance responses of (a) LSM electrode, (b) 0.8 mg cm^{-2} GDC-impregnated LSM electrode, and (c) 5.8 mg cm^{-2} GDC-impregnated LSM electrode as with respect to cathodic current treatment time at 200 mA cm^{-2} and 700°C in air [128]

2.4.1. Catalyst promoted cathodes

As discussed above, lowering the working temperature of the fuel cell stack has several benefits [129, 130]; however the cathode overpotential increases dramatically at lower temperatures. One effective way to enhance the activity and performance of

cathode is to introduce catalysts into the cathode microstructure. The idea of using catalyst in the microstructure of the electrodes to compensate the performance drop was first elaborated by Watanabe et al [96]. They reported considerable decrease in cathode overpotential by adding Pt catalyst to an LSM cathode. Figure 2.24 compares the overpotential of the pure and Pt added LSM catalyst at different temperatures and demonstrate that the change in overpotential as a result of catalyst addition is more pronounced at lower temperature.

Figure 2.24 Polarization curves for LSM cathodes with (●) and without (○) loading of 0.5 mg cm^{-2} Pt microcrystalline catalyst at (a) 1000, (b) 900 and (c) 800°C in oxygen atmosphere [96]

Cobalt infiltration was also reported to be effective for enhancing the performance of an LSM/SYSZ (Sc_2O_3)_{0.1}(Y_2O_3)_{0.01}(ZrO_2)_{0.89} cathode material as reported by

Yamahara et al [131]. They investigated influence of cobalt infiltration into an LSM/SYSZ support on the electrochemical characteristics by comparison of identically prepared cells with and without cobalt infiltration. The size of cobalt nano particles was estimated to be around 25 nm by TEM studies. Figure 2.25 shows the differences in the electrochemical characteristics of the cells with and without Co infiltration. Cobalt infiltration increased the peak power density by a factor of two. The dramatic improvement by Co infiltration is mainly due to the significant reduction in non-ohmic resistance.

Figure 2.25 Current–voltage and power density characteristics of co-fired LSM/SYSZ supported SOFCs with Co infiltration (solid lines) and without Co infiltration (dashed lines) at three different temperatures. Note that the catalyst infiltration significantly reduces the reaction overpotentials [131]

Imanishi et al [132] co-infiltrated a $\text{Co}_3\text{O}_4/\text{CeO}_2$ solution to the LSM/YSZ composite cathode and reported better performance and long term stability of the cathode as compared to both pure LSM/YSZ and LSM/YSZ infiltrated by single phase Co_3O_4 catalyst. Figure 2.26 shows current/overpotential curve for the LSM/YSZ cathode with and without Co_3O_4 at different temperatures. Over studied temperature range Co containing cell shows lower overpotential compare to pure LSM/YSZ cathode. Decrease in overpotential is more pronounced at lower temperature. They evaluated the performance of the cathode electrode for 100 h and observed that the cathode overpotential is increased with time. The degradation of the cell performance is most likely due to the loss of catalytic activity of the cobalt oxide phase resulting from sintering and agglomeration of nano sized cobalt oxide particles. Impregnating cerium oxide phase to the microstructure of the LSM/YSZ- Co_3O_4 cathode enhances the oxygen reduction catalytic activity. The best resistance against agglomeration was reported at the molar ratio of 0.8:1.2 for Co:Ce.

Figure 2.26 Overpotential versus current curves for oxygen reduction on LSM/YSZ electrodes with and without Co_3O_4 with respect to temperature. $\circ$: without Co_3O_4 at 600°C, $\square$: without Co_3O_4 at 700°C, Δ : without Co_3O_4 at 800°C, $\bullet$: with Co_3O_4 at 600°C, $\blacksquare$: with Co_3O_4 at 700°C, $\blacktriangle$: with Co_3O_4 at 800°C [132]

Wan et al reported that by applying a very thin layer of sputtered Pt for just five second on the surface of a perovskite $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF) cathode, a considerable 40% decrease in cathode overpotential was achieved [133]. The sputtered catalyst layer was in the shape of fine isolated particles and did not cover the surface of the electrode. Figure 2.27 shows a comparison of overpotential of an SCF cathode without and with Pt and Ag catalyst at 800°C. The results show that Ag catalyst gives a modest improvement, while Pt sputtering reduces the cathode overpotential by 40%. The reason for reduction in cathode overpotential was explained by the increased tendency of dissociative chemisorption of oxygen molecules as a result of presence of Pt phase.

Figure 2.27 Overpotentials at 800°C of an SCF cathode without and with Ag or Pt catalyst sputtering deposited on the electrode surface [133]

Liang et al [134] developed a novel nano-structured Pd added YSZ cathode electrode for intermediate temperature applications and reported high catalytic activity of Pd/YSZ composite cathode for oxygen reduction reaction. With the Pd loading of 1.4 mg cm^{-2} , the electrode polarization resistance for the oxygen reduction reaction on cathode electrode at 700°C is reported to be 0.22 $\Omega \text{ cm}^2$. The activation energy for the O_2

reduction on Pd/YSZ cathode was 105 kJ mol^{-1} , which is lower than $130\text{--}201 \text{ kJ mol}^{-1}$ for the cathodes such as LSM, LSM+YSZ, LSM+GDC and LSCF. This indicates that the nano-structured Pd+YSZ composite cathode is particularly suitable for IT-SOFC applications. Nano-structured Pd also has a significant enhancing effect on the oxygen reduction reaction of LSM based cathodes. Incorporation of Pd to the microstructure of the LSM/YSZ composite cathode yields electrode polarization resistance of $0.9 \text{ } \Omega \text{ cm}^2$ at 600°C , considerably lower than $70 \text{ } \Omega \text{ cm}^2$ for pure LSM/YSZ cathode at the same temperature as reported by Liang et al [135]. The maximum power density for a full cell consisting of a Ni/YSZ anode, a thin YSZ electrolyte and an LSM/YSZ cathode shows a dramatic increase by adding 0.6 mg cm^{-2} Pd to the cathode electrode. At 600°C a maximum power density of 1.42 W cm^{-2} was obtained on Pd added cell which is much higher than 0.2 W cm^{-2} for the cell without palladium [136]. Figure 2.28 illustrated a comparison between reaction sites (TPB) in four different type of microstructure of cathode electrodes [136]. High power output and low electrode polarization resistance of the cathode electrodes containing catalyst material can be explained clearly by this picture. In the Figure 2.28(a) where pure LSM is in contact with the electrolyte layer, the only site for oxygen reduction reaction is the contact points between LSM particles and the electrolyte at the interface. Mixed microstructure containing both LSM and YSZ particles increases the number of TPB by extending the reaction sites into bulk of the electrode and the average path required for the electrons to reach to the TPB is decreased. Figure 2.28(c) shows that if the electronic conductive phase is finely dispersed over the surface of the ionic conductive backbone, then the number of TPBs is increased substantially. In an improved configuration shown in Figure 2.28(d), the reaction sites are

dispersed all over the porous structure and the transfer of the electrons take place through both LSM particles in the mixed structure and connected network of the catalyst particles on the surface. This structure yields the least electrode polarization resistance and highest performance as compare to other structures.

Figure 2.28 Schematic illustrations of various cathode microstructures: (a) LSM; (b) conventionally mixed LSM-YSZ; (c) impregnated LSM + YSZ; and (d) Pd impregnated Pd + LSM-YSZ, showing the paths of transport for electrons and oxygen ions and reaction sites for O₂ reduction reactions [136]

2.4.2. Long time stability of catalyst agents

A problem for cells containing nano-sized catalysts at elevated temperature and long-time operation is the coarsening of the catalyst phase as a result of agglomeration of fine catalyst particles which leads to the overall performance drop in the cell [137, 138]. Figure 2.29 shows a stability test on a Pd/YSZ cathode as well as on a Mn stabilized Pd catalyst on YSZ backbone [139]. For the pure Pd catalyst, the cathode overpotential increases around 9%, after tested for 30h at 750°C under cathodic current passage of 200 mA cm⁻², while the overpotential for Mn alloyed Pd catalyst is not only stable, but also have lower overpotential under identical polarization condition. However, the activation energy for both pure Pd/YSZ and Mn stabilized Pd/YSZ composites are similar. By comparing the SEM pictures of both pure and Mn stabilized Pd on YSZ backbone after 30 h testing at high temperature, Liang et al. showed that presence of Mn inhibits grain growth of Pd phase and finer distribution of the catalyst particles is achieved. The results indicate that the reason for the performance drop is primarily due to the micro-structural change and consequently presence of Mn enhances the micro-structural stability.

Chen and co-workers [140] used palladium catalyst in the microstructure of a La_{0.8}Sr_{0.2}Co_{0.5}Fe_{0.5}O_{3-δ} (LSCF) cathode and reported a more than fifty percent reduction in the area specific resistance of the cathode. The electrode polarization resistance for the pure LSCF cathode was 0.22 Ω cm² at 750°C and reduced to 0.1 Ω cm² by adding 1.2 mg cm⁻² PdO to the cathode microstructure. Cathodic current treatment has almost negligible effect on the impedance response of the LSCF cathode at 700°C and 200 mA cm⁻². Pd containing LSCF cathode shows substantially smaller electrode polarization resistance at the beginning of the test, but the electrode polarization resistance was increased by

around 37% after 60 min cathodic current passage at 700°C. The reason for the increasing electrode polarization resistance was attributed to agglomeration of fine PdO particles which resulted in decreasing the TPBs.

Figure 2.29 Performance and stability of Pd + YSZ and Pd_{0.95}Mn_{0.05} + YSZ cathodes under a constant cathodic current of 200 mA cm⁻² for 30 h at 750°C in air [139]

Sholklapper et al [141] infiltrated silver catalyst into a pre-sintered backbone of scandia stabilized zirconia (SSZ) to make a composite cermet cathode. The SSZ backbone provides an ion conducting pathway throughout the electrode. Ag was selected as the second constituent for making the cermet electrode because it not only provides electronic conductivity for the cermet, but also has a special property for conducting the oxygen ion in its bulk. In the SSZ/Ag cermet, oxygen ion can diffuse through the silver bulk to the boundary between silver and the electrolyte where the oxygen reduction reaction will occur. Figure 2.30 shows SEM image of a cross-sectioned Ag infiltrated electrode before and after conditioning treatment in which spreading of the silver after

conditioning is clearly observable. The origin of this effect might be related to the electrochemical migration of Ag, but exact understanding of this phenomenon needs more clarification. The activation effect of Ag is somehow different from activation of LSM cathode materials. They also show that the Ag/LSM nano composite electrode has smaller cell impedance than either of its component.

Figure 2.30 SEM micrographs of a focused ion beam cross-sectioned Ag infiltrated electrode (a) as infiltrated and (b) after conditioning [141]

Figure 2.31 shows the impedance spectra for the cathode electrode made of silver, LSM and silver/LSM materials. The size of impedance arc is much smaller in the case of silver/LSM composite compared to that of Ag and LSM cathodes. Also Ag/LSM electrode shows higher power output and better long time stability.

Figure 2.31 Impedance spectra measured on Ag (■), LSM (●) and Ag-LSM (▲) infiltrated cathode electrodes at 700°C [141]

2.5. Summary

From one perspective, we may divide the materials for anode electrode application into two groups, which are Ni-containing and Ni-free materials. Addition of Catalyst to both groups shows a very significant improving effect. Catalyzing Ni-free materials is crucial because it improves the low activity of the electrode materials towards fuel cell reactions. Catalyzing Ni-containing anode electrodes not only improves the activity of the electrode, but also might be helpful for solving the problem of carbon deposition in direct utilization of hydrocarbons in SOFCs. The working temperature of any kind of electrode can be lowered by using catalyst materials, because in the presence of a catalytic agent, the desired catalytic activity from the electrode is achievable at a lower temperature. The stability of the catalyzed electrode systems has not been widely studied.

There is a strong desire to lower the working temperature of SOFCs below 800°C. Kinetic of the chemical and electrochemical reactions taking place at SOFC electrodes

decreases significantly as a result of lowering the working temperature of the cell. To compensate that performance reduction, adding catalyst phase into both anode and cathode of SOFCs is proved to be an effective method. Precious metals such as Ru, Rh, Pd, Pt, Ir, Ag, etc... are the most effective catalysts for SOFC anode electrodes even at a very low catalyst loading.

There are some disagreements in the literature on whether or not a catalytic agent has a positive effect on hydrogen oxidation similar to hydrocarbon oxidation. While almost all the reports indicate that precious metal catalysts are effective for hydrocarbon oxidation, some works indicate that hydrogen oxidation is not considerably affected by the presence of catalytic nano particles. The impedance studies show that presence of catalytic nano particles affects the low frequency segment of the impedance spectra, indicating that catalytic agent mainly influence the adsorption/dissociation/diffusion processes in fuel oxidation reactions.

It is noted that some precious metal catalysts are most effective when they are used on some particular substrates. This observation implies that the proper catalyst/substrate couple should be selected to maximize the catalytic activity. Pt and Pd are shown as very strong catalysts for both anode and cathode electrodes of solid oxide fuel cells. Co, Pd, Ag and Pt are also reported to be very effective in the performance enhancement for the O₂ reduction reaction on cathode; however cathode performance degrades with time. This performance drop is mostly attributed to the agglomeration of catalyst particles and micro-structural change in the cathode electrodes at elevated working temperatures. Alloying of catalyst materials has been shown to be effective to enhance the performance stability.

The improving effects of different type of catalyst on the electrochemical performances of anode and cathode electrodes were investigated by the researchers, but the mechanism of the performance enhancement of the catalyst nano particles is still not clearly understood. There is apparently a lack of detailed studies on the mechanisms of the electro-catalytic promotion of catalyst agents, particularly for the fuel oxidation reactions on both Ni-based and Ni-free anodes. In a number of studies the performance improvement is attributed to the increased number of triple phase boundary sites, but this conclusion cannot explain the specific catalytic properties of some precious metals like Pt and Pd. Thus, understanding of the enhancing mechanism of metallic catalysts is very important because by knowing the promoting mechanisms of the catalyst agents, the electrode materials can be manipulated in such a way that the desired catalytic properties could be obtained with significantly reduced precious metallic catalyst loading or by using materials with more reasonable price.

The objective of this PhD thesis is to investigate the mechanisms of performance improvement by metallic catalyst on the anode electrode of SOFC. The mechanistic study is required for both hydrogen and hydrocarbon fuels. For this purpose two categories of anode materials are selected, which are Ni/GDC composite materials and Ni-free LCCM/GDC composite materials. Palladium catalyst, which is a well known metallic catalyst, is selected as the catalyst in this study. Also, the performance enhancement of Pd catalyst on the cathode electrode of SOFC will be investigated to some extent.

CHAPTER THREE

3. Experimental procedures and characterization

3.1. Sample preparation

As the main purpose of this work is to investigate the effect of Pd impregnation on the reaction mechanisms and kinetics of the electrode reactions, in particular the anodic electrode, a half cell design with a three electrode arrangement on an electrolyte supported cell was selected in the present study. In the half cell design working electrode, either anode or cathode, is located on one side of the dense electrolyte substrate, while counter and reference electrodes is positioned on the other side. The material used as the counter and reference electrodes was platinum paste and the materials used for the working electrode were Ni/ $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) and $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LCCM)/GDC for the anode investigation and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) for the cathode study. Figure 3.1 shows a schematic diagram of the test cell configuration and electrical connection arrangement used. Pt paste was not used as the current collector; instead Au and Pt meshes in direct contact with the working electrode were used as the current collector to eliminate the possible interference of the Pt paste to the oxidation reaction of the fuel gases or reduction of oxygen. Similar Au and Pt meshes were used for the

distribution of electrical charges on the counter electrode and connecting the reference electrode to the circuit.

Figure 3.1 Schematic of a test cell arrangement [53]

Dense electrolyte substrates were prepared by mixing yttria stabilized zirconia (8 mole % Y_2O_3 - ZrO_2 , YSZ, Tosoh, Japan) powder with 2 wt % poly-vinyl-butylal (PVB) binder followed by roll milling the mixture in isopropanol media for 24 h. The slurry was then poured in a Petri dish and dried in an oven at 80°C overnight. The resultant powder was then die pressed by an unidirectional stainless steel die to make green pellets. The obtained green pellets were sintered at 1500°C for 4 h in air using a zirconia crucible. The YSZ discs obtained after sintering had a diameter of about 19 mm and a thickness of about 0.9 mm. In some experiments the electrolyte thickness was reduced to about 0.7 mm. The surfaces of the pellets were ground by sandpaper in order to increase the surface roughness of the electrolyte for better overlaying of the working and counter electrodes on the electrolyte.

Two groups of anode materials were used in this study, namely, a conventional Ni/GDC cermet anode and a Ni free ceramic LCCM/GDC composite anode. Gadolinium doped ceria powder ($\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$, GDC) with the specific surface area of $6.5 \text{ m}^2/\text{g}$ is purchased from Fuel Cell Materials Inc. (USA) and the Ni oxide was from J.T.Baker Inc (USA). Lanthanum calcium chromium manganite (LCCM) powder with the composition of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ was prepared by a glycine nitrate process. For this purpose a stoichiometric amount of hydrated nitrate salt of lanthanum, calcium, chromium and manganese (all from Sigma-Aldrich) was weighed and dissolved in distilled water with simultaneous addition of glycine ($\text{C}_2\text{H}_5\text{NO}_2$). The resultant solution was then boiled until the liquid phase was fully evaporated and the LCCM precursor was formed in a form of fine powder. The fine powder was then sequentially calcined at 800°C for 8 h and at 1200°C for 2 h, respectively. Formation of the LCCM perovskite structure was investigated by X-ray diffraction (XRD) technique. XRD pattern of the synthesized LCCM powder completely matched the corresponding reference data for the LCCM powder in database, indicating formation of the perovskite structure.

For preparation of the Ni/GDC anode electrodes, nickel oxide (NiO) powder was coarsened in a furnace at 700°C for 2 h in air and then mixed with $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) powder with a weight ratio of 65/35 for NiO and GDC powders. Graphite (5wt%) was added to the NiO and GDC mixture as the pore former and the mixture was then ball milled in isopropanol for 24 h. The resultant slurry was heated in an oven to obtain a dry powder mixture. For preparation of the final slurry, Ink Veh 500 (Fuel Cell Materials Inc.) was added to the powder mixture and the slurry was homogenized in a mortar before overlaying to the electrolyte substrate. The surface of the YSZ electrolyte was cleaned

with alcohol and the prepared ink was applied to the YSZ pellets by slurry painting method. The overlaid layer was in the form of a circle in the center of the electrolyte disc with the surface area of 0.5 cm^2 . The painted electrode was sintered in the furnace at 1400°C for 2 h in air. Figure 3.2 shows a SEM micrograph of a Ni/GDC anode sintered at 1400°C for 2 h showing the porous structure of the electrode with appropriate connection between the particles.

Figure 3.2 SEM micrograph of a Ni/GDC anode sintered at 1400°C for 2 h

Nickel oxide in the anode electrode was reduced in situ to metallic nickel in hydrogen stream before commencement of the test. Preparation of the LCCM/GDC composite ceramic anode was quite similar to the above mentioned process for Ni/GDC cermet. Calcined LCCM powder was mixed with GDC powder with the weight ratio of 50/50. Graphite (5 wt %) was added to the powder mixture to increase porosity. Ink Veh was added to the powder mixture to make the slurry and overlaying of the anode electrode was done by similar slurry painting method. The ideal sintering temperature of

the LCCM/GDC anode electrode was investigated in the temperature range of 1150 to 1350°C with the temperature interval of 50°C. Sintering time was 2h.

For investigation on the cathode electrode, pure $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) powder (surface area $5.78 \text{ m}^2 \text{ g}^{-1}$) from Fuel Cell Materials Inc. was mixed with 5 wt. % graphite and roll milled for better distribution of pore former between LSM particles. The process of slurry preparation and overlaying on the electrolyte was similar to those for the anode. LSM cathode was sintered at 1100°C for 2h in air. Thickness of the working electrode was $\sim 30\text{-}40 \text{ }\mu\text{m}$ after sintering for all types of electrode materials.

Pt paste from Metalor Company (Swiss) was used as the counter and reference electrodes. Counter electrode was painted with a fine brush opposite to the working electrode with the same shape and size as the working electrode and the reference electrode was painted as a ring around counter electrode on the circumference of the electrolyte discs. The gap between counter and reference electrodes was 4 mm. The painted Pt electrode was baked in the furnace at 850°C for 15 min.

Addition of palladium nano particles to the microstructure of anode or cathode was carried out by impregnation method. Palladium nitrate solution ($\text{Pd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Alfa Aesar) with concentration of 0.05, 0.1 and 0.2 mole was used for impregnation of Pd catalyst. A droplet of palladium nitrate solution was placed on the surface of the working electrode and the solution infiltrated into the porous structure by capillary force. Excess solution was then wiped out from the surface of the electrode by using a soft tissue, followed by calcinations of the electrodes at 700°C for 30 min. The impregnated PdO loading was obtained by measuring the weight of the cell before and after impregnation treatment. One impregnation of the porous electrode with a 0.2 mole solution yields a

PdO loading of ~ 0.07 - 0.08 mg cm^{-2} . Lower loading was achieved by using lower concentration solutions and higher loading was obtained by repeating the impregnation sequence. Ni/GDC electrodes with PdO loading of 0.04, 0.07, 0.11 and 0.15 mg cm^{-2} were selected for the electrochemical testing. In the case of LCCM/GDC anodes, samples with PdO loading of 0.02 and 0.06 mg cm^{-2} were selected. Nevertheless, it should be pointed here that under fuel oxidation conditions, impregnated palladium would most likely exist as metallic palladium. The use of PdO loading is for the convenience of measurement of the impregnated Pd loading. In the investigation of LSM cathode electrode the main objective was study of the stability of Pd and Pd based catalysts, thus, for this purpose $\text{Pd}(\text{NO})_3$ and $\text{Pd}_{1-x}\text{M}_x(\text{NO}_3)_y$ ($\text{M} = \text{Co}, \text{Mn}$ and Ag ; $x = 5\%$ and 20%) impregnation solution were prepared from $\text{Pd}(\text{NO})_3$, $\text{Co}(\text{NO}_3)_2 \cdot$, AgNO_3 and $\text{Mn}(\text{NO}_3)_2 \cdot$ nitride solutions (all from Alfa Aesar) and infiltrated into the microstructure of LSM cathode. Samples with 0.08 and 0.25 mg cm^{-2} catalyst loading were tested to investigate the effect of catalyst loading on the performance and stability of the catalysts.

Humidified hydrogen ($97\% \text{H}_2/3\% \text{H}_2\text{O}$) and methane ($97\% \text{CH}_4/3\% \text{H}_2\text{O}$) were used as the fuel gas with the flow rate of 80 mL min^{-1} over the anode electrode. In the case of methanol and ethanol fuels, nitrogen-saturated methanol and ethanol by passing nitrogen through pure methanol and ethanol at 60 and 70°C , respectively, was also used as the fuel gas. In the case of methanol and ethanol fuels, the alcohol content in nitrogen was $\sim 17 \text{ vol\%}$. During cathode electrode studies the working electrode was left in open air. In all the experiments the counter and reference electrodes were exposed to open air.

3.2. Characterization

Electrochemical activity and performance of anode and cathode electrodes were characterized by using a couple of electrochemical measurement techniques including electrochemical impedance spectroscopy (EIS), linear sweep voltammetry, chrono amperometry and chrono potentiometry using an Autolab data analyzer (PGSTAT302).

3.2.1. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a very powerful technique for characterizing many electrical properties of materials and their interfaces with electronically conducting electrodes. It might be used to investigate the dynamics of the bound or mobile charges at the interface of any type of liquid or solid materials including ionic, mixed ionic-electronic, semiconducting and even insulating materials [142]. AC impedance spectroscopy is extensively used in the field of electrochemistry and solid state ionics to differentiate interfacial and bulk contributions from the alternating-current response of a material. In AC impedance spectroscopy, an alternating voltage or current with a defined frequency is applied to the interface and the phase shift and amplitude of the resulting current are measured at the defined frequency. Then the impedance is evaluated as a function of alternating current frequency using either analogue circuit or fast Fourier transform (FFT) analysis of the response. This measurement is performed for a set of individual frequencies. A useful style for presenting the impedance data is the complex impedance diagram (Cole-Cole or Nyquist plot). In this type of plot the imaginary part of the impedance (Z'' , capacitance) is plotted versus the real part of the impedance (Z' , resistance). Experimentally obtained impedance data for a given electrode-materials system can be analyzed by using an exact mathematical model based

on a plausible physical theory that predicts theoretical impedance $Z_t(\omega)$ or by a relatively empirical equivalent circuit whose impedance predictions might be denoted by $Z_{ec}(\omega)$. In either cases the parameters can be estimated and the experimental $Z_e(\omega)$ data compared and fitted to either the predicted equivalent circuit impedance $Z_{ec}(\omega)$ or to the theoretical impedance $Z_t(\omega)$. An analysis of the charge transport processes will often suggest an equivalent circuit of ideal resistors and capacitors. (RC circuits). Figure 3.3 shows a schematic presentation of an equivalent circuit (Figure 3.3a) which is used for fitting the experimental data on Figure 3.3b. Analysis of the experimental data, such as that in Figure 3.3, can provide an estimate of the parameters R and C. If more than one semicircle is observed in the impedance spectra, then more parameters will be added to the equivalent circuit [142].

Figure 3.3 Schematic of an equivalent circuit (a) consisting of a pure capacitor and a pure resistor used for fitting the experimental impedance spectra in (b)

In this work, the EIS measurements were generally performed in the frequency range of 10 mHz to 100 kHz with an amplitude of 10 mV. The impedance data were collected at the open circuit potential as well as under different applied potentials up to 0.25 V. Varying of applied potential may help to understand the chemical or electrochemical nature of a particular reaction. In an EIS experiment, the ohmic resistance of the cell was directly measured from a high frequency intercept at the real

impedance axis of the Nyquist plot and the electrode polarization resistance or area specific resistance (ASR) was calculated from the difference of the high and low frequency intercepts at the same axis.

3.2.2. DC polarization

DC polarization techniques were used to characterize the power generating ability of a SOFC under current loading. Current/voltage (I-V) performances were evaluated with linear sweep and chrono amperometry or potentiometry methods. Linear sweep voltammetry was performed by gradually sweeping the potential in a range starting from OCP to a specified potential and then measuring the corresponding current density within that potential range. The step potential and scan rate were 0.005 V and the 0.02 V/s, respectively. Chrono amperometry method was based on applying a fixed overpotential to the cell and measuring the corresponding current density over the time. In contrast, chrono potentiometry was performed by drawing a particular current density from the cell and measuring the induced overpotential in the cell in a defined time domain. All the electrochemical measurements except EIS might be referred to as polarization test in this context. The electrochemical measurements were carried out over a temperature range of 650-900°C.

3.2.3. Other characterization techniques

The surfaces and cross-sections of the working electrodes were inspected using a JEOL 5600LV scanning electron microscope (SEM) and a JEOL 6340F field emission scanning electron microscope (FESEM). The chemical composition of the electrodes was

examined by energy dispersive spectrometer (EDS) equipped on the SEM used. X-Ray photoelectron spectroscopy (XPS) measurements of the Pd impregnated Ni/GDC cermet anodes, before and after reduction in hydrogen at 700°C for 1 hr, were conducted using a Kratos AXIS Ultra spectrometer at room temperature with the Pd 3d spectra being recorded using an Al K α X-ray source. X-ray diffraction (XRD) measurements were performed using a PW 1830 Philips diffractometer.

CHAPTER FOUR

4. Hydrogen oxidation on Pd promoted Ni/GDC anode

In this chapter the results of electrochemical evaluation of hydrogen oxidation reaction on the palladium impregnated Ni/GDC anode electrode are presented and compared with those measured on the anode electrode without Pd catalyst. These measurements were carried out at open circuit potential as well as under applied anode potential to investigate chemical or electrochemical nature of the reaction. Study of the impedance spectra of the anode electrode reveals a considerable decrease in electrode polarization resistance of the anode electrode as a result of introduction of the Pd catalyst. The incorporation of the Pd catalyst in the electrochemical oxidation reaction of the hydrogen mainly decreases the resistance against adsorption/dissociation/diffusion of the fuel molecules. The presence of palladium catalyst in the form of nano particles in the structure of cermet anode is studied by SEM and EDS. The chemical states of Pd particles before and after reduction in the hydrogen gas were studied by XPS and the possible role of Pd and PdO particles on the improvement of hydrogen oxidation reaction is discussed.

4.1. Experimental

Dense YSZ electrolytes with the diameter and thickness of about 19 and 0.9 mm, respectively, were used for the cell preparation purpose. The electrolytes were sintered at 1500°C. Ni and GDC powders with a weight ratio of 65 to 35, respectively, were used for the preparation of Ni/GDC electrodes and the resultant cermet was sintered at 1400°C for 2h. Pt paste was used to prepare the counter and reference electrode. A palladium nitrate solution was used for the impregnation of the Pd catalyst into the Ni/GDC electrodes. The impregnation treatment was repeated to increase the loading of the Pd nano particles. The Ni/GDC electrodes with the PdO loadings of 0.04, 0.07, 0.11 and 0.15 mg cm⁻² were selected for the electrochemical measurements. The EIS experiments were performed in the frequency range of 0.1 Hz to 0.1 MHz. The electrochemical measurements were performed in the temperature range of 650 to 900°C. Humidified hydrogen (97% H₂/3% H₂O) was used as the fuel gas with a flow rate of 80 mL min⁻¹. FESEM and XPS were used to characterize the surface morphology, bonding structure and chemical composition of the electrodes.

4.2. Hydrogen oxidation reaction on Pd-Ni/GDC anodes

Figures 4.1 and 4.2 show the impedance curves for the hydrogen oxidation reaction on the Ni/GDC cermet anodes as a function of impregnated Pd loading in the wet hydrogen at different temperatures. For the oxidation reaction of hydrogen on the pure Ni/GDC anode, the impedance responses are characterized by a large impedance arc with no clear separation in the impedance frequency range studied. At 850°C the electrode polarization (interfacial) resistance, R_E , is 0.59 Ωcm^2 for the reaction on the pure Ni/GDC

anode. The impedance arc for the hydrogen oxidation reaction on Ni/GDC anodes decreases with presence of impregnated Pd nano particles, indicating significant effect of the impregnated Pd on the hydrogen oxidation reaction. In the case of the 0.11 mg cm^{-2} Pd added Ni/GDC, electrode polarization resistance (R_E) is $0.17 \text{ } \Omega\text{cm}^2$ at 850°C (Figure 4.1 a), less than 30% of the R_E value ($0.59 \text{ } \Omega\text{cm}^2$) for the reaction on a Ni/GDC anode without Pd impregnation. Most interestingly, the impedance responses of the reaction on Pd impregnated Ni/GDC anodes become clearly separated at low and high frequencies. The appearance of the impedance arcs at low and high frequencies indicates that the hydrogen oxidation reaction on Pd-impregnated Ni/GDC anodes is controlled by at least two electrode processes, similar to that observed for the reaction on Ni/YSZ and Ni/GDC cermet anodes by others [55-57]. The reduction and separation of the electrode process indicate that the impregnated palladium promotes the electrode processes and the promotion effect is also preferential towards particular one of the processes taking place in the anode. At lower temperatures, the decreasing trend of electrode polarization resistance with increasing the loading of Pd catalyst is observable similar to the case for the one at higher temperature, but the separation of the arcs is not as clear as it is at higher temperature of 850°C .

Figure 4.1 Impedance spectra for hydrogen oxidation reactions on Pd-impregnated Ni/GDC cermet anodes as a function of impregnated PdO loading in 97% H_2 /3% H_2O at (a) 850 and (b) 800°C. The numbers are frequencies in Hz

Figure 4.2 Impedance spectra for hydrogen oxidation reactions on Pd-impregnated Ni/GDC cermet anodes as a function of impregnated PdO loading in 97% H_2 /3% H_2O at (a) 700 and (b) 650°C. The numbers are frequencies in Hz

Figure 4.3 shows the impedance responses for the oxidation reaction on a 0.11 mg cm^{-2} Pd-Ni/GDC cermet anode in wet hydrogen at different temperatures. In the Figure 4.3 symbols are the experimental data and lines are the fitted results according to an equivalent circuit as shown in Figure 4.3. In the equivalent circuit, R_H and R_L are the electrode polarization resistances at high and low frequency arcs, Q_H and Q_L are the capacitance elements at high and low frequency arcs. R_H' and Q_H' are the electrode polarization resistance and capacitance element at extra high frequency arc which only occurs at low temperatures. The fitting between the experimental result and the calculated one is reasonable, indicating the applicability of the applied equivalent circuit. The impedance responses for the reaction on a 0.11 mg cm^{-2} Pd impregnated Ni/GDC anode are generally characterized by two impedance arcs at high and low frequencies. At 900°C , the electrode polarization resistance for the electrode processes at high and low frequencies (R_H and R_L) is 0.086 and $0.079 \text{ }\Omega\text{cm}^2$ and R_H/R_L ratio is 1.1 , close to unit. The similar magnitude in R_H and R_L indicates that the hydrogen oxidation reaction is almost equally controlled by the electrode processes associated with the high and low frequencies.

Figure 4.3 Impedance spectra for hydrogen oxidation reactions on (a) 0.11 mg cm^{-2} Pd-Ni/GDC and (b) 0.15 mg cm^{-2} Pd-Ni/GDC cermet anodes measured in $97\% \text{H}_2/3\% \text{H}_2\text{O}$ at different temperatures. Symbols are the experimental data and lines are the fitted data. The equivalent circuit used for curve fitting is shown in (a), and the numbers are frequencies in Hz

By decreasing the temperature, the high frequency arc becomes more and more dominant (Figure 4.3) and at 700°C, the low frequency arc almost completely disappears and the reaction is limited by the electrode process associated with the high frequency arc. Further reduction in the temperature to 650°C leads to the appearance of an impedance arc at extra high frequencies (R_H' and Q_H'). R_H' and Q_H' were added to the equivalent circuit to represent impedance arc at extra high frequencies, as shown under dashed line in Figure 4.3a. The appearance of the additional frequency arc at high frequencies is probably related to the oxygen ion conduction related to the electrolyte material. Similar results were also found for the reaction on the Pd impregnated Ni/GDC anodes with different Pd loadings. Table 4.1 shows the evaluated impedance parameters of individual electrode processes of the hydrogen oxidation on the Ni/GDC anodes with different loading of palladium over the temperature range of 650-900°C. At lower temperatures the low frequency arc is negligible and could not be measured. Data in the brackets show the contribution of the electrode resistance of individual reaction steps to the sum of all electrode polarization resistances. In the case of a 0.11 mg cm^{-2} Pd-Ni/GDC, at 900°C, the electrode resistance related to low frequency arc is ~48% of the total electrode polarization resistance. By decreasing the temperature to 750°C about 25% of the total electrode resistance is from the low frequency arc and the rest belongs to the electrode process associated with the high frequency arc. The impedance responses for the hydrogen oxidation reaction on other Pd impregnated Ni/GDC anodes were also evaluated using the equivalent circuit shown in Figure 4.3a.

Table 4.1. Impedance data calculated from the curve fitting of the impedance spectra for the hydrogen oxidation reactions on (a) Ni/GDC, (b) 0.04 mg cm⁻² Pd-Ni/GDC, (c) 0.07 mg cm⁻² Pd-Ni/GDC (d) 0.11 mg cm⁻² Pd-Ni/GDC and (e) 0.15 mg cm⁻² Pd-Ni/GDC in wet hydrogen. The data in the brackets are the ratios of R_i to $R_{H^+}+R_H+R_L$ at the respective temperatures

(a) Ni/GDC				
T (°C)	R_{H^+} (%)	R_H (%)	R_L (%)	R_E
850	-	0.538 (62%)	0.33 (38%)	0.586
800	-	0.631 (53%)	0.554 (47%)	0.749
700	-	2.22 (49%)	2.33 (51%)	2.570
650	-	5.380 (100%)	-	5.380

(b) 0.04 mg cm⁻² Pd-Ni/GDC				
T (°C)	R_{H^+} (%)	R_H (%)	R_L (%)	R_E
850	-	0.315 (66%)	0.16 (34%)	0.411
800	0.109 (14%)	0.461 (60%)	0.195 (25%)	0.642
750	0.048 (4%)	0.858 (67%)	0.378 (29%)	0.930
700	0.032 (2%)	1.46 (98%)	-	1.450
650	-	2.73 (100%)	-	2.730

(c) 0.07 mg cm⁻² Pd-Ni/GDC				
T (°C)	R_{H^+} (%)	R_H (%)	R_L (%)	R_E
900	-	0.127 (62%)	0.0787 (38%)	0.181
850	-	0.161 (66%)	0.0833 (34%)	0.208
800	-	0.202 (60%)	0.136 (40%)	0.254
750	-	0.492 (100%)	-	0.490
700	-	0.766 (100%)	-	0.760
650	-	1.59 (100%)	-	1.590

(d) 0.11 mg cm⁻² Pd-Ni/GDC				
T (°C)	R_{H^+} (%)	R_H (%)	R_L (%)	R_E
900	-	0.086 (52%)	0.079 (48%)	0.150
850	-	0.110 (57%)	0.082 (43%)	0.173
800	-	0.193 (66%)	0.098 (34%)	0.248
750	-	0.322 (75%)	0.109 (25%)	0.348
700	-	0.551 (100%)	-	0.551
650	0.54 (33%)	1.120 (67%)	-	1.390

	(e) 0.15 mg cm⁻² Pd-Ni/GDC			
T (°C)	R _H (%)	R _H (%)	R _L (%)	R _E
950	-	0.106 (58%)	0.078 (42%)	0.168
900	-	0.1 (56%)	0.079 (44%)	0.158
850	-	0.141 (64%)	0.08 (36%)	0.198
800	-	0.199 (71%)	0.083 (29%)	0.254
750	-	0.502 (100%)	-	0.531
700	0.225 (21%)	0.848 (79%)	-	0.880
650	0.883 (38%)	1.461(62%)		1.670

Figure 4.4 shows the activation plots of the electrode polarization resistance associated with the low and high frequency arcs for the reaction on the Pd-impregnated Ni/GDC electrodes. Activation energy of the individual electrode polarization resistance of the oxidation reaction was calculated from the slope of the Arrhenius plots. The results are summarized in Table 4.2. For the hydrogen oxidation reaction on the pure Ni/GDC cermet anode, the activation energy values are 98.5 and 119.5 kJmol⁻¹ for the electrode process at high and low frequencies, respectively. With the impregnation of palladium, the Arrhenius plots of the R_H are shifted in parallel and the activation energy of the electrode process associated with the high frequency arc is in the range of 91.3 – 94.5 kJmol⁻¹ and does not change significantly with the Pd loading (Figure 4.4a). This indicates that impregnation of Pd phase does not change the electrode process associated with the high frequency arc.

Figure 4.4. Arrhenius plots of electrode processes corresponding to (a) R_H , (b) R_L and (c) R_E for hydrogen oxidation reactions in 97% H_2 /3% H_2O . The values in the legends are the loadings of impregnated PdO in Pd-Ni/GDC cermet anodes

Table 4.2. Activation energies for hydrogen oxidation reaction (R_E), high frequency arc process (R_H) and low frequency arc process (R_L) of Pd-Ni/GDC samples

Sample	Activation Energy (kJ.mol^{-1})		
	R_E	R_H	R_L
Ni/GDC	98.3	98.5	119.5
0.04 mg cm^{-2} Pd -Ni/GDC	79.6	94.5	82.8
0.07 mg cm^{-2} Pd -Ni/GDC	80.2	94.5	57.9
0.11 mg cm^{-2} Pd -Ni/GDC	78.2	94.1	22.9
0.15 mg cm^{-2} Pd -Ni/GDC	77.5	91.3	4.4

On the other hand, the slopes of the Arrhenius plots of the R_L gradually decrease with the impregnated Pd loading (Figure 4.4b). This indicates that the activation energy for the electrode process associated with low frequencies decreases with the impregnated Pd loading. For the reaction on a Ni/GDC anode with the PdO loading 0.04 mg cm^{-2} , activation energy of R_L is 82.8 kJ mol^{-1} and it decreases to 22.9 kJ mol^{-1} when the PdO loading increases to 0.11 mg cm^{-2} . With further increase of PdO loading to 0.15 mg cm^{-2} , the activation energy for the electrode process at low frequency arc is 4.4 kJ mol^{-1} , 27 times smaller than that on the Ni/GDC cermet anode without the impregnated Pd nano particles for the same electrode process. The impedance results clearly indicate that the impregnation of Pd nano particles to the Ni/GDC anode significantly reduces the activation energy for the electrode process associated with low frequencies, resulting in the overall reduction in the activation energy for the hydrogen oxidation reaction on Pd-impregnated Ni/GDC cermet anodes, as shown in Figure 4.4c.

Figure 4.5 shows the plots of the activation energy of R_H and R_L as a function of Pd loading. Activation of R_L decreases almost linearly with the increasing of Pd loading, while the activation energy value for R_H remains constant within the range of

impregnated Pd loading studied. Therefore the main contribution of the addition of palladium phase to the Ni/GDC anode can be considered to facilitate the electrode process associated with low frequency arc. According to Table 4.2, the decrease in the activation energy for the overall electrode polarization resistance (R_E) is relatively small. The activation energy for the reaction on a Ni/GDC cermet anode with 0.15 mg cm^{-2} PdO loading is 77.5 kJmol^{-1} , ~20% smaller than 98.3 kJmol^{-1} measured for the reaction on the pure Ni/GDC anode. This indicates that the hydrogen oxidation reaction on Ni/GDC cermet anodes with and without Pd would be primarily dominated by the electrode process associated with high frequency arc.

Figure 4.5 Activation energies corresponding to high frequency arc resistance (R_H) and low frequency arc resistance (R_L) with respect to impregnated PdO loading for hydrogen oxidation reactions on Pd-impregnated Ni/GDC cermet anodes

4.3. Hydrogen oxidation reaction under dc bias

Figure 4.6 shows the impedance spectra for hydrogen oxidation reaction on Ni/GDC and Pd-Ni/GDC cermet anodes at 850°C under different applied potential, from zero up to 0.15 V. Applied potential zero means open circuit potential (OCP= - 1.09 V) and applied potential 0.1 means that the potential of the anode with respect to the reference electrode is - 0.99 V. Anode potential is the sum of the anode overpotential and iR loss of the anode. As the purpose is to study the effect of dc bias on the electrode behavior under more or less identical conditions, anode potential rather anode overpotential was used in this study for the purpose of simplicity. In the impedance graphs of Figure 4.6 symbols are the measured data and the lines are fitted one. Figure 4.6(e) shows the equivalent circuit used for curve fitting of the impedance spectra. According to Figure 4.6(a), the anode impedance spectrum for Ni/GDC anode at open circuit potential is apparently one single arc with the electrode polarization resistance of $0.58 \Omega \text{ cm}^2$. Infiltration of palladium catalyst to the microstructure of the Ni/GDC anode decreases the ASR to $0.282 \Omega \text{ cm}^2$ and at the same time splits the impedance arc into two different semicircles located at high and low frequencies, similar to the results reported in section 4.1 and reported in the literature [52, 143]. By applying an anode potential, the size of the anode impedance arc for the both Ni/GDC and Pd-Ni/GDC anodes becomes smaller.

Figure 4.6 Impedance spectra for hydrogen oxidation reactions over Ni/GDC and Pd-Ni/GDC anodes at (a) OCP and applied anode potentials (b) 0.05, (c) 0.10 and (d) 0.15 V at 850°C. (e) shows the equivalent circuit used for curve fitting of the spectra. The numbers are frequencies in

Hz

The effect of anode potential on the low and high frequency semicircles of the hydrogen oxidation impedance spectra is demonstrated in Figure 4.6. According to the curve fitting results, the magnitude of electrode polarization resistance for the high frequency arc is decreased from about $0.198 \Omega \text{ cm}^2$ at OCP to about 0.168, 0.108 and $0.095 \Omega \text{ cm}^2$ as a result of applying 0.05, 0.1 and 0.15 V anode potentials, respectively. Figure 4.7 shows the plot of electrode polarization resistance at high and low frequencies as a function of dc bias (anode potential) which is derived from the fitted curves in Figure 4.6. As can be seen in the Figure 4.7, both high and low frequency arcs of the impedance arc show a decreasing trend in size and magnitude by increasing dc bias. The ohmic resistance of the cell also shows a decreasing trend with increasing anode potential.

Figure 4.7 Electrode polarization resistances at high and low frequencies (R_H & R_L) and ohmic resistance (R_Ω) as a function of anode potential for hydrogen oxidation reactions on a Pd-promoted Ni/GDC anode at 850°C

The electrode polarization resistance for the high frequency arc at 0.15 V is 52 % less than that measured at the OCP. It is believed that the high frequency arc in the impedance spectra is representing the charge transfer step of the reaction [143], and in principle the charge transfer reaction is more facile under polarization condition. The electrode

polarization resistance of the reaction which occurs in the low frequency portion of the impedance spectra also shows a similar decreasing trend with anode potential. By applying the above mentioned anode potential steps, the low frequency ASR decreases from about $0.152 \Omega \text{ cm}^2$ at OCP to about 0.125, 0.109 and $0.075 \Omega \text{ cm}^2$, respectively. Total decrease in the polarization resistance of low frequency arc is 51 % at 0.15 V, relative to that at the OCP. These data show that both steps of the hydrogen oxidation reaction on a Pd-Ni/GDC electrode at high and low frequencies are sensitive to applied potential with a similar degree of magnitude. Adsorption of hydrogen on the surface of group XIII of transition metals is a very facile process which occurs easily especially at elevated temperature. The fact that the reaction at low frequencies (adsorption, dissociation and diffusion) is facilitated by applying potential implies that after the initial adsorption of H_2 molecules on the surface of anode electrode, the molecules dissociate into H^+ species which later diffuse toward the triple phase boundary (TPB) sites. Then the H^+ species combine with oxygen ions and form the final product of the reaction, which is water. The dissociation and diffusion are probably the processes that are reinforced by applied anode potential. In order to estimate the share of each step of hydrogen oxidation reaction over a Ni/GDC anode electrode, four different impedance spectra are compared together in Figure 4.8 and the related ASR data are compared in table 4.3. In this Figure curves 1 and 2 are anode impedance for pure and Pd impregnated Ni/GDC anodes, respectively. The size of curve 2 is much smaller than that of curve 1 clearly due to the presence of palladium catalyst in Ni/GDC anode. The charge transfer resistance retained its original value at this stage because according to the results in section 4.1, the presence of the Pd catalyst does not affect the activation energy for

charge transfer reaction at high frequencies. The charge transfer resistance is even thought to be relatively independent of anode materials [53]. Curve 3 shows impedance spectra for a Pd-Ni/GDC anode electrode under 0.05 V anode potential. Subsequent decrease in ASR from curve 2 to curve 3 is shared almost equally by two electrode processes at high and low frequencies and the net reduction in charge transfer resistance from curve 2 to 3 is only $0.1 \Omega \text{ cm}^2$ according to the measurements of fitted results. Thus the majority of decrease in the size of impedance arc from curve 1 to curve 3 has obtained by assisting the anode electrode for better reception of hydrogen species in the triple phase boundary sites. Curve 4 also shows the impedance response of a Ni/GDC anode electrode under anode potential which is consisted of two semicircles however they are not distinguishable at this stage. Finally, from Figure 4.8 a conclusion can be drawn that the impedance response for the reaction on pure Ni/GDC anode is mainly dominated by the adsorption, dissociation and diffusion processes of hydrogen species.

Figure 4.8 Impedance spectra for hydrogen oxidation reactions at 850°C for Ni/GDC anode at (I) OCP and (IV) 0.15 V applied anode potential, and Pd-Ni/GDC anode at (II) OCP and (III) 0.15 V applied anode potential

Table 4.3 Area specific resistance (ASR) for pure and 0.08 mg cm⁻² Pd impregnated Ni/GDC anodes at OCP and under applied anode potential of 0.15 V

Ni/ GDC anode	ASR / Ωcm^2		Reduction%
	OCP	v = 0.15	
Pure	0.56	0.34	39
0.08 Pd	0.26	0.12	54
Reduction%	54	65	

4.4. Microstructure and redox behavior of Pd-impregnated Ni/GDC anodes

Figure 4.9 shows the SEM micrographs of Pd-impregnated Ni/GDC anodes after tested in hydrogen. The particle size of Ni/GDC cermet anodes is in the range of 0.5 – 1 μm . Figure 4.9a shows the microstructure of a Ni/GDC cermet anode with Pd loading 0.07 mg cm⁻² just after reduction in hydrogen but before testing. The average Pd particle size is 20-30 nm and the distribution seems concentrated on the surface of nickel grains. After exposure to high temperature (650-900°C) for about 8 hrs the Pd particles has became significantly larger as a result of agglomeration and particles with different size up to 100 nm are detected (Figure 4.9b). In the sample with higher amount of impregnated palladium (PdO loading 0.15 mg cm⁻²), the Pd particles form a continuous network on the surface of composite anode and cover the whole surface area of the anode microstructure as demonstrated in Figures. 4.9 c and d.

Figure 4.9. SEM micrographs of Pd impregnated Ni/GDC anodes. (a) 0.07 mg cm^{-2} Pd-Ni/GDC after reduction in hydrogen and before testing, (b) 0.07 mg cm^{-2} Pd -Ni/GDC after testing, (c) and (d) 0.15 mg cm^{-2} Pd -Ni/GDC after testing showing the formation of almost continuous network of Pd particles

Pd 3d spectra for the Pd impregnated Ni/GDC anode before and after hydrogen reduction treatment are shown in Figure 4.10 together with their deconvolution. The XPS characteristics of the respective Pd surface species are summarized in Table 4.4. Before the hydrogen reduction treatment, the Pd 3d core-level spectra of the Pd-impregnated Ni/GDC anode comprised a principle doublet centered around 336.9 (spin-orbital coupling of 5.28 eV), in excellent agreement with literature values for PdO [144, 145]. Hydrogen reduction treatment at 700°C resulted in attenuation of this high energy state, concomitant with the emergence of a low binding energy peak. Spectral deconvolution revealed the presence of two distinct components for the Pd impregnated Ni/GDC cermet after the hydrogen reduction treatment, corresponding to a dominant feature at 335.45 eV and a second feature at 336.31 eV (Figure 4.10 b). Both the absolute position and peak shift of this new feature relative to PdO component are consistent with the formation of

metallic Pd⁰. Despite the hydrogen reduction treatment at high temperatures, there is still ~27% of the surface of the impregnated Pd nano particles remained as PdO. Fox et al [146] studied the reducibility of bimetallic PdCu/CeO₂ catalysts and showed that mutual interaction between Cu, Pd and CeO₂ components affects the reduction process. The presence of copper significantly retards the reducibility of Pd on ceria at high temperatures probably due to the greater oxygen affinity of copper over palladium. Similarly, the presence of nickel could also retard the reduction of palladium, forming PdO on the surface of Pd nano particles on Ni. This appears to be supported by the observation that in the case of Pd impregnated La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O₃/YSZ composite anodes, the existence of PdO after the hydrogen reduction treatment at 800°C for 2 h and at 900°C for 0.5 h is extremely small [107].

Figure 4.10 XPS Pd 3d spectra together with their deconvolutions for the Pd impregnated Ni/GDC anodes (a) before and (b) after hydrogen reduction treatment at 700°C for 1 hr

Table 4.4 Deconvolution results of XPS Pd 3d spectra of Pd impregnated samples before and after reduction in hydrogen as shown in Figure 4.10

Deconvoluted Peaks		Binding Energy (eV)	
		Pd 3d _{5/2}	Pd 3d _{3/2}
Before reduction	1	336.94	342.32
	2	337.36	343.13
	3	338.75	345.39
After reduction	1	335.45	340.73
	2	336.31	341.63

4.5. Electrocatalytic effect of Pd nano particles

There are extensive studies on the mechanism and kinetics of the hydrogen oxidation reactions in solid oxide fuel cells. According to previous studies on the hydrogen oxidation reaction on Ni/YSZ cermet anodes, the impedance responses can be separated into two electrode processes at low and high frequencies; the low frequency process corresponds to the adsorption, dissociation and diffusion step of the reaction on Ni surface while the high frequency step is associated with the charge transfer process at the three phase boundaries [53, 54]. Two electrode processes were also observed for the hydrogen oxidation reaction on Ni/GDC cermet anodes. Ihara et al. [147] investigated in detail the dependence of polarization and interfacial conductivity of Ni/YSZ cermet anode on the partial pressure of hydrogen and proposed a model in which the rate determining step is the Langmuir-type reaction of adsorbed hydrogen and oxygen species at the TPB. The possible role of interstitial hydrogen and hydroxyl formation at the TPB

for the hydrogen oxidation reaction is also suggested by Holtappels et al [148, 149] and Mogensen et al [150].

As shown in this study, impregnation of Pd nano particles not only reduces significantly the overall electrode polarization resistance but also separates the electrode processes at low and high frequencies. This indicates that the hydrogen oxidation reaction on Pd-impregnated Ni/GDC cermet anodes is controlled by at least two limiting electrode processes, similar to that of the Ni/YSZ cermet anodes. The reported observation of the significant reduction of the size of the low frequency arc with the addition of H₂O content [53, 54, 151] for the hydrogen oxidation reaction on Ni and Ni/YSZ cermet anodes supports the view that the low frequency arc is associated with an adsorption and dissociation or a diffusion process of hydrogen species on the Ni surface rather than a pure hydrogen gas phase diffusion. The dissociation of H₂O at SOFC operation temperatures would increase the concentration of O_{ads} sites on the Ni surface, leading to the formation of sub-surface oxide sites on the Ni surface. The presence of O_{ads} sites or the formation of sub-oxide sites enhance the hydrogen adsorption/ dissociation and hydrogen diffusion processes on the Ni metal surface through the spillover mechanism [53]. According to Curtis-Conner Jr et al [152], spillover enhances the kinetics of adsorption processes. The XPS analysis of the impregnated Pd nano particles shows the significant amount of PdO (~27%) of the impregnated Pd nano particles on Ni/GDC grains after reduction treatment in hydrogen (Figure 4.10), indicating the existence of Pd/PdO redox couple on the surface of Ni/GDC grains during the hydrogen oxidation reaction. Dutta et al investigated the hydrogen spillover on CeO₂/Pt by a combination of density function theory (DFT) approach and experimental verification [153]. The

hydrogen adsorbed on CeO₂/Pt catalysts is ~30 times higher than over Pt metal particles due to the enhanced adsorption of hydrogen on the Pt-ceria surface via spillover to the oxide support. Dissociative adsorption of hydrogen gas favorably occurs on a metal surface which has a high density of d-electron states such as Ni, Pt and Pd. The presence of Pd/PdO redox couple would substantially promotes the adsorption and diffusion of hydrogen species via the hydrogen spillover mechanism. On the other hand, recent studies of the O₂ reduction on Pd-impregnated YSZ and (La,Sr)MnO₃ cathodes showed that the addition of Pd nano particles not only provides electrochemically active sites but also significantly promotes the electro-catalytic activity of YSZ and LSM/YSZ composite cathodes for the O₂ reduction reaction, facilitating the dissociation, diffusion, and exchange of oxygen species on the electrode surface [68, 69].

The promotion effect of Pd nano particles on the hydrogen oxidation reaction is schematically illustrated in Figure 4.11. Without Pd/PdO redox couple, the hydrogen oxidation reaction would proceed primarily at the three phase boundaries (TPB), where the hydrogen, Ni anode and YSZ (or GDC phase in the anode) electrolyte phases meet (i.e., the path A in the Figure). The activity of the Ni/GDC anode would depend strongly on the microstructure of the anode, and this is in turn critically related to the distribution of the electronic conducting Ni phase and ionic conducting GDC phase [75, 154]. The presence of palladium nanoparticles on the surface of Ni/GDC anode would significantly enhance both the hydrogen dissociation and diffusion and oxygen diffusion process via spillover mechanism over the Pd/PdO redox couple, resulting in a significant reduction of the electrode polarization resistance and particularly the electrode process associated with the hydrogen dissociation and diffusion. This reaction mechanism is illustrated by the

reaction path B in Figure 4.11. In this case, the whole surface of Ni and GDC grains would be active for the electrochemical oxidation of hydrogen. This is indeed indicated by the dramatic reduction of the size of impedance arcs, in particular the low frequency arc, for the hydrogen oxidation reaction on the Pd-impregnated Ni/GDC cermet anodes. The increase of the PdO loading will increase the interconnectivity between the Pd/PdO redox couple, thus increasing the electrocatalytic activities of the anode due to the fast process of the hydrogen dissociation and diffusion. This is clearly supported by the significant reduction in the activation energy of the electrode process associated with hydrogen dissociation and diffusion (see Figure 4.4). On the other hand, Pd exhibits a very special property when exposed to hydrogen atmosphere. Palladium has very high permeability for hydrogen atoms and it has been used as a membrane for purifying hydrogen [155, 156]. The ability of palladium to accept a large amount of hydrogen atoms in its crystal structure could also facilitate the adsorption and diffusion processes of hydrogen.

Figure 4.11 Schematic diagram of electrocatalytic effect of Pd nano particles on hydrogen oxidation reaction on Ni/GDC cermet anode

4.6. Summary

The effects of the addition/impregnation of Pd nano particles to the Ni/GDC cermet anodes on the hydrogen oxidation reaction were investigated in detail. The results showed that when hydrogen was used as a fuel gas, the electrode polarization resistance was decreased significantly as a result of the presence of Pd nano particles in the anode microstructure. A detailed electrode impedance analysis showed that a major function of the Pd nano particles was to decrease the electrode impedance associated with the adsorption/dissociation/diffusion processes. As a result of introducing 0.15 mg cm^{-2} PdO to the microstructure of Ni/GDC anode, the activation energy for the charge transfer reaction (high frequencies) decreases by around 7%, while the activation energy for the adsorption and diffusion step of the reaction (low frequencies) decreases by almost 96% and the decrease in the activation energy of the whole anode reaction is around 21%. The significantly enhanced adsorption and diffusion processes of the impregnated Pd nano particles were related to the significantly promoted hydrogen and oxygen spillovers over the Pd/PdO redox couple and the hydrogen permeability through the Pd phase. Comparison of the impedance spectra of the Pd-Ni/GDC anodes for the hydrogen oxidation reactions at the open circuit potential and under the anode potentials revealed that the both steps of each anode electrode reaction, which were “adsorption/dissociation/diffusion” and “charge transfer”, were almost equally facilitated (around 50%) by applying 0.15 V in anode potentials.

CHAPTER FIVE

5. Hydrocarbon oxidation on Pd-promoted Ni/GDC anode

In this Chapter, the results of electrochemical performance of the pure and palladium impregnated Ni/GDC anodes operated in methane, methanol and ethanol fuels were presented and discussed. The measurements were performed at the open circuit potential as well as under applied dc bias. The electrochemical impedance spectroscopy study revealed that, similar to the results obtained in the hydrogen gas, the electrode polarization resistances of the anode electrodes decreased remarkably in the presence of Pd catalyst and the polarization performances showed that higher performance and stability could be obtained. Activation energy for the methanol oxidation reaction decreased around 33% as a result of impregnating 0.15 mg cm^{-2} PdO catalyst into the Ni/GDC anode. Study of the microstructure of Pd-promoted Ni/GDC anodes by SEM and EDS before and after hydrocarbon oxidation reactions showed that carbon deposition occurred mainly on the Ni particles and the Pd impregnation could not eliminate the carbon deposition.

5.1. Experimental

YSZ discs after sintering at 1500°C for 4 h with the diameter of 19 mm and thickness of 0.7 mm were used as the electrolyte. Ni/GDC cermet was overlaid on the YSZ electrolytes and sintered together at 1400°C for 2 h. Pt paste was used to make the counter and reference electrodes and baked at 850°C for 15 min. A Pd nitrate solution was used for the infiltration of the Pd catalyst phase into the anode electrodes and the impregnated electrodes were baked at 700°C for 30 min. The electrodes with PdO loadings of 0.04, 0.07, 0.11 and 0.15 mg cm⁻² were selected for electrochemical testing. Wet methane with a flow rate of 80 mL min⁻¹ was used as the fuel gas. Also, methanol and ethanol which was produced by passing wet nitrogen gas (40 mL/min) through liquid methanol and ethanol at 60 and 70°C, respectively, were used as the fuel gases. EIS, linear sweep voltammetry and steady state polarization tests were used to evaluate the electrochemical activities of the Ni/GDC electrodes for the oxidation of hydrocarbon fuels. FESEM and EDS were used to characterize the surface morphology, microstructure and chemical composition of the electrodes.

5.2. Impedance behavior of oxidation reactions of methane, methanol and ethanol

The EIS measurements were performed on the pure and Pd-impregnated Ni/GDC cermet anodes in wet methane, methanol and ethanol fuel gases. Figure 5.1 shows the impedance curves for the pure and Pd impregnated Ni/GDC anodes in the wet methane at 800 and 700°C. Figures 5.2 and 5.3 illustrate the impedance curves for the pure and Pd

impregnated Ni/GDC anodes when 17% methanol or ethanol in N₂ was used as the fuel at the same temperatures. The impedance spectra were taken at the open circuit potential. The results show that the electrode polarization resistance of the oxidation reaction in wet methane, methanol and ethanol decreases significantly on Pd impregnated Ni/GDC anodes, similar to that reported on the Pd-impregnated LSCM/YSZ anode [107]. In the case of methanol and ethanol fuel, the effect of palladium impregnation is more pronounced particularly at lower temperature (700°C). For the oxidation reaction of ethanol on the pure Ni/GDC anode at 700°C (Figure 5.3b), impedance responses are characterized by a high frequency arc and a very long tail at low frequencies. The electrode polarization resistance for the electro-oxidation of ethanol on Ni/GDC anode could be as high as 60 $\Omega \text{ cm}^2$. With the impregnation of 0.07 mg cm⁻² Pd nano particles, the impedance for the ethanol oxidation reaction is characterized by a semicircle and the diffusion tail at low frequencies disappears (Figure 5.3b). The electrode polarization resistance is 1.6 $\Omega \text{ cm}^2$, substantially smaller than 60 $\Omega \text{ cm}^2$ observed for the reaction on the Ni/GDC anode without Pd impregnation. The results indicate that Pd nano particles are particularly effective in the promotion of the electrochemical oxidation reaction in ethanol fuel, consistent with the results for the Pd-impregnated LSCM/YSZ anode [157]. Nevertheless it is observed that the impedance responses of the Pd-impregnated Ni/GDC anodes in wet methane, methanol and ethanol fuels were fluctuated and not very stable, indicating that the electrochemical activity of the Pd-impregnated Ni/GDC anodes under hydrocarbon fuel is not stable. After the tests in wet methane, methanol and ethanol, carbon deposits can be seen on the electrode surface, indicating that the impregnation of palladium may not be sufficient to suppress the carbon cracking on Ni/GDC anodes.

Figure 5.1. Impedance spectra for the oxidation reactions on pure and Pd impregnated Ni/GDC cermet anodes in wet methane (97%CH₄/3%H₂O) at (a) 800 and (b) 700°C. The numbers are impregnated PdO loadings

Figure 5.2. Impedance spectra for the oxidation reactions on pure and Pd-impregnated Ni/GDC cermet anodes in methanol (17%CH₃OH/83%N₂) at (a) 800 and (b) 700°C. The numbers are impregnated PdO loadings

Figure 5.3. Impedance spectra for the oxidation reactions on pure and Pd-impregnated Ni/GDC cermet anodes in ethanol (17% CH₃CH₂OH/83% N₂) at (a) 800 and (b) 700°C. The numbers are impregnated PdO loadings

The impedance responses for the oxidation reactions of methanol over the pure and Pd impregnated Ni/GDC anodes were measured over the temperature range of 650-900°C. Based on the EIS results, the Arrhenius plots of the electrode polarization resistances for the methanol oxidation reactions are drawn and presented in Figure 5.4. As can be seen the slopes of the fitted lines are decreased by introducing the Pd catalyst into the microstructure of the Ni/GDC anodes and a further increase in Pd content reduces the

slopes of the fitted lines more considerably. This shows that the activation energy for the methanol oxidation reaction decreases by increasing Pd content.

Figure 5.4 Arrhenius plots of the electrode polarization resistances for wet methanol (17%CH₃OH/83%N₂/3%H₂O) oxidation reactions. The values in the legend are the loading of impregnated PdO in Pd-Ni/GDC cermet anodes

Base on the data in Figure 5.4, the activation energies for the methanol oxidation reactions over the Ni/GDC anodes with and without Pd catalyst are calculated and depicted in Figure 5.5. The activation energies for the wet methanol oxidation reactions are 150.3 kJ mol⁻¹ over the pure Ni/GDC anode and decreased to 142.77 kJ mole⁻¹ after introducing a small amount of Pd catalyst (0.04 mg cm⁻²) into the anode microstructure. By increasing the PdO content to 0.07, 0.11 and 0.15 mg cm⁻², the activation energies decrease more considerably to 105.9, 104.7 and 101.4 kJ mol⁻¹, respectively. The overall

decrease in activation energy for the methanol oxidation reaction after the impregnation of 0.15 mg cm^{-2} PdO into the Ni/GDC anode is about 33%. The decreasing in the activation energy with increasing Pd loading indicates that the presence of Pd catalyst is effective for the methanol oxidation reactions particularly at low operating temperatures.

Figure 5.5. Activation energy as a function of impregnated PdO loading for methanol oxidation reactions on Pd-impregnated Ni/GDC cermet anodes

5.3. Polarization performance

The polarization performances of Ni/GDC composite anodes for the oxidation reaction in wet methane as a function of impregnated palladium loading at different temperatures are shown in Figure 5.6.

Figure 5.6. Polarization performances of Pd-Ni/GDC anodes for reactions in wet methane as a function of PdO loading at (a) 850, (b) 800 and (c) 700°C. The numbers in the graphs are PdO loadings

As demonstrated in Figure 5.6, the anode overpotential decreases significantly with the impregnation of palladium nano particles. For the methane oxidation reaction on a pure Ni/GDC anode at 850°C, anode overpotential was as high as 147 mV at a current density of 100 mA cm⁻². After impregnation of 0.11 mg cm⁻² PdO, overpotential decreased rapidly to 85 mV, a reduction of more than 1.7 times in the polarization potential. Decrease in the overpotential is more considerable at low temperatures. At 800°C reduction in overpotential as a result of impregnation of 0.11 mg cm⁻² PdO is around 2.5 fold at the same conditions and at lower temperature of 700 °C decrease in overpotential is even more remarkable. This shows effectiveness of the Pd catalyst for improvement of methane oxidation reaction especially at low temperatures.

The polarization behavior of the Ni/GDC anode in ethanol fuel as a function of Pd loading at 850 and 800°C is shown in Figure 5.7. At 850°C, at a current density of 100 mA cm⁻², the overpotential was 93 mV for the pure Ni/GDC anode and decreased to 37.5 mV with impregnation of 0.11 mg cm⁻² PdO, which show a reduction of 2.5 fold, while at 800°C decrease in overpotential at the same condition is around 3.7 times. Similar to the result for methane fuel, the effectiveness of the loaded Pd catalyst is more considerable at lower temperatures.

Figure 5.7. Polarization performance for reactions in wet ethanol as a function of PdO loading at (a) 850 and (b) 800°C. The numbers in the graphs are PdO loading

Figure 5.8 compares the overpotential of the oxidation reaction of methane and ethanol as a function of PdO loading, measured at 100 mA cm⁻². The plots clearly demonstrate that the impregnation of Pd nano particles is very effective in the reduction of the reaction overpotential, particularly at low temperatures. However, further increase

in Pd loading does not lead to the significant decrease in the overpotentials and even causes a slight increase in the anode overpotentials. This indicates that Pd nano particles mainly promote the dissociation and diffusion of the methane and ethanol molecules on the Ni/GDC anodes, similar to the hydrogen oxidation reaction on Pd-promoted Ni/GDC anodes. Thus high PdO loading may lead to the excess coverage of the anode surface by palladium particles and reducing the active triple phase boundary points as can be seen in Figure 4.6(c) resulting in the increase in the polarization resistance with excess PdO impregnation as shown in Figure 5.8.

Figure 5.8. Anode overpotentials for the oxidation reactions of methane and ethanol over pure and Pd-impregnated Ni/GDC anodes as a function of Pd loading at 100 mA cm⁻² and 800°C

5.4. Hydrocarbon oxidation reaction under dc bias

Electrochemical oxidation of methanol over Pd-impregnated Ni/GDC anodes at 850°C was investigated at open circuit potential as well as under applied anode potential, and corresponding electrochemical impedance spectra are presented in Figure 5.9. The

PdO loading was 0.15 mg cm^{-2} . The electrochemical measurements were performed 45 minutes after switching the inlet gas from hydrogen to wet methanol which is long enough to ensure that no hydrogen is remained inside gas passages in the cell. Similar to the impedance responses for the hydrogen oxidation reaction (see in Figure 4.1a), the impedance response for CH_3OH oxidation on a Pd-Ni/GDC electrode at OCP is consisted of two semicircles at high and low frequencies. The frequencies representing the low and high frequency arcs are very similar to those in hydrogen oxidation reaction.

Figure 5.9 Impedance spectra for methanol oxidation reactions on a 0.15 mg cm^{-2} Pd-Ni/GDC anode under different applied anode potentials at 850°C

By gradual applying the anode potential up to 0.25 V, the overall size of the anode impedance decreases from $0.665 \text{ } \Omega \text{ cm}^2$ at OCP to $0.267 \text{ } \Omega \text{ cm}^2$ at 0.25 V. Analysis of the fitted data for the size of low and high frequency arcs under different applied anode potentials shows that the percentage of reduction for the size of both semicircles are almost similar compare to the corresponding values at OCP. Chen et al [119] studied the

impedance behavior of a $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM)/GDC anode in wet methane as a function of dc bias at 850°C. They reported that by applying dc bias of 50, 100, 200 and 300 mV during impedance measurement only low frequency part of the arc is affected and the high frequency part is independent of the applied dc bias. Considering that the charge transfer process is basically sensitive to bias potential, the high frequency arc for the impedance spectra of LSCM/GDC anode in their work may not be attributed to the charge transfer reaction. The trend for decreasing magnitude of electrode polarization resistance for low and high frequency arcs for methanol oxidation reaction as a result of applying anode potential is extracted from Figure 5.9 and depicted in Figure 5.10 along with similar data for hydrogen oxidation reaction which is extracted from Figure 4.6.

Figure 5.10 Anode electrode polarization resistances for the high and low frequency reactions versus applied anode potentials for hydrogen and methanol oxidation reactions and ohmic resistance over a Pd-Ni/GDC anode on a thick YSZ electrolyte at 850°C

As can be seen in Figure 5.10, the behavior of low and high frequency arcs of the impedance spectra for methanol oxidation reaction under applied anode potential are very similar to those in hydrogen oxidation reactions and the only difference is that the resistances against both reaction steps for methanol fuel are larger than those for hydrogen. Dissociation of the relatively large methanol molecule and formation of charged species on the surface is probably the main limiting step in the reaction. The mechanism of the carbon formation in the oxidation of methane on the Pd, Ni and Pd-Ni catalyst is summarized by Nabae et al [98, 100]. They explained that CH_4 decomposes on (100) and (110) crystallographic planes of the Pd, Ni and Pd-Ni catalyst particles and the released C atom diffuses on the surface of Ni particle until it find a (111) plane and then combines with other C atoms to form a carbon fiber. They also reported that deposition of carbon as well as formation of hydrogen gas is strongly depends on the type of materials used as catalyst support. For example, while Pd-Ni/ SiO_2 yields high hydrogen formation rate and carbon deposition level, Pd-Ni/ LaSrCrO_3 catalyst shows no activity for hydrogen formation and carbon deposition. The ohmic resistance of the cell in the methanol test remains constant up to an anode potential of 100 mV and then shows a relatively quick decrease when the anode potential reaches 250 mV. The trend for the decreasing ohmic resistance of the cell with increasing anode potential is seen in the experiments for the both hydrogen and methanol oxidation reactions under dc bias. However, some deviations exist in the results.

Comparison between oxidation reactions of hydrogen and methanol fuel gases was also performed by observing the impedance response of the anode electrode while switching the inlet gas from H_2 to CH_3OH . The time interval between individual

impedance measurements was 15 min. Figure 5.11 shows a set of impedance spectra for the oxidation reaction of the fuel gas right before and after changing the fuel gas from hydrogen to methanol over a 0.11 mg cm^{-2} Pd impregnated Ni/GDC anode at 850°C at open circuit potential.

Figure 5.11 Impedance spectra for hydrogen and methanol oxidation reactions on a Pd-Ni/GDC anode right before and after switching the inlet gas from hydrogen to methanol at 850°C at OCP.

The interval between measurements is 15 min

As can be seen in Figure 5.11, the immediate response to fuel change is mainly observed in the low frequency part of the impedance curve. The size of low frequency arc increases very quickly while the changing rate in the size of high frequency arc is relatively slow. The considerable increase in electrode resistance in the low frequency arc of impedance spectra implies an increased resistance against the adsorption and dissociation processes of the methanol molecules on the electrode surface. The increase in the size of low frequency arc could be due to the gradual coverage of active surface areas of the nickel particles by the cracked carbon.

The effect of the fuel change from hydrogen to methane on the impedance behavior of Pd-Ni/GDC anode is also studied at 850°C with a time interval of 15 min between individual EIS measurements. As demonstrated in Figure 5.12(a), at the open circuit potential, by switching the feed gas from hydrogen to methane a very quick increase in the sizes of the both low and high frequency arcs is observed. Different to the results for the methanol fuel, the high frequency arc also increases in size very quickly after the gas is switched to methane which is an indication of a much more difficult charge transfer process between CH₄ molecules and electrode surface when compared to a similar process for H₂ and CH₃OH molecules with the electrodes. By applying an anode potential of 0.05 V to the cell, the increase in the electrode impedance is significantly smaller with the change of the fuel as compared to that measured under the OCP as shown in Figure 5.8b. In particular, it appears that dc bias is more effective in suppressing the electrode process associated with the high impedance arc, indicating again that the electrode reactions at the high frequencies are associated with the charge transfer process, which is consistent with the above results.

Figure 5.12 Impedance spectra for hydrogen and methane oxidation reactions on a Pd-Ni/GDC anode right before and after switching the inlet gas from hydrogen to methanol at 850°C at (a) OCP and (b) 0.05 V anode potential. The interval between measurements is 15 min

From Figures 5.11 and 5.12, the size of the low and high frequency arcs for methane and methanol oxidation reactions over Pd-Ni/GDC anode are measured and compared with those for hydrogen, then the trend for the change in the electrode polarization resistance at low (R_L) and high (R_H) frequencies as a result of switching the fuel from hydrogen to hydrocarbons over a limited period of time is depicted in Figure 5.13. As can be seen in Figure 5.13a, increase in the magnitude of low frequency arc is much more considerable compare to the one for high frequency arc. After 60 min passage of the methanol over Pd-Ni/GDC anode at OCP, the low frequency arc increases 224% in size, almost 4 times of the increase in the high frequency arc size which is 54%. In the

case of methane fuel in Figure 5.13b, both high and low frequency arcs show a relatively rapid increase in the magnitude at OCP and the low and high frequency impedance arcs increases 550 and 272%, respectively. By applying 0.05 V anode potential the percentage of increase in the low frequency arc sinks significantly to about one third of that at OCP (~100%), while high frequency arc affects moderately and the percentage of increase after 60 min passage of the methane over Pd-Ni/GDC under 0.05 V dc bias becomes 400%.

Figure 5.13 Change in electrode polarization resistances at low (R_L) and high frequencies (R_H) as a function of time, when the inlet fuel gas is switched from hydrogen (time zero) to (a) methanol and (b) methane at OCP (solid symbols) and 0.05 V anode potential (hollow symbols)

5.5. Stability of Pd-promoted Ni/GDC anode for oxidation of methanol fuel

Stability test was performed on both Ni/GDC and Pd-Ni/GDC anodes at a current density of 100 mA cm^{-2} alternatively in hydrogen and methanol fuel and the results are presented in Figure 5.14. The cell was first stabilized in hydrogen for 3 h. While the OCP for both Ni/GDC and Pd-Ni/GDC anodes was $\sim -1.09 \text{ V}$, the anode potential when drawing a current density of 100 mA cm^{-2} from the cell stabilized at 0.89 and 0.86 V for Pd-Ni/GDC and Ni/GDC anodes, respectively. Then the inlet gas was switched to wet methanol. After initial sharp potential drop for both anodes, a more gradual decreasing trend of anode potential is observed in both anodes. After around 10 h operation of the Ni/GDC electrode in methanol fuel performance became unstable and significant potential fluctuations are observed. However, Pd added Ni/GDC anode shows a more stable performance and a potential level of 0.62 V is maintained over 13 h operations in methanol fuel. After switching the fuel gas back to the hydrogen, the anode potential for both cells returned to the initial value at the beginning of the operation. Better stability of Pd promoted Ni/GDC anode during the time course of 13 h in this experiment shows effectiveness of the Pd catalyst in direct utilizing of hydrocarbons in Ni containing anode materials, however more work is needed to understand the enhancing effect of Pd catalyst on the stability of the cell.

Figure 5.14 Stability performances of Ni/GDC and Pd-Ni/GDC anodes in hydrogen-methanol-hydrogen fuel for 1400 min. The cell is polarized at 100 mA cm^{-2} and 850°C

5.6. Microstructure of Pd-promoted Ni/GDC anode and carbon deposition

Figure 5.15 shows the SEM micrographs of a Ni/GDC and a 0.11 mg cm^{-2} Pd impregnated Ni/GDC electrodes after test in methane and ethanol fuel. The SEM study clearly shows that in the case of ethanol fuel, carbon is mostly deposited on the nickel particles of the anode (Figure 5.15a & b). Points (1) and (2) in Figure 5.15b were analyzed by EDS technique and the results are presented in Figure 5.16 and Table 5.1. The points 1 and 2 corresponds to Ni and GDC phase of the anode as shown by the EDS analysis. Significant amount of the carbon was detected on the Ni particle surface (point 1, Figure 5.15b); while no carbon was detected on the GDC surface (point 2, Figure 5.15b). Similar carbon deposition was found when methanol was used as the fuel gas. In

the case of methane fuel, in addition to carbon deposition on Ni particles, fibrous deposits were found on the Pd-impregnated Ni/GDC anode surface and EDS analysis indicates that the fiber deposits were carbon (Figure 5.15c & d). Most of the internal surface of the alumina testing tube was covered by the carbon residues when ethanol was fed as the fuel, while in the cases of methanol the carbon deposition was restricted to the anode electrode area. Although the carbon deposition on the testing tube does not relate to the anode and the electrochemical oxidation of the fuel and in fact it relates to the thermodynamic issues, it reminds the high possibility of carbon cracking for ethanol. In the EDS results as shown in Table 5.1 some data may not be precise. For example the oxygen content cannot be measured exactly by EDS technique. The SEM results indicate that the Pd impregnation is not able to prevent the carbon deposition despite the fact that the Pd nano particles substantially promote the electro-catalytic activities of the Ni/GDC anodes.

Figure 5.15 SEM micrographs of (a) Ni/GDC and (b) 0.11 mg cm^{-2} Pd-Ni/GDC anodes exposed to ethanol; (c) and (d) 0.11 mg cm^{-2} Pd -Ni/GDC surface after testing in methane, showing the formation of fibrous carbon on the surface and (e) Pd-Ni/GDC anode before test showing the presence of Pd nano particles. Points 1 and 2 in (b) are Ni and GDC particles, respectively, and point 3 in (d) is a fibrous carbon formed in hydrocarbon fuel

The carbon deposition on the Pd-impregnated Ni/GDC anodes could cause the degradation of the anode performance and contribute to the instability of the impedance responses of the anodes in the methane, methanol and ethanol fuels. The Pd nano particles cannot completely suppress the carbon deposition when the hydrocarbons are used as the fuels. However, substantially decreased electrode impedance for the oxidation reaction on the Pd-impregnated Ni/GDC anode proves that the Pd nano particles have a considerable catalytic effect for the oxidation reactions of the methane, methanol and ethanol fuels.

Figure 5.16 EDS analysis results of (a) point 1, (b) point 2 and (c) point 3 as shown in the SEM micrographs of Figure 5.15

Table 5.1 Relative intensity analysis of EDS spectra for points 1, 2 and 3 as indicated in Figure 5.16

Element	Point 1 (wt %)	Point 2 (wt %)	Point 3 (wt %)
C (K)	14.26	0	71.31
O (K)	30.58	23.87	20.66
Ni (K)	29.93	28.93	6.03
Pd (L)	2.2	1.9	-
Ce (L)	20.76	40.13	2
Gd (L)	2.26	5.18	-
Total	100	100	100

A comparison between molecular structure of methane, methanol and ethanol may help to understand why methanol behave more benign on the carbon deposition issue in comparison with the filament type carbon residues in the case of methane and a rather messy carbon contamination around the anode in the case of ethanol. Figure 5.17 shows the molecular structure of methane, methanol and ethanol molecules. Based on the information in the literature, it is believed that in the presence of metallic catalytic agents, particularly Pd catalyst, dissociation process of hydrocarbon molecules proceeds through a gradual dehydrogenation of hydrocarbon molecules [158-160] which is more energetically feasible as compared to instantaneous cracking of the hydrocarbon molecules. Several groups studied dissociative adsorption of methane on the surface of metallic catalysts [158, 161, 162]. Klier et al [163] reported that on the metallic catalyst surface, methane chemisorption gives rise to formation of surface methyl species as primary products, and further dissociation of the C–H bonds proceeds stepwise all the way to carbon. Dehydrogenation of a CH₄ molecule yields deposition of one carbon atom on the surface of metallic catalyst. The deposited carbon has a chance to either be removed from the surface by combining with an oxygen atom to form CO molecule or

joining to other carbon nuclei existing on the surface and forming a carbon filament as explained by Nabae et al [100]. The oxygen atom required for removal of C atom might be supplied from the cathode through electrolyte or from the water molecules present in the anode compartment.

Figure 5.17 Molecular structures of (a) methane, (b) methanol and (c) ethanol

Dissociation of methanol on the surface of precious metal catalysts is also studied [164-166]. Mehmood et al [167] performed a comprehensive study about probable routes for dehydrogenation of methanol in the presence of palladium and reported that Methanol dehydrogenation through hydroxymethyl (CH_2OH), hydroxymethylene (CHOH), formyl (CHO), and carbon monoxide (CO) is the most favorable reaction pathway and a competing dehydrogenation pathway through methoxy (CH_3O) and formaldehyde (CH_2O) is slightly less favorable. Each of these pathways results in formation of CO and H_2 . Pathways involving C-O bond cleavage are less energetically favorable. The $(\text{CH}_2\text{OH}) \rightarrow (\text{CHOH}) \rightarrow (\text{CHO}) \rightarrow (\text{CO})$ route is also suggested by Schauermann et al [160]. What is important in this dehydrogenation process is that there is a high possibility that CO detaches from the surface according to the calculation by Mehmood et al, so, the only

carbon in the hydrocarbon molecule will be removed automatically from the surface [167]. Thus, the surface of Pd-impregnated Ni/GDC anode in methanol is significantly cleaner as compared to that in methane. However, a competing reaction of combining two CO molecules and formation of one CO₂ molecule plus one C atom (Boudourd reaction) may cause deposition of carbon. So, Boudourd reaction is not a favorable reaction under SOFC operation conditions.

Ethanol dissociation process is also studied [168, 169]. Li et al [159] systematically investigated the ethanol dehydrogenation process using self-consistent periodic density functional theory and found that the most likely decomposition path for ethanol in the presence of Pd is $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHOH} \rightarrow \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} \rightarrow \text{CH}_2\text{CO} \rightarrow \text{CHCO} \rightarrow \text{CH} + \text{CO} \rightarrow \text{CO} + \text{H} + \text{CH}_4 + \text{C}$. As can be seen in this reaction route, carbon is the direct product of ethanol decomposition. That is probably why using ethanol yields significant amounts of carbon deposit in our experiments.

Comparing the above mentioned dehydrogenation routes implies that methanol provides the less chance for depositing C residues on the surface of metallic catalyst. While both methane and ethanol need external oxygen for the removal of the carbon atom. The carbon resulting from Boudourd reaction in all the hydrocarbons needs external oxygen for removal.

Increased stability of the Pd-Ni/GDC anode as compared to the Ni/GDC one for the oxidation of methanol might be due to the enhancing effect of Pd for dehydrogenation of the molecules according to the route suggested by Schauermaun and Mehmood [160, 167].

Nabae et al. investigated the effect of addition of Pd-Ni catalyst to the LSCr/SDC composite anode for the direct oxidation of methane and observed that low frequency arc of impedance spectra is affected as a result of addition of Pd or Pd-Ni catalyst [98]. Eguchi et al. also reported that decreased electrode impedance in the oxidation reaction of methane over Ni/YSZ cermet anode in the presence of precious metals is a consequence of the enhanced diffusion process [55]. In the present study, the electrode impedance associated with the low frequency arc for the oxidation reaction in hydrogen, methane, methanol and ethanol is also significantly reduced by addition of palladium nano particle catalyst. The significantly enhanced adsorption and diffusion processes via the spillover of hydrogen and oxygen species over the Pd/PdO redox couple and Pd nano particles as discussed previously could also explain the significant improvement in the electrochemical activities of the Pd-impregnated Ni/GDC anodes in methane, methanol and ethanol fuels as compared to Ni/GDC anodes without impregnated Pd nano particles. Supported Pd systems are widely recognized as the excellent catalysts for methane and other important oxidation reactions. The effectiveness of Pd as an oxidation catalyst depends on its complex interactions with gas phase O_2 to form surface PdO or non-stoichiometry PdO_x and on the redox reactions, which in turn is a complex function of temperature and O_2 partial pressure [170, 171]. The presence of uniformly distributed and nano-sized Pd/PdO over the surface of Ni and GDC grains would provide an effective source or pathway for the oxygen diffusion and exchange thus promoting the electro-catalytic oxidation of hydrocarbon fuels such as methane, methanol and ethanol. This is supported by the experimental results as shown in Figures.5.1, 5.2 and 5.3.

5.7. Summary

Electrochemical performance of Pd-impregnated Ni-GDC anode electrode for the oxidation reaction of methane, methanol and ethanol fuels was investigated at open circuit potential and under dc bias. The results showed that the impregnation of Pd nano particles substantially reduced the electrode polarization resistance of the oxidation reaction of the hydrocarbon. The presence of the palladium nano particles mainly reduces the electrode polarization resistance of the reaction in the low frequency portion of the impedance arcs. The introduction of the Pd nano particles into the microstructure of the Ni/GDC anodes results in a significant decrease in activation energy for the methanol oxidation reaction over the Ni/GDC anode electrode. The activation energy for the methanol oxidation process decreased by $\sim 33\%$ as a result of impregnation of 0.15 mg cm^{-2} PdO, i.e., from about 154.3 to 101.4 kJ. mol⁻¹. This remarkable decrease in activation energy revealed the effectiveness of the Pd nano particles in promoting the oxidation of the methanol fuel, especially, at low temperatures.

The study of the impedance response of oxidation reaction of the methanol fuel under applied anode potentials revealed that the both steps of fuel oxidation reaction, which were adsorption/dissociation/diffusion and charge transfer, were almost equally facilitated under applied anode potentials. The electrodes containing the Pd catalyst showed a higher stability in operation with the methanol fuel. The presence of Pd nano particles could not suppress the carbon deposition over the Ni/GDC cermet anodes. The carbon deposition occurs mainly on the Ni particles of the Ni/GDC cermets in the hydrocarbons tested.

CHAPTER SIX

6. Hydrogen and methane oxidation on Pd-promoted LCCM/GDC anode

In this Chapter the results of the oxidation reactions of hydrogen and methane on the Ni-free LCCM/GDC composite anodes with and without Pd impregnation were presented. Traditional Ni containing anode materials like Ni/YSZ and Ni/GDC cermets have high catalytic activities for the hydrogen and methane oxidation reactions but suffers from the carbon deposition problem. One approach to operate an anode in methane without coking is to substitute Ni with another carbon-tolerant phase. It was shown that the pure ceramic oxide composite materials like LSCM/GDC and LCCM/YSZ exhibited a good tolerance to the carbon deposition. However, the catalytic activities of the lanthanum chromite perovskite oxide-based composite anodes are not as high as those of the Ni-containing anodes. It was shown that introducing transition metals such as Pt and Ru promoted the catalytic activities of the anode materials for the hydrogen oxidation reactions. Thus, it is interesting to investigate the electrochemical activity of the LCCM/GDC composite anode for the hydrogen and methane oxidation reactions in SOFCs and the effects of incorporating Pd nano particle into the microstructure of the electrodes on the mechanisms of hydrogen and methane oxidation reactions.

6.1. Experimental

Electrochemical impedance spectroscopy (EIS) and steady state polarization techniques were used to study the electro-catalytic activity and performance of the Pd impregnated LCCM/GDC anodes for the oxidation reactions of hydrogen and methane. The optimum sintering temperature for the composite LCCM/GDC electrode on the YSZ electrolyte was investigated using EIS and SEM. XRD examination of the LCCM and YSZ or GDC powders after heated at 1350°C for 2 h was performed to investigate any possible interaction between the phases after sintering at high temperature. Dense YSZ with a thickness of about 0.9 mm was used as the electrolyte. Pt paste was used to fabricate both counter and reference electrodes and Pt mesh was used as the current collector in contact with all the electrodes. Pd-impregnated anode electrodes with the PdO loadings of 0.02 and 0.06 mg cm⁻² were selected for the electrochemical measurements over the temperature range of 750-850°C. Humidified hydrogen and methane were used as the fuel gases with a flow rate of 80 mL min⁻¹. The microstructure of the Pd impregnated anodes and the possibility of coke formation on the Pd impregnated LCCM/GDC anodes were characterized with FESEM.

6.2. Effect of sintering temperature

In order to find the optimum sintering temperature of the LCCM and GDC particles on the YSZ electrolyte, the prepared anodes were sintered at the temperatures of 1150, 1200, 1250, 1300 and 1350°C. This temperature range was selected based on the suggested sintering temperatures for the compositions close to LCCM/GDC mixture in

the literature. Normally the sintering temperature which is corresponding to the lowest ohmic and electrode polarization resistance is selected as the optimum sintering temperature. Figure 6.1 shows the electrochemical impedance spectra for the hydrogen oxidation reaction on the LCCM/GDC composite anodes measured at 800 and 850°C in the wet hydrogen at the open circuit potential.

Figure 6.1 Impedance curves for hydrogen oxidation reactions, measured at (a) 850 and (b) 800°C in wet hydrogen on LCCM/GDC anodes sintered at. i) 1150; ii) 1200; iii) 1250; iv) 1300 and v) 1350°C

The impedance responses were generally characterized by two separated impedance arcs at low and high frequencies, similar to that observed on (La,Sr)(Cr,Mn)O₃/YSZ composite anodes by Jiang et al [69]. The sintering temperature shows a significant effect on the electrode polarization resistance and in particular the electrode ohmic resistance, R_{Ω} , of the LCCM/GDC composite anodes. R_{Ω} decreases with the increase of the sintering

temperature and reaches the minimum for the anodes sintered at 1300°C. At a sintering temperature of 1150°C, R_{Ω} is 6.93 Ωcm^2 at a testing temperature of 850°C and is reduced to 2.13 Ωcm^2 when the sintering temperature increased to 1300°C. The important role of the sintering temperature on the R_{Ω} was also reported for the Ni/YSZ cermet anodes [172, 173]. The significantly reduced ohmic resistance is most likely due to the enhanced interfacial contact between the YSZ electrolyte and the LCCM and GDC phases in the composite anodes. The impedance responses for the hydrogen oxidation reaction on the LCCM/GDC anodes also show that the electrode polarization resistance is affected by the anode sintering temperature. Electrode polarization resistance for the anode samples sintered at 1300°C is 0.43 Ωcm^2 at 850°C, considerably smaller than 1.28 Ωcm^2 for the reaction on the anodes sintered at 1150°C. Figure 6.2 shows the plots of R_{Ω} and electrode polarization resistance, R_E , of the LCCM/GDC composite anodes as a function of the sintering temperature. As shown in Figure 6.2, further increase in the anode sintering temperature to 1350°C leads to increase of R_{Ω} and electrode polarization resistance again. As demonstrated by the XRD results (see Figure 6.4), there is no phase formation between LCCM and YSZ or GDC after heat treatment at 1350°C. Thus, the most likely reason for increasing the R_E and R_{Ω} magnitude could be related to the sintering and coarsening of LCCM and GDC phases of the anodes. The grain growth and agglomeration of the LCCM and GDC particles could reduce the interface contact between the LCCM/GDC anode and YSZ electrolyte, leading to the increase in both R_{Ω} and electrode polarization resistance [174]. Based on the above mentioned results, the LCCM/GDC composite anodes sintered at 1300°C would produce the lowest electrode ohmic resistance and electrode polarization resistance for the hydrogen oxidation reaction.

Figure 6.2 Electrode ohmic resistance (R_{Ω}) and area specific resistance (ASR) of LCCM/GDC composite anodes as a function of anode sintering temperature. R_{Ω} and ASR for hydrogen oxidation reactions on LCCM/GDC anodes were measured at 800 and 850°C

Figure 6.3 shows the polarization performance of the LCCM/GDC anodes measured at 800°C and 850°C in humidified hydrogen (3% water). The anodes were sintered at different temperatures. The results show that the anodes sintered at 1250 and 1300°C have the lowest overpotential (η) values. The overpotential value measured at 50 mAcm^{-2} for the anode sintered at 1250 and 1300°C is ~33 mV at 800°C, about one third of the 98 mV for the anodes sintered at 1150°C and 1200°C. As the sintering temperature increase to 1350°C, the overpotential for the reaction on the LCCM/GDC composite anode increases again. The polarization behavior of the anodes sintered at different temperatures is in a good agreement with their impedance behavior. Thus, based on the impedance and polarization results, the best electrode performance can be obtained on the

LCCM/GDC composite anodes sintered at 1300°C. Without specification, the anodes presented in following sections were sintered at 1300°C.

Figure 6.3 Polarization performances of hydrogen oxidation reactions on LCCM/GDC composite anodes at (a) 850 and (b) 800°C. The anodes were sintered at different temperatures

In order to investigate the possible interaction between LCCM and YSZ or GDC, the LCCM powder was mixed individually with GDC and YSZ powders and heated at 1350°C for 2 h and the composite LCCM/GDC and LCCM/YSZ powders were also

examined by XRD. As shown in Figure 6.4, there is no phase change between LCCM/GDC and LCCM/YSZ composite powders after heat treatments at 1350°C.

Figure 6.4 XRD patterns of (a) LCCM-GDC, LCCM and GDC and (b) LCCM-YSZ, LCCM and YSZ powders sintered at 1350°C for 2 h in air

The nature of the observed arcs in the impedance spectra of the hydrogen oxidation reaction on LCCM/GDC electrode was investigated by studying the impedance response of the hydrogen oxidation reaction as a function of hydrogen flow rate as shown in Figure 6.5. The impedance results show increasing size of low frequency arc as a result of decreasing hydrogen partial pressure, which suggests that the low frequency arc is related to diffusion and/or adsorption of hydrogen, similar to what is commonly believed for Ni/YSZ and Ni/GDC electrodes.

Figure 6.5 Impedance spectra for hydrogen oxidation reactions on a LCCM/GDC anode electrode at 850°C at different hydrogen partial pressures

6.3. Effect of Pd impregnation on hydrogen oxidation reaction

Pd-impregnated LCCM/GDC anodes with different Pd loading were tested in humidified hydrogen at different temperatures. Figure 6.6 shows the impedance

responses of the LCCM/GDC composite anode in wet hydrogen at 750°C and 850°C with different PdO loading. For the hydrogen oxidation reaction on a pure LCCM/GDC anode, the impedance responses are characterized by a depressed arc which appears to consist of two to three semicircles.

Figure 6.6 Impedance curves of LCCM/GDC composite anodes in wet hydrogen, measured at (a) 850 and (b) 750°C as a function of the impregnated PdO loading. The anodes were sintered at 1300°C. The numbers in the graphs are frequencies in Hz

The overall electrode polarization resistances are 0.45 and 1.01 $\Omega \text{ cm}^2$ at 850 and 750°C, respectively. The electrode polarization resistance for the hydrogen oxidation reaction on the LCCM/GDC composite anode (e.g., 0.45 $\Omega \text{ cm}^2$ at 850°C) is also much lower than the reported value for the reaction on LCCM/YSZ composite anode (e.g., 1.4 $\Omega \text{ cm}^2$ at 900°C) [106]. The much lower electrode polarization resistance for the reaction

on the LCCM/GDC composite anodes is most likely related to the catalytically active GDC phase as compared to the YSZ phase in the composites. With the Pd impregnation, the overall impedance arcs are reduced considerably. For the hydrogen oxidation on the LCCM/GDC anode with impregnation of 0.02 mg cm^{-2} PdO, the electrode polarization resistance is $0.17 \text{ } \Omega \text{ cm}^2$ at 850°C , significantly smaller than $0.45 \text{ } \Omega \text{ cm}^2$ for the reaction on a pure LCCM/GDC composite anode. With the increase of the impregnated Pd loading to 0.06 mg cm^{-2} , electrode polarization resistance decreased to $0.13 \text{ } \Omega \text{ cm}^2$. Also a significant change is observed in the impedance behavior for the hydrogen oxidation reaction. In the case of the 0.06 mg cm^{-2} Pd-impregnated LCCM/GDC anode, the impedance responses are characterized by a single distorted impedance arc at high frequencies and the low frequency impedance arcs associated with the reaction on the pure LCCM/GDC anode disappear (Figure 6.6a). Similar trend was also observed for the anodes measured at a lower temperature of 750°C (Figure 6.6b). The results show that impregnation of Pd not only reduces the size of the impedance arcs, but also changes significantly the characteristics of the impedance behavior for the hydrogen oxidation on LCCM/GDC composite anodes. The remarkable change in the impedance characteristics indicates that the impregnated Pd particles have a pronounced effect on the electrode processes associated with low frequencies, similar to that observed on the Ni/GDC cermet anodes. Kim *et al.* [175] reported that the maximum power density of a cell consisting of LSCM/YSZ anode, thin YSZ electrolyte and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3/\text{YSZ}$ cathode operated in hydrogen fuel is increased almost five folds by introducing 0.5 wt % Pd to the anode electrode at 700°C . The Pd introduced was considered to play a catalytic role, facilitating the hydrogen oxidation reaction.

The ASR data for the hydrogen oxidation reaction on the Pd-impregnated LCCM/GDC composite anodes, measured at different temperatures are summarized in Figure 6.7. The substantial reduction in the electrode polarization resistance is achieved by adding 0.02 mg cm⁻² PdO, and further increasing the Pd loading to 0.06 mg cm⁻² has a much smaller effect on the reduction in the electrode polarization resistance. This indicates that a very small dosage of catalytic material such as palladium can considerably reduce the polarization resistance of the hydrogen oxidation reaction on LCCM/GDC composite anodes. The significant reduction in the low frequency impedance arc of the reaction on Pd-impregnated LCCM/GDC anodes indicates that the impregnated Pd may primarily accelerate the dissociation and diffusion processes of the reaction.

Figure 6.7 ASRs for hydrogen oxidation reactions on Pd-impregnated LCCM/GDC composite anodes, measured at different temperatures. The anodes were sintered at 1300°C

The significant improvement in the electrode polarization resistance was also confirmed by the polarization performance. Figure 6.8 shows the plots of polarization performance for the hydrogen oxidation reaction on the LCCM/GDC anodes as a function of the loading of the impregnated Pd, measured at 850°C and 750°C in wet hydrogen. The polarization potential for the hydrogen oxidation reaction on the LCCM/GDC composite anodes decreases significantly with the increase in the impregnated Pd. At 850°C under a current density of 100 mA cm⁻², η was 38mV for the reaction at 850°C on a pure LCCM/GDC anode and reduced to 20mV for the reaction on the 0.06 mg cm⁻² Pd-impregnated LCCM/GDC anode (Figure 6.8a). The reduction in the overpotential is even more substantial at lower temperatures. For example at 750°C under a current density of 50 mA cm⁻², η was 12 mV on the 0.06 mg cm⁻² Pd-impregnated LCCM/GDC composite anode, 4 times smaller than 51 mV for the reaction on the pure LCCM/GDC anode (Figure 6.8b). The results of polarization performance are consistent with the impedance data of the LCCM/GDC composite anodes.

Figure 6.8 Polarization performance of hydrogen oxidation reactions for Pd-impregnated LCCM/GDC anodes measured at (a) 850 and (b) 750°C. The anodes were sintered at 1300°C

6.4. Effect of Pd impregnation on methane oxidation reaction

Pd-impregnated LCCM/GDC composite anodes with different Pd loading were also evaluated in wet CH₄ at different temperatures. Figure 6.9 shows the impedance curves of

the LCCM/GDC anodes with and without Pd-impregnation in wet CH₄ measured at 750 and 850°C under open circuit condition. Symbols are the experimental data and the lines are the fitted results. The equivalent circuits for the fitting are given in Figure 6.9c. In the circuit, R_{Ω} is the electrode ohmic resistance, Q is the constant phase element (CPE), R is the electrode polarization resistance and W is the Warburg diffusion parameter. The subscript, H, M, and L, represents the high, medium and low frequency arcs. For the CH₄ oxidation reaction on the pure LCCM/GDC anode, the impedance response is characterized by a high frequency arc and a large tail at low frequencies. Appearance of the low frequency tail is an indication of the dissociation and diffusion limiting process for the methane oxidation reaction on LCCM/GDC composite anodes. This appears to be supported by the poor reforming or catalytic activity of (La,Sr)CrO₃-based perovskite in methane fuel [176]. In this case, the impedance responses were fitted with the equivalent circuit with a Warburg diffusion parameter (circuit II in Figure 6.9c). The fitting between the equivalent circuit and experimental data is reasonable, indicating the applicability of the circuit II for the methane oxidation reaction on pure LCCM/GDC composite anodes at 850°C (Figure 6.9a). The overall electrode polarization resistance was $\sim 2.2 \Omega \text{cm}^2$ and the Warburg diffusion parameter is $0.238 \Omega \cdot \text{s}^{-1/2}$ in this case. Similar observation and conclusions can also be drawn for the reaction on the LCCM/GDC composite anodes at 750°C and the corresponding Warburg diffusion parameter is $0.395 \Omega \cdot \text{s}^{-1/2}$ (Figure 6.9b).

Figure 6.9 Impedance curves of LCCM/GDC composite anodes in wet CH_4 , measured at (a) 850 and (b) 750°C as a function of impregnated PdO loading. Symbols are the experimental data and the lines are fitted results. The numbers on the curves are frequencies in Hz. The equivalent circuits used for the fitting are given in (c). The anodes used were sintered at 1300°C

With the Pd impregnation, the size of the impedance arc is significantly reduced and there are also substantial changes to the impedance behavior for the methane oxidation reaction on the LCCM/GDC composite anodes. The overall electrode polarization resistance decreases remarkably with the increase in the Pd loading. In the case of the reaction on the 0.02 mg cm^{-2} Pd-impregnated LCCM/GDC composite anode, the long and large low frequency tail disappears with the consequent formation of two impedance arcs at medium and low frequencies (Figure 6.9a). The impedance responses can be characterized by three clearly separated arc at high, medium and low frequencies. With further increase of the impregnated Pd to 0.06 mg cm^{-2} , the size of the impedance arc decreases and the low frequency arc appears to be undetectable. The disappearance of the low frequency tail and the evolution of the impedance arcs at medium and low frequencies indicate that the impregnated Pd plays an important catalytic role in the enhancement of the dissociation and diffusion process for the methane oxidation reaction on LCCM/GDC composite anodes. In the case of the CH_4 oxidation reaction on Pd-impregnated LCCM/GDC composite anodes, the impedance responses were fitted with the equivalent circuit consisted of three RQ components in series (Circuit I, Figure 6.9c). The fitting between the calculated data based on the equivalent circuit I and the experimental data is very good, indicating that the methane oxidation reaction on Pd-impregnated LCCM/GDC composite anode is limited by three electrode processes associated with high, medium and low frequencies. The significant change in the impedance behavior of the Pd-impregnated LCCM/GDC anodes compare to that on pure LCCM/GDC anodes is also clearly demonstrated for the reaction at 750°C (Figure 6.9b).

The enhancement of the methane oxidation reaction by adding Pd nano particles is also confirmed by the polarization performance, as shown in Figure 6.10. The polarization potential for the reaction on the Pd-impregnated LCCM/GDC is much lower than that on the pure LCCM/GDC anode. At a testing temperature of 750°C, η is 398 mV at 40 mA cm⁻² for the reaction on the pure LCCM/GDC composite anodes and is reduced substantially to 38 mV on the 0.06 mg cm⁻² Pd-impregnated LCCM/GDC anode, a 10-fold reduction in the η values for the methane oxidation reaction. In the case of a cell with Pd/ceria impregnated LSCM/YSZ composite anode, YSZ electrolyte and LSF/YSZ cathode, Kim *et al.* [177] also reported a high power density of 400 mWcm² in methane fuel at 700°C.

Figure 6.10 Polarization performances for methane oxidation reactions on Pd-impregnated LCCM/GDC anodes at 750°C. The anodes used were sintered at 1300°C

Long time test was performed on a 0.06 mg cm⁻² Pd impregnated LCCM/GDC anode at a current density of 25 mA cm⁻² in hydrogen and methane with the gas flow rate

of 20 mL min^{-1} . The results are shown in Figure 6.11. The cell was first stabilized in hydrogen for 120 min and then the fuel gas was switched to methane. After switching the gas the potential decreased from - 0.94 to - 0.815 V gradually and remained stable for the polarization period from 600 to 1400 min. After switching back to hydrogen the polarization potential returned to a stable value of - 0.95V, slightly different from - 0.94V before the stability test in the wet CH_4 . This small difference might be due to an experimental error in the measurements. The overall exposure time in wet CH_4 is 1200 min (i.e., 20 h). The stable and close polarization potential of the Pd Impregnated LCCM/GDC composite anodes in hydrogen before and after exposure to CH_4 for 20 h indicates that the exposure of the Pd-impregnated LCCM/GDC anode in methane has no detrimental effect on the performance and activity of the anode under the conditions studied. The stable potential of the Pd impregnated LCCM/GDC composite anodes in methane at 0.815 V for about 900 min shows applicability of palladium promoted LCCM/GDC anodes for the direct utilization of methane.

Figure 6.11 Stability performance of a 0.06 mg cm^{-2} Pd-impregnated LCCM/GDC anode in hydrogen-methane-hydrogen fuel for 2000 min. The cell is polarized at 25 mA cm^{-2} and 850°C

After the tests in wet methane, the surface of the Pd-impregnated LCCM/GDC composite anodes was examined. Surfaces of the Pd-impregnated LCCM/GDC composite anodes were clean after testing in methane fuel and no carbon deposits were detected on anode surface by EDS analysis. Figure 6.12 shows the SEM pictures of Pd impregnated LCCM/GDC composite anodes after the polarization test. The Pd loading of the composite anode was 0.02 and 0.06 mg cm⁻² PdO, respectively. The LCCM and GDC particles are typically in the range of ~1 μm and are intimately connected. Pd nano particles with the range of 20-50 nm were clearly visible and finely distributed in the porous LCCM/GDC structure. In the case of 0.02 mg cm⁻² Pd-impregnated LCCM/GDC composite anodes, the Pd nano particles were in the range of 20 nm (Figure 6.12a). As the Pd loading increased to 0.06 mg cm⁻², the number of the Pd nano particles increased significantly and the particle size is in the range of 50 nm (Figure 6.12b). There appears no preferential distribution of Pd nano particles on the surface of the LCCM and GDC grain and at the anode/YSZ electrolyte interface. From the cross section of the Pd-impregnated LCCM/GDC composite anodes, the microstructure of the anodes appears to be highly porous; indicating that impregnation of small amount of Pd does not have any effect on the porosity of the anodes (Figure 6.12c). The SEM results indicates that nano sized Pd particles were successfully introduced to the LCCM/GDC composite anodes by the impregnation method.

Figure 6.12 SEM micrographs of Pd-impregnated LCCM/GDC anodes with (a) 0.02 mg cm^{-2} PdO (b) 0.06 mg cm^{-2} PdO and (c) cross section of a 0.06 mg cm^{-2} Pd-impregnated LCCM/GDC anode with YSZ electrolyte after fuel cell test

The impedance results reveals that the impregnation of the Pd phase primarily promotes the electrode processes associated with medium and low frequencies, which could be mainly correlated to the adsorption and diffusion step of the fuel oxidation reactions [53, 71]. The promotion effect of Pd nano particles in the hydrogen and CH_4 oxidation reaction on the LCCM/GDC anodes could also be explained similarly to what was discussed for the Pd-impregnated Ni/GDC anode. The detailed mechanism of the methane oxidation reaction is not clearly understood. Nevertheless, in the case of the methane oxidation over a heterogeneous Pd catalyst, the breaking of the C-H bond to form carbon containing species could be involved, followed by the subsequent oxidation reaction of the surface species [178]. The impregnated Pd nano particles could play a catalytic role to facilitate the breaking of the C-H bond and to provide a low activation

energy path for the adsorption and dissociation of reaction species of the methane oxidation reaction probably through the spillover mechanism via the Pd/PdO couple under fuel cell operation conditions. However, significantly more work is needed to understand the fundamentals of the catalytic role of nano-sized Pd in the oxidation of hydrogen and in particular methane on the LaCrO₃-based perovskite oxide anodes.

6.5. Summary

LCCM/GDC composite anodes were investigated for hydrogen and methane oxidation reactions in solid oxide fuel cells. The performance of the LCCM/GDC anodes was significantly affected by the sintering temperature and the best performed LCCM/GDC composite anodes were obtained on the anodes sintered at 1300°C. ASRs of the LCCM/GDC anodes were about 0.47 Ωcm^2 for the hydrogen oxidation reaction and $\sim 2.2 \Omega\text{cm}^2$ for the methane oxidation reaction at 850°C. Addition of Pd nano particles to the LCCM/GDC composite anodes significantly improved the electro-catalytic activity of the anodes for the oxidation reaction of both hydrogen and methane. The impregnation of the Pd nano particles also significantly changed the impedance behavior of the reaction particular for the methane oxidation reaction. In the case of methane oxidation reaction, the impregnation of Pd in the LCCM/GDC composite anodes led to the disappearance of the low frequency diffusion tail and the evolution of the impedance arcs at medium and low frequencies. The stable and close polarization potentials of the Pd-impregnated LCCM/GDC composite anodes in hydrogen before and after exposure to CH₄ for 20 h indicated that the exposure of the Pd-impregnated LCCM/GDC anodes in methane had

no detrimental effect on the performance and activity of the anodes under the conditions studied. No carbon deposition was detected after operating of the Pd-impregnated LCCM/GDC composite ceramic anodes in the methane fuel.

CHAPTER SEVEN

7. Performance and stability of Pd-based catalyst promoted LSM cathode

This Chapter investigates the effects of catalyst loading, operation temperature and co-infiltration of palladium based catalysts on the performance and stability of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) cathode electrodes. The ASR and overpotential of LSM electrodes for the O_2 reduction reactions increase sharply in the intermediate temperature range of 600-800°C. The application of the metal catalyst materials in the microstructure of the SOFC electrodes showed a considerable effect on lowering the overpotential and increasing the performance of the fuel cells. However, the stability of the impregnated metal nano particles was a serious concern due to the inevitable agglomeration and grain growth of the nano particles under the high operation temperatures of the SOFCs.

Thus, it is important to investigate the performance and stability of the Pd-based catalyst-impregnated LSM cathode and develop more stable Pd-based catalysts by the co-impregnation method. The results showed that the co-impregnation of two catalytic species could effectively inhibit the agglomeration of the catalytic nano particles at high temperatures, while at low operating temperatures the agglomeration issue was not very serious. On the other side, a high loading of a catalyst agent increased the possibility of

nano particle agglomeration while a low loading of the same catalyst enhanced the stability of the catalyst nano particles in the microstructure of the electrodes.

7.1. Experimental

LSM cathodes impregnated with Pd and $\text{Pd}_{1-x}\text{M}_x$ ($\text{M}=\text{Co}$, Mn and Ag ; $x = 0.05$ and 0.20) were studied at temperatures of 750 and 850°C . The temperature of 750°C was selected to study the behavior of the Pd-LSM cathode in the intermediate temperature range of SOFCs. But, because the individual arcs of the impedance spectra of the Pd-LSM electrode at 750°C were merged together and the details of the arcs are not clear, a higher temperature of 850°C was also selected for the measurements. The cathode samples with 0.08 and 0.25 mg cm^{-2} catalyst loadings were used to investigate the effect of loading on the performance and stability of the cathodes. After the infiltration treatment, the cells were heated at 700°C for the deposition of the impregnated catalyst solution and for the formation of the PdO-based nano particles in the microstructure of the LSM electrodes. The loading of 0.25 mg cm^{-2} PdO was selected as the high loading for the experiments as the primary microstructural studies showed that at this loading, right after the calcinations treatment, most of the electrode surface was covered by the catalyst nano particles. A loading of 0.08 mg cm^{-2} PdO was the loading at which the catalytic properties of the Pd-LSM electrode were well activated, while the catalyst nano particles were individually arranged on the catalyst surface and the chance for sintering of the particles together was minimized. Impedance spectroscopy and polarization measurements were used for the electrochemical evaluation of the impregnated cathodes and the microstructure of the electrode was studied by FESEM. YSZ electrolyte with

respective thickness and diameter of about 0.7 and 19 mm was used as the electrolyte. Pt paste was used as counter and reference electrodes and the LSM was sintered at the temperature of 1100°C for 2 h.

7.2. Effect of PdO catalyst loading

It is well known that the effectiveness of palladium as oxidation catalysts depends strongly on its complex reaction with gas-phase oxygen to form surface PdO or non-stoichiometry PdO_x and on the redox reactions, which in turn is a complex function of temperature and oxygen partial pressure [170, 171]. The TGA results by Liang et al indicate that there is a phase transfer between PdO and metallic Pd at a temperature of about 830°C in air [139]. The calculation of Gibbs free energy of formation of PdO using a mathematical formula as suggested by Nell and O'Neill [179] indicates that $\Delta G_{\text{PdO}}^{\text{f}}$ at a temperature around 869°C becomes zero. By increasing the temperature above 869°C the palladium species turns from PdO to Pd. Thus it is interesting and important to study the chemical states of the palladium catalyst at the test conditions of this study. Figure 7.1 shows the XRD spectra for the palladium samples heat-treated at 800 and 900°C in air. The results show that at 800°C palladium primarily exists in the form of PdO. This is consistent with the observations that the impregnated palladium mainly exists as PdO in the case of Pd-impregnated LSM/YSZ composite cathode calcined at 750°C [135]. As the temperature increased to 900°C, metallic palladium species is dominant, however a trace of PdO is also observed. This indicates that the impregnated palladium nano particles in the LSM cathode may exist as Pd/PdO or non-stoichiometry PdO_x, depending on the temperature and oxygen partial pressure, which in turn is related to the overpotential or

current in the case of fuel cell reactions. Thus, it should be emphasized here that the use of Pd catalysts and PdO catalysts loading instead of Pd/PdO or PdO_x catalysts in the present study is for the purpose of simplicity.

Figure 7.1 XRD spectra for palladium oxide samples heat treated at 800 and 900°C in air for 1h

The effect of PdO catalyst loading on the performance and stability of the LSM cathode was studied on the electrodes impregnated with 0.08 and 0.25 mg cm⁻² PdO catalysts. Figure 7.2 is the impedance spectra for the O₂ reduction reaction on Pd-impregnated LSM electrodes before and after the polarization treatment at 850°C and 200 mA cm⁻² in air for 2, 22 and 44 h. For the pure LSM electrode without palladium impregnation the electrochemical impedance responses are characterized by a large and depressed impedance arc and the electrode polarization resistance of the LSM electrode is 2.05 Ωcm² before the polarization treatment (Figure 7.2a). With the polarization treatment at 200 mA cm⁻², the impedance arc decreased significantly and after polarized for 44 h, the electrode polarization resistance decreased to 0.15 Ωcm², much smaller than

2.05 Ωcm^2 at the beginning of the polarization treatment. The significant reduction in the electrode polarization resistance for the reaction on the LSM cathode with the polarization treatment is clearly due to the activation effect of the polarization on the electro-catalytic activity of LSM-based cathode [180, 181]. The impedance responses after polarized for 44 h (inset graph, Figure 7.2a) clearly show the separation and existence of three semicircles at high, medium and low frequencies, indicating the presence of at least three electrode steps for the O_2 reduction on LSM cathode at 850°C, consistent with results in the literature [182-184]. For the LSM electrode impregnated with 0.08 mg cm^{-2} PdO catalyst loading, the impedance arc also decreased significantly and after polarization at 200 mA cm^{-2} for 44h, the ASR is 0.018 Ωcm^2 (inset graph, Figure 7.2b), 8 times smaller than 0.15 Ωcm^2 measured on pure LSM under identical polarization treatment conditions. For the LSM electrode with a higher loading of 0.25 mg cm^{-2} PdO, the polarization resistance after polarization at 200 mA cm^{-2} for 44h is 0.28 Ωcm^2 (inset graph, Figure 7.2c), even higher than 0.15 Ωcm^2 measured on pure LSM under identical polarization treatment conditions. This shows that high palladium catalyst loading is detrimental to the electrochemical activity of LSM cathode and this may be the reason for the contradictory reports regarding the enhancement of palladium to the activity of LSM cathodes [185, 186].

Figure 7.2 Electrochemical impedance spectra for O₂ reduction reactions on (a) pure LSM, (b) 0.08 mg cm⁻² Pd-impregnated LSM and (c) 0.25 mg cm⁻² Pd-impregnated LSM electrodes at 850°C. The impedance curves were measured at open circuit potential before and after polarized at 200 mA cm⁻² for different periods. The insets show enlarged graphs of the impedance spectra after polarized for 44 h. The numbers in the graphs are frequencies in Hz

Figure 7.3 shows the polarization curves for LSM cathodes at low and high loading of Pd catalyst at 850°C and 200 mA cm⁻². The electrode polarization resistance, R_E , and ohmic resistance, R_Ω were obtained from the electrochemical impedance curves and overpotential, η , was obtained by subtracting the iR losses from the measured cathodic polarization potential, E_{cathode} . Similar to the impedance behavior, polarization potential for the O₂ reduction on pure and Pd-impregnated LSM cathodes decreased significantly with the cathodic polarization (Figure 7.3a). For the reaction on 0.08 mg cm⁻² Pd-impregnated LSM, the cathode overpotential is 21 mV after polarized for 44 h, significantly smaller than 130 mV in the case of pure LSM cathode measured under the same polarization conditions. This indicates the addition of the Pd/PdO nano particles significantly promotes the electro-catalytic activity of the LSM cathode. In the case of LSM with high PdO catalyst loading of 0.25 mg cm⁻² the initial overpotential is low, 17 mV under a cathodic current of 200 mA cm⁻², but it gradually increases with the polarization and finally reached ~44 mV, which is higher than 21 mV for the reaction on a LSM with a low PdO catalyst loading of 0.08 mg cm⁻². This shows that high catalytic loading is not beneficial for the stability of the electro-catalytic activity of the LSM cathode.

Figure 7.3 Polarization performance for (a) pure LSM, (b) 0.08 mg cm^{-2} PdO/LSM and (c) 0.25 mg cm^{-2} PdO/LSM electrodes at 850°C and 200 mA cm^{-2} for 44 h in air

Bidrawn et al [187] reported that the calcination temperature of the LSM/YSZ cathode influences the catalytic effect of added dopants on the LSM/YSZ cathodes and concluded that the observed enhancing effect as a result of addition of a catalyst agent is associated with electrode structure, and not the electrochemical or catalytic activity enhancement. Other reports correlate the performance enhancements to the catalytic activity of the infiltrated materials [132, 133]. The fact that sputtering of a very thin layer of Pt metal on the surface of cathode electrode cause a significant enhancement in cathode overpotential [133] suggest that change in electrode structure might not be the only reason for performance enhancement. As explained in Chapter 4, spillover of the gas molecules over the catalytic agents is probably one of the major enhancement mechanisms in catalyst promoted electrodes.

The polarization behavior of LSM cathode without and with Pd impregnation was also studied at 750°C and 100 mA cm⁻². Figure 7.4 shows the plots of overpotential of the O₂ reduction reaction on pure LSM and Pd promoted LSM electrodes with different PdO catalyst loadings at 750°C. The cathode overpotential increased with the polarization time and reached a maximum after polarized for ~500 min, followed by a steady decrease with the polarization time. The dependence of the overpotential on the polarization time appears to be different from that observed at a higher temperature of 850°C. At this stage the reasons for the appearance of the maximum peak of the overpotential with the current passage time are not clear. Similar to that observed at 850°C addition of Pd catalyst also remarkably decreases the overpotential of the reaction on LSM cathode at 750°C. In the case of pure LSM, the overpotential for the reaction after polarization for 44 h is ~400 mV, significantly higher than ~100 mV for 0.08 mg cm⁻² Pd-impregnated LSM and ~90

mV for 0.25 mg cm^{-2} impregnated LSM. Pure Co, Mn and Rh were also infiltrated to the LSM cathode, but no remarkable enhancing effect was observed.

Figure 7.4 Cathode overpotentials versus time for pure LSM, 0.08 mg cm^{-2} PdO/LSM and 0.25 mg cm^{-2} PdO/LSM cathodes at 750°C and 100 mA cm^{-2}

7.3. Effect of co-infiltration with Co, Mn and Ag

Cobalt, manganese and silver were co-infiltrated with palladium during the impregnation treatments. Figure 7.5 shows plots of overpotential versus polarization time for the LSM cathodes impregnated with Pd-Mn, Pd-Co and Pd-Ag solutions with composition of 5 and 20 mol% of co-infiltrated Mn, Co and Ag, measured at 850°C and 200 mA cm^{-2} . The infiltrated catalyst loading was 0.08 mg cm^{-2} . The overpotential data for Co and Mn impregnated LSM cathode is also included in Figure 7.5 for comparison.

As shown in Figure 7.5, the performance and stability of the catalyst impregnated LSM cathodes depend strongly on the composition of the Pd-Mn, Pd-Co and Pd-Ag catalyst solutions. In the case of Pd-Mn and Pd-Co, $\text{Pd}_{0.95}\text{Mn}_{0.05}$ and $\text{Pd}_{0.95}\text{Co}_{0.05}$ -infiltrated LSM cathodes show a substantially low overpotential for the O_2 reduction reaction as compared to that on pure Co and Mn and on the $\text{Pd}_{0.8}\text{Mn}_{0.2}$ and $\text{Pd}_{0.8}\text{Co}_{0.2}$ -infiltrated LSM cathodes. The reason may be due to the low solubility of cobalt and manganese oxides with palladium and in the case of the $\text{Pd}_{0.8}\text{Mn}_{0.2}$ and $\text{Pd}_{0.8}\text{Co}_{0.2}$ infiltrated LSM, cobalt and manganese oxides could be segregated and co-exist with palladium [188]. The segregated cobalt and manganese oxides are not electro-catalytically active for the O_2 reduction reaction at high temperatures, resulting in the high overpotential as shown by the high overpotentials of Co and Mn-impregnated LSM cathodes (Figure 7.5). Sholklapper et al recently [141] investigated the performance of Ag-LSM cathode electrode and showed the enhancement of infiltrated Ag to the activity of LSM cathodes. Both $\text{Pd}_{0.95}\text{Ag}_{0.05}$ and $\text{Pd}_{0.8}\text{Ag}_{0.2}$ infiltrated LSM cathodes show good performance and stability, indicating the co-impregnation of Pd and Ag may result in alloy formation, leading to the improved stability of the Pd based catalyst [189]. The best performance and performance stability were observed on the LSM cathodes impregnated with 0.08 mg cm^{-2} $\text{Pd}_{0.95}\text{Co}_{0.05}$ and $\text{Pd}_{0.8}\text{Ag}_{0.2}$. The degradation in performance for the O_2 reduction reaction is negligible.

Figure 7.5 Cathode overpotentials as a function of polarization time for LSM cathodes co-impregnated with Pd-Mn, Pd-Co and Pd-Ag with 5 or 20% Mn, Co and Ag and pure Co and Mn in the impregnation solutions. The catalyst loading is 0.08 mg cm^{-2} and the polarization is carried out at 850°C and 200 mA cm^{-2}

Figure 7.6 is the plots of the overpotentials for the O_2 reduction reaction on LSM cathodes impregnated with Pd, $\text{Pd}_{0.95}\text{Co}_{0.05}$ and $\text{Pd}_{0.8}\text{Ag}_{0.2}$ catalyst as a function of polarization at 200 mA cm^{-2} and 850°C (Figure 7.6a) and 100 mA cm^{-2} and 750°C (Figure 7.6b). The catalyst loading was 0.25 mg cm^{-2} . At 850°C , performance of the Pd-impregnated LSM cathode showed stable performance for the initial ~ 700 min and then degraded significantly with the polarization time (Figure 7.6a), indicating that instability of Pd-impregnated LSM cathode. The significant increase in the overpotential for the reaction on Pd-impregnated LSM cathodes is most likely due to the significant grain growth of impregnated Pd/PdO nano particles [190]. The performance stability of the both $\text{Pd}_{0.95}\text{Co}_{0.05}$ and $\text{Pd}_{0.8}\text{Ag}_{0.2}$ infiltrated LSM cathodes improved significantly and there

is basically no considerable change in the overpotential during the polarization period of 2500 min at 850°C. In the case of Pd_{0.95}Co_{0.05} infiltrated LSM cathode, cobalt could substitute palladium site to form Pd_{0.95}Co_{0.05}O solid solutions, similar to Pd_{0.95}Mn_{0.05}O as reported earlier [190]. For Pd-Ag system, the formation of PdAg solid solution occurs in a wide range of Pd and Ag compositions [191]. Thus the good stability of the Pd_{0.95}Co_{0.05} and Pd_{0.8}Ag_{0.2} infiltrated LSM cathodes could be attributed to the formation of Pd_{0.95}Co_{0.05}O and Pd_{0.8}Ag_{0.2}O solid solution nano particles.

Figure 7.6 Cathode overpotentials as a function of polarization time for LSM cathodes impregnated with PdO, Pd_{0.95}Co_{0.05} and Pd_{0.8}Ag_{0.2} catalysts at (a) 850 and (b) 750°C. The catalyst loading is 0.25 mg cm⁻² and polarization is carried out at 100 and 200 mA cm⁻² at 750 and 850°C, respectively

Similar results were also observed for the reaction at 750°C (Figure 7.6b). The co-infiltration of Pd_{0.8}Ag_{0.2} and Pd_{0.95}Co_{0.05} catalysts not only increases the electro-catalytic activity of the LSM cathode for the O₂ reduction reaction but also enhances significantly the performance stability. As shown in Figure 7.6, LSM cathodes impregnated with Pd_{0.8}Ag_{0.2} and Pd_{0.95}Co_{0.05} catalysts show significantly lower overpotential and are stable over the test period of 44h at both 750 and 850°C. LSM cathode impregnated with Pd_{0.8}Ag_{0.2} catalysts showed a slightly better performance as compared to that impregnated with Pd_{0.95}Co_{0.05} catalysts especially at 850°C.

7.4. Microstructure of impregnated LSM electrodes

The microstructure of Pd and co-infiltrated LSM electrodes was examined by SEM. Figure 7.7a shows SEM micrograph of palladium particle distribution on the surface of a 0.08 mg cm⁻² Pd-impregnated LSM cathode before the polarization test. PdO particles with particle size of ~20 nm on the surface of LSM grains were observable. After polarization test at 100 mA cm⁻² and 750°C for 44h, PdO particles grow and the average particle size is around 30-40 nm (Figure 7.7b). With the increase of the operation temperature to 850°C the Pd catalyst particles grow significantly to 70-90 nm after polarized for 44 h for the reaction on the Pd-impregnated LSM with the same PdO loading of 0.08 mg cm⁻² (Figure 7.7c). In the case of Pd-impregnated LSM electrodes with a high PdO loading of 0.25 mg cm⁻², significant agglomeration of the catalyst particles can be seen after polarized at 850°C for 44h (shown by arrow in Figure 7.7d). The size of the agglomerates is as high as 1200 nm. For the Pd promoted LSM electrode

system, the growth and agglomeration of Pd catalyst particle growth at 850°C is significant as compared to that operated at 750°C. This shows that the grain growth and agglomeration depend strongly on the operation temperature as well as the catalyst loading. Agglomeration and sintering of the catalyst particles decreases the active surface area of the catalyst and consequently decreases catalytic activity for the oxygen reduction process. This explains the significant overpotential increase for the O₂ reduction reaction on the 0.25 mg cm⁻² Pd-impregnated LSM cathodes polarized at 200 mAcm⁻² and 850°C (Figure 7.6a).

Figure 7.7 SEM micrographs of PdO-impregnated LSM cathode electrodes with (a) 0.08 mg cm^{-2} PdO before polarization, (b) 0.08 mg cm^{-2} PdO after polarization at 750°C , (c) 0.08 mg cm^{-2} PdO after polarization at 850°C and (d) 0.25 mg cm^{-2} PdO after polarization at 850°C . The arrow in (d) points at bigger PdO agglomerates

Grain growth was also observed for the co-infiltrated LSM electrodes. Figure 7.8a shows SEM micrograph of a 0.25 mg cm^{-2} $\text{Pd}_{0.8}\text{Ag}_{0.2}$ -infiltrated LSM electrode after polarized at 200 mA cm^{-2} and 850°C for 44 h. The size of the $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ catalyst particles grew to 70-100 nm, significantly larger than the original size of $\sim 20 \text{ nm}$ (the

original particle size of $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ was similar to PdO , see Figure 7.7a). However, different from 0.25 mg cm^{-2} Pd-infiltrated LSM cathode (see Figure 7.7d), there is no significant agglomeration of infiltrated $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ catalytic particles. $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ particles are uniformly distributed on the LSM grain surface and LSM grain boundaries (Figure 7.8a). Presence of well separated individual $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ particles in the LSM cathodes is likely the reason for the enhanced stability of the LSM cathode with co-infiltrated catalyst. On the other hand, there is a formation of distinct crystal facets on the $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ catalyst nano particles (see Figure 7.8b). The presence of crystal facets on the catalyst nano particles could be beneficial for the O_2 reduction reaction, similar to the high activity reported for the O_2 reduction reaction on faceted Pt nano particles in proton exchange membrane fuel cells [192].

Figure 7.8 SEM micrographs of 0.25 mg cm^{-2} $\text{Pd}_{0.8}\text{Ag}_{0.2}$ -impregnated LSM cathode electrode after polarization at 850°C and 200 mA cm^{-2} with a high magnification view shown in (b)

7.5. Summary

Performance and stability of LSM cathode electrodes impregnated with Pd and Pd-Mn, Pd-Co and Pd-Ag were investigated at catalyst loadings of 0.08 and 0.25 mg cm^{-2} and operation temperatures of 750 and 850°C . Addition of 0.08 mg cm^{-2} PdO to the LSM cathode substantially decreased the cathode overpotentials from about 130 to 21 mV and the performance of the cell was quite reasonable during 44 polarization of the cell. The higher catalyst loading of 0.25 mg cm^{-2} was detrimental to the performance stability particularly at the operation temperature of 850°C . The instability of the cell was mainly due to agglomeration and grain growth of the PdO catalyst nano particles at the SOFC operation temperature. Co-impregnation of Pd with Mn, Co and Ag mitigated the agglomeration and sintering, and among the catalyst systems tested, $\text{Pd}_{0.8}\text{Ag}_{0.2}$ and $\text{Pd}_{0.95}\text{Co}_{0.05}$ compositions showed significantly enhanced performance and good stability.

In the case of the LSM impregnated with Pd_{0.8}Ag_{0.2} nano particles, the formation of special crystallographic orientation and facets on the surface of the Pd_{0.8}Ag_{0.2} nano particles could also be beneficial for the O₂ reduction reaction. The results indicated that the co-impregnation was effective to enhance the activity and improve the stability of the SOFC cathodes.

CHAPTER EIGHT

8. Conclusions and Recommendations

8.1. Conclusions

The main objective of this PhD project was to systematically study the mechanisms and kinetics of the oxidation reactions of different fuels including H_2 , CH_4 , CH_3OH and C_2H_5OH , which took place over Pd-impregnated electrodes such as Ni/GDC and LCCM/GDC anodes under a wide range of temperatures. The stability of the Pd based catalyst-impregnated LSM cathodes for O_2 reduction reactions was also investigated. Based on the results obtained in this research, the following main conclusions were drawn:

- ✓ The electrode polarization resistances of the fuel oxidation reactions decreased significantly as a result of the presence of Pd nanoparticles in the anode microstructures. However, in the cases of hydrocarbon fuels; carbon deposition was not suppressed over the Ni/GDC cermet anodes.
- ✓ The major function of the Pd nanoparticles was to decrease the electrode impedance associated with the adsorption, dissociation and diffusion processes in the Ni/GDC electrodes, while the charge transfer process was not affected by the presence of Pd nanoparticles.

- ✓ The activation energies of the adsorption, dissociation and diffusion processes of the anodic reactions over the Ni/GDC anodes decreased significantly as a function of impregnated Pd loading.
- ✓ The significantly enhanced adsorption and diffusion processes by the impregnated Pd nanoparticles were considered to be related to the significantly promoted hydrogen and oxygen spillovers over the Pd/PdO redox couple and the hydrogen permeability through the Pd phase.
- ✓ Addition of the Pd nanoparticles to the LCCM/GDC composite anodes significantly improved the electro-catalytic activities of the anodes for the oxidation reactions of both H_2 and CH_4 .
- ✓ The impregnation of the Pd nanoparticles in the electrodes also significantly changed the impedance behavior of the reactions. In the case of CH_4 oxidation reactions, the impregnation of the Pd nanoparticles in the LCCM/GDC composite anodes led to the disappearance of the low frequency diffusion tails and the evolution of the impedance arcs at medium and low frequencies.
- ✓ The stable and close polarization potentials of the Pd-impregnated LCCM/GDC composite anodes in H_2 before and after exposure to CH_4 for 20 h indicated that the exposure of the Pd-impregnated LCCM/GDC anodes in CH_4 had no detrimental effect on the performance and activity of the anodes under the conditions studied.
- ✓ No carbon deposits were detected on the Pd-impregnated LCCM/GDC composite anodes after the tests with the CH_4 fuel.

- ✓ Addition of 0.08 mg cm^{-2} Pd/PdO to the LSM cathodes substantially decreased the cathode overpotentials from about 130 to 21 mV and the performance of the fuel cell was quite reasonable during the polarization of the cell for 44 h.
- ✓ A high catalyst loading of 0.25 mg cm^{-2} was detrimental to the performance stability of the LSM cathodes, in particular, at the operation temperature of 850°C . The instability of the LSM cathodes was mainly due to the significant agglomeration and grain growth of the Pd nanoparticles at SOFC operation temperatures.
- ✓ The co-impregnation of Pd with Mn, Co and Ag mitigated the agglomeration and sintering, and among the catalyst systems tested, $\text{Pd}_{0.8}\text{Ag}_{0.2}$ and $\text{Pd}_{0.95}\text{Co}_{0.05}$ compositions showed more significantly enhanced performance and stability.
- ✓ In the case of LSM cathodes impregnated with the $\text{Pd}_{0.8}\text{Ag}_{0.2}$ nanoparticles, the formation of special crystallographic orientation and facets on the surfaces of the $\text{Pd}_{0.8}\text{Ag}_{0.2}$ nanoparticles could also be beneficial for the O_2 reduction reactions.
- ✓ The co-impregnation not only enhanced the stability of the SOFC cathodes, but also the electrochemical activities of the catalyst phases compared to the pure Pd.

8.2. Novelty and contributions

- The Ni/GDC and LCCM/GDC anode electrodes promoted by the Pd nanoparticles based catalysts were investigated for various hydrogen and hydrocarbon oxidation reactions for the first time in this PhD research.

- Use of Pd nanoparticles as a catalyst clearly disclosed the presence of different steps in the oxidation reactions of hydrogen and hydrocarbons via electrochemical impedance spectroscopic measurements.
- The effects of the presence of the Pd nanoparticles on reducing the activation energies of adsorption/dissociation/diffusion processes of the reactions were systematically studied with electrochemical measurements.
- The different steps of the fuel oxidation reactions were studied under a dc bias.
- The Pd-Ag alloys were also successfully explored to improve the performance and stability of the cathode electrodes for the first time.

8.3. Recommendations

- The promoting effect of Pd on different composite anode materials (non-GDC) might be studied to obtain a more comprehensive database for a better understanding of the proposed spillover mechanism for SOFC electrodes.
- The idea of coke free operation of conventional Ni-containing anode materials in hydrocarbon fuels under low operating temperature and high current density [112, 193] can be exploited for the development of Pd promoted anodes as the previous experimental results have shown effectiveness of some Pd based catalysts in enhancing the performance and lowering the operating temperature of SOFC.
- Catalyst materials other than Pd, such as Pt and Ru, on GDC based anodes can be explored to see whether they have a similar splitting phenomenon in the

impedance curve. Then, similar set of experiments can be repeated to conclude similar or different promoting role of catalysts materials.

- Based on the promising performance of Pd/Ag alloy catalyst, the Pd/Ag alloys may also be applied to some other cathode and anode materials [194] especially for low temperature operations of SOFCs.
- Combination of catalytic analysis of Pd-impregnated Ni/GDC for methane, methanol and ethanol reforming and partial oxidation reaction with the electrochemical analysis could be effective to evaluate the reaction steps under SOFC operation condition.

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