Anodes for Solid Oxide Fuel Cells Operating at Low Temperatures

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Anodes for Solid Oxide Fuel Cells Operating at Low Temperatures

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A thesis submitted in fulfillment of the requirement for the award of the Degree of Doctor of Philosophy

Department of Energy Conversion and Storage, Risø Campus

TECHNICAL UNIVERSITY OF DENMARK

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'Possession of knowledge lies in the art of awakening one’s natural curiosity'
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Mohammed Hussain, Risø DTU
Abstract

An important issue that has limited the potential of Solid Oxide Fuel Cells (SOFCs) for portable applications is its high operating temperatures (800-1000 °C). Lowering the operating temperature of SOFCs to 400-600 °C enables a wider material selection, reduced degradation and increased lifetime. On the other hand, low-temperature operation poses serious challenges to the electrode performance. Effective catalysts, redox stable electrodes with improved microstructures are the prime requisite for the development of efficient SOFC anodes.

The performance of Nb-doped $SrTiO_3$ (STN) ceramic anodes with various loadings of Ni-CGO by infiltration technology is illustrated. The Knudsen and bulk gas phase diffusion in the porous electrode and its influence on the gas diffusion impedance have been studied in detail. The new contributions of these studies include combined electrocatalysts materials (Ni, Pt, Pd, Ru and CGO (Gd-doped $CeO_2$)), which could significantly enhance the electrode performances. The best electrode performance is obtained using ternary catalyst i.e., anode polarization resistance of 0.1 and 0.3 $\Omega cm^2$ at 600 and 500°C, respectively for the combination of Pt, Ni and a CGO. At 400°C, the polarization resistance was 2 $\Omega cm^2$, these values were determined in moisturized hydrogen.

STN based ceramic anodes have been prepared with the novel concept of a palladium functional layer at the interface of electrode/electrolyte. Pd nanoparticles formed at the interface have a significant effect in reducing the polarization losses compared to Pd-CGO infiltrated anodes without modifications. Similarly, the interfacial modification of the electrode/electrolyte with a ceramic functional layer (e.g. CGO) infiltrated with Pd-CGO electrocatalysts, yielded rather a low polarization resistance of 1.5 $\Omega cm^2$ at 400°C. The potential of using $WO_3$ ceramic as an alternative anode materials has been explored. The relatively high electrode polarization resistance obtained, 11 $\Omega cm^2$ at 600 °C, proved the inadequate catalytic activity of this system for hydrogen oxidation. At the end of this thesis, an investigation on the effect of application of cathodic polarization on Ni-YSZ anodes is described.
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Chapter 1

Introduction

Fuel cells are promising energy conversion devices for pollution free sustainable energy production. Among the various types of fuel cells, solid oxide fuel cells (SOFCs) and molten carbonate fuel cells (MCFCs) operate at high temperatures (800-1000 °C). One of the earliest study (1937) on SOFC was reported by Baur and Preis[1]. SOFC has the ability to convert various fuels (hydrogen, natural gas, methane, methanol etc..) in to electrical energy. Other significant advantages of SOFCs includes [2],

- High power conversion efficiencies not limited by the Carnot efficiency as in the case of combustion type systems.
- Continuous power generation for long periods without maintenance.
- The size and shape (modularity) of the SOFCs are independent of performance.
- The major technological impact of SOFCs developed are due to its combined heat and power (CHP) management capability[3], which provides an opportunity in various stationary fuel cells application including residential applications (1-10 kW), building industry (25-250 kW) and large power plants (>1000 kW)[4].

The recent research on SOFCs have been focused on lowering the operating temperature in the range of 500-800 °C. Low temperature operation of SOFCs might provide improved start-up and shutdown cycles facilitating its usage in portable and mobile applications (e.g., electronics, military and transportation sector, 1-
10 kW). Moreover, lowering the operating temperature enables wider range of materials selection and use of lower cost materials. Other major benefits include stability and reliability of SOFC components. An extensive research is still underway to introduce commercially viable, cost effective intermediate temperature SOFCs (IT-SOFCs) into the market. The major challenges faced by researchers in the development of IT-SOFCs besides 'stability issues' are

- Low ionic conductivities of electrolyte materials (ohmic losses).
- Charge transfer at the electrode/electrolyte interfaces (activation and polarization losses) and,
- Mass transfer limitations (concentration losses).

Reducing the ohmic resistance of the electrolyte is significant at low temperatures of operation. Various attempts were made to improve the ionic conductivity in electrolyte materials. One such attempt has been to reduce the thickness of the electrolyte. However, the majority of the losses in SOFC i.e., 23 and 56 % were from anode and cathode, respectively measured in $H_2 / 25\% H_2O$[5] Hence, focus is required to develop electrode materials for efficient SOFCs production.

### 1.1 Principle of Solid Oxide Fuel Cells

SOFCs are solid state electrochemical cell that converts chemical energy from fuels into useful electrical energy by electrochemical combustion reactions. A continuous flow of fuel gas such as hydrogen to the anode compartment and air or oxygen to the cathode compartment is required for the electrochemical combustion of $H_2$ and $O_2$. Oxidation of $H_2$ (HOR) and reduction of $O_2$ (ORR) takes place at anode and cathode compartment, respectively with $H_2O$ as by-product. An electrolyte e.g., YSZ ($Y_2O_3$-stabilized $ZrO_2$) is a dense gas impermeable ceramic, which physically separate the anode from the cathode compartment i.e., the electrolyte prevents the direct combustion of $H_2$ with oxidant gas. The flow of electrons from anode is forced towards the cathode through an external load resulting in an electric current. Figure 1.1 is a schematic representation of the SOFC working principle.

Both electrodes must be porous and should be electron and oxide ion. Owing to the $O_2$ partial pressure ($pO_2$) differences between cathode ($pO_2=1$ to
0.01 atm) and anode ($pO_2 = 10^{-13}$ to $10^{-27}$ atm) compartment, the change in chemical potential results in diffusion of $O^2−$ ion through the electrolyte and the electrochemical combustion reactions take place in each compartment as described.

At the anode compartment, $H_2$ dissociates and electrochemically react with oxygen ions, $O^2−$ to give away the electrons to the external circuit. The half cell reaction at the anode compartment can be written as,

$$H_2 + O^2− \rightarrow H_2O + 2e−$$

Cermet of metal and ceramic e.g., Ni-YSZ is a well established anode materials used in SOFC.

At the anode compartment, $O_2$ is reduced into $O^2−$ ions by the electrons received from the anode compartment through the external circuit. The half cell reaction in the cathode compartment is given by,

$$\frac{1}{2}O_2 + 2e− \rightarrow O^2−$$

The well known cathode materials are perovskite type oxides e.g., LSM
(La$_{0.9}$Sr$_{0.1}$MnO$_{3-\delta}$) and LSCF (La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$).

The overall electrochemical reaction of a SOFC is expressed as,

\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \]

At open circuit voltage (OCV), an equilibrium has been established between the diffusional force of oxide ions and electric field. This results in a Nernst-Voltage ($E_N$) between the anode and cathode, which is given by equation 1.1

\[ E_N = \frac{RT}{n_f} \ln \left( \frac{P_{O_2}^{\text{anode}}}{P_{O_2}^{\text{cathode}}} \right) \quad (1.1) \]

$E_N$ in terms of Gibbs free energy ($\Delta G$) is expressed by the equation 1.2

\[ E_N = -\frac{\Delta G}{n_f} \quad (1.2) \]

The temperature and partial pressure dependence of $\Delta G$ is expressed by equation 1.3

\[ \Delta G = \Delta G_o + RT \ln \left( \frac{P_{H_2O}^{\text{anode}} \sqrt{P_{H_2}^{\text{anode}}}}{P_{O_2}^{\text{cathode}} \sqrt{P_{O_2}^{\text{cathode}}}} \right) \quad (1.3) \]

where, $\Delta G_o$ is the standard Gibbs free energy. Substituting equation 1.3 in 1.2 yields equation 1.4, a Nernst-Voltage of a SOFC.

\[ E_N = -\frac{\Delta G}{n_f} - \frac{RT}{2f} \ln \left( \frac{P_{H_2O}^{\text{anode}}}{P_{O_2}^{\text{cathode}} \sqrt{P_{H_2}^{\text{anode}}}} \right) \quad (1.4) \]
1.2 SOFC Performance, Losses and Evaluation

The performance of SOFCs are measured as the voltage output as the function of current drawn. The current-voltage characteristics indicating the different losses in a SOFC are shown in Figure 1.2. The deviations in cell voltage \( E \) at a given current density relative to Nernst-Voltage \( E_N \) are polarization losses (overpotential, \( \eta \)), which is given by the expression 1.5

\[
E = E_N - \eta_{activation} - \eta_{ohmic} - \eta_{concentration}
\]  

Kinetic losses, such as activation loss, \( \eta_{activation} \) are associated with charge transfer at the interface of electrode and electrolyte, which is described as a barrier to prevent the spontaneous reactions and requires an activation energy to overcome this barrier. Activation loss (charge transfer limitation) illustrates the absorption-desorption chemistry of the electrochemically active species of the fuel gas (\( H_2 \)) at the three phase boundary (TPB) i.e., electrode, electrolyte and the fuel gas are in contact. Butler-Volmer equation describes the effect of activation polarization or loss on the current density. However, multiple reaction steps and variation in reaction rate depending on the electrode microstructure and catalyst used makes the determination of rate limiting step as complex entity.

The ohmic losses, \( \eta_{ohmic} \) primarily arising from the ionic and electronic conduction limitation in electrolyte and electrode materials, respectively. At low temperature, the electrolyte ohmic resistance dominates this overpotential depending on the ionic conductivity of the electrolyte used; furthermore, a small contribution is observed from the conductivity of electrodes and current collector. One of the major drawbacks of using highly conductive mixed ionic and electronic composites (MIEC) electrolyte materials is leakage current associated with its high transference number i.e., a ratio of electronic conductivity to that of total conductivity at low \( pO_2 \). In general, MIEC electrolytes, for example, CGO (Gd-doped \( CeO_2 \)) shows a leakage current at low \( pO_2 \) leading to a drop in theoretical voltage as shown in the figure 1.2.

The mass transfer limitations (concentration loss), \( \eta_{concentration} \) at high current densities are due to the gas diffusion and conversion. Gas diffusional limitation arises due to slow mass transfer of the gases to the porous electrodes mainly owing to its microstructure.
1.2.1 Electrochemical Impedance Analysis

Electrochemical impedance spectroscopy (EIS) is an important tool to analyse the loss contribution in SOFC. The impedance of an electrochemical system is determined by applying an AC potential and measuring the current and phase displacement through the system or by applying a current signal (AC) and measuring the resulted voltage and phase displacement. Electrochemical impedance in SOFC is measured using a small excitation signal (5-50mV) in order get a linear response. The applied excitation voltage depends on the cell impedance. With an application of excitation signal \( E_t = E_0 \sin(\omega t) \), results in a current signal \( I_t = I_0 \sin(\omega t + \phi) \), which has the same sinusoidal response as that of the applied voltage, but with a phase shift \( \phi \). The impedance \( Z \) is a ratio of applied voltage to that of resulted current signal\[6\].

Impedance, \( Z(\omega) \) as a complex quantity is represented in equation\[1.6\],

\[
Z(\omega) = \frac{E_t}{I_t} = \frac{E_0 \exp(j\omega t)}{I_0 \exp(j\omega t - \phi)} = Z_0 \exp(j\phi) = Z_0(\cos\phi + jsin\phi) \tag{1.6}
\]

where, \( Z_0 \) is the magnitude of the impedance with the phase shift \( \phi \).
The impedance of an electrochemical cell in a defined frequency range for example, 1MHz to 0.1 Hz is represented by plotting the real part of the complex impedance on the X-axis and the imaginary part on the Y-axis. The resulted plot is shown in Figure 1.3. The high frequency intercept of the semicircle essentially indicates the ohmic resistance of the cell (electrolyte, electrode and current collector) and the low frequency intercept is similar to the resistance value calculated from the I-V characteristics. The difference between the low frequency and high frequency intercept is the polarization resistance of the electrochemical cell, which is usually a sum of several contributing losses. To analyse the impedance spectrum in detail, an equivalent circuit elements, such as RQs are used. A (RQ) is a resistance (R) in parallel with constant phase element (Q). Each semicircle fitted with a RQ in a impedance spectrum has a characteristics time constant, $\tau_{RQ} = (RQ)^{1/n}$. In case of pure capacitance (a perfect semicircle), n has the value of 1, however in practice one observes a depressed semicircle due to the distributed relaxation times [7].

1.3 Thesis Motivation

Lowering the operating temperature of SOFC has an real impact on its technological advancement. The need to produce high performance SOFC electrodes is a predominant requirement to demonstrate a power efficient SOFC. In particular to anode, consideration of alternative redox stable anode materials and improved catalyst materials are required.
The SOFC 400 project has been focused to demonstrate a SOFC operating at 400°C. The goal of this study has been to improve the electrochemical performance of existing anode materials and to develop new anode materials. An anode area specific resistance (ASR) of 0.5 Ωcm² at 400 °C in H₂ (with YSZ electrolyte) has been set as a target based on the best results reported in the literature. In the course of this project, emphasis has been given to demonstrate highly efficient anodes operating at low temperatures (400-600 °C), which would allow to reach the project target at 500°C, if not at 400°C.

Nanostructured anodes are the preliminary requirement to produce highly efficient anodes. Infiltration technology facilitates for the production of nanostructured anodes. Repetitive infiltration steps is known to improve the performance, but results in unwanted pore filling leading to gas diffusion impedance within the porous electrode. A detailed investigation has been reported in this work on the gas diffusion impedance in the infiltrated anodes.

Understanding the synergistic effect of noble metals - nickel infiltrated nanostructured electrodes has been given importance in this study. Modification of the electrode/electrolyte interface with metal and ceramic catalyst with a novel electrode design and exploiting the potential of new anode material are the other major dimensions of this study.

1.4 Thesis Outline

- Chapter-3 describes the electrochemical performance of Ni-CGO infiltrated electrocatalyst in a STN backbone. Substantial improvement in performance has been achieved with incremental loading of electrocatalyst. The gas diffusion limitations in these infiltrated electrodes have been investigated.

- Chapter-4 is the exploitation of various electrocatalyst materials used in combination with CGO. Binary electrocatalyst such as Pd-CGO, Ru-CGO and Pt-CGO have been electrochemically analyzed with reference to Ni-CGO electrocatalyst. Ternary electrocatalysts, namely Ni-Pd-CGO and Ni-Pt-CGO have also been studied. In addition, the synergistic effect of multicablestall Ni-Pd-Ru-CGO studied using Transmission Electron Microscopy.

- Chapter-5 is about the modification on the electrode/electrolyte interface by
introducing Pd in the form of thin film deposited by sputtering. The electrochemical performance of the Pd modified backbone has been improved and this modification has a greater impact in boosting the performance of Pd-CGO infiltrated STN anodes. The microstructural characterizations using Transmission Electron Microscopy showed the distribution of Pd nanoparticles at the interface.

- Chapter-6 illustrates the modification on the electrode/electrolyte interface by introducing CGO in the form of a thin film deposited by spin coating. Ce is believed to be slightly dissolved in STN backbone. The modification resulted in a drastic reduction in electrochemical performance of the anode. The CGO-modified backbone has been further infiltrated with Pd-CGO electrocatalyst and the electrochemical properties are discussed.

- Chapter-7 concentrates on development of WO$_3$ – CuO anodes for SOFC operating at low temperatures. The preliminary studies have shown a good current collection in WO$_3$-infiltrated W-Cu-YSZ anodes with less adequate catalytic activity for hydrogen oxidation. The high area specific resistance indicates the need for further studies and improvement on this material to demonstrate a working SOFC anode.

- Chapter-8 is a brief review on the effect of application of cathodic bias on a Ni-YSZ anode. A considerable improvement in performance was observed in Ni-YSZ anode with the application of cathodic bias.
Chapter 2

Ceramic Anode, Electrocatalyst And Infiltration Technology

2.1 Ceramic Anode

Strontium titanate (SrTiO$_3$) is an perovskite type oxide having its potential in energy conversion device applications. $ABO_3$ is the structure of ideal perovskite type oxide as shown in Figure 2.1. A-site at the corners of the cubic unit cell is a larger cations (Sr$^{2+}$) with 12-fold coordination. B-site is a smaller cation (Ti$^{4+}$) surrounded by 6-fold octahedral coordination with O$^{2-}$-ions. The two main intrinsic point defects in a host perovskite compound (e.g., SrTiO$_3$) are positively charged strontium and negatively charged oxygen ion vacancies. Aliovalent ions i.e, having difference in valence to that of native atoms (A or B-site), replaced in host compound are dopants. Doping host perovskite compound with aliovalent

![Figure 2.1: Schematic of perovskite oxide structure ($ABO_3$).](image_url)
ions results in creation of extrinsic point defects affecting the properties tremendously. The electroneutrality conditions of the host compound will be affected by aliovalent doping[8].

2.1.1 Niobium-doped Strontium Titanate

Niobium-doped strontium titanate, $Sr_{0.94}Ti_{1-x}Nb_xO_3$, $x<0.2$ is a perovskite type oxide with a donor dopant ($Nb^{5+}$) having higher valence state than that of host cation ($Ti^{4+}$). To balance the effect of substituting the B-site ($Ti^{4+}$) by $Nb^{5+}$, strontium deficiency was introduced. The doping results in an electronic conduction in this material, which was very high in reducing atmosphere (low $P_{O_2}$). Under this reducing condition, a reduction of $Ti^{4+}$ to $Ti^{3+}$ occurs i.e., change in lattice parameter from 0.605 to 0.67 Å for $Ti^{4+}$ to $Ti^{3+}$ due to the increase in ionic radius[9]. This has been also learned from the change in lattice parameter between the $Sr_{0.94}Ti_{1-x}Nb_xO_3$ samples sintered in air and reducing conditions. Based on the defect model for donor-doped $SrTiO_3$, Ti-rich secondary phases is expected to be detected in the reduced samples.

High electronic conductivity (410 and 250 S/cm at 400 and 600 °C, respectively), good redox stability and compatibility with electrolyte (i.e., thermal expansion coefficient of YSZ and $Nb-doped SrTiO_3$ (STN) is $12.1 \times 10^{-6} K^{-1}$ and $10 \times 10^{-6} K^{-1}$, respectively) are the main properties that makes strontium titanates as a potential anode material for LT-SOFCs[9]. Additionally, they are tolerant to carbon and sulfur poisoning, leading to the possible utilization of hydrocarbon fuels. However, high oxide ionic conductivities as well as catalytic activity are required for SOFC anodes and these are the major drawbacks for STN based anodes.

Various attempts had been made to understand the defect transport mechanism of doped-strontium titanates to enhance the ionic conductivity and catalytic activity[10]. Despite the attempts, STN has not been demonstrated as a stand-alone anode for SOFCs due to the high electrode polarization resistance. A composite of STN/YSZ can facilitate oxide ion conductivity in the anode[11]. On the other hand, both catalytic activity and ionic conductivities in STN had been improved with STN/CGO composites prepared by infiltration technology (details in section 2.3).
2.2 Reaction Pathways and Catalyst Materials

The stability of the surface-adsorbed $H_2$ (hydrogen spillover) and $O_2$ (oxygen spillover) on various transitional metals were calculated in literature using density-functional theory (DFT)[12]. Oxygen spillover and hydrogen spillover on the surface of the Ni are the two predominant reactions mechanism described to investigate the catalytic activity for SOFC anodes.

The ability of the metals to attract oxygen have an influence on its catalytic activity. Ni has a highest catalytic activity with intermediate oxygen adsorption energy. The simplified scheme for oxygen spillover pathway for Ni is shown below[12]

$$O_2^{−}(ads, electrolyte)+H_2(gas) \leftrightarrow O^*(ads, Ni)+H_2(gas)+2e− \leftrightarrow H_2O(gas)+2e^−$$

Figure 2.2 illustrates the formation of electrochemically active species at the TPB of Ni-YSZ anode as a result of hydrogen oxidation illustrated by hydrogen spillover mechanism[13]. The rate at which the reactions proceeds on the electrode surface depends on the coverage of the species absorbed on the catalyst used and the temperature.

Figure 2.2: Electrochemical active species on Ni-YSZ anode (Hydrogen spillover mechanism). Image: courtesy of Jens Høgh.
The catalyst is either a metal or ceramic oxides depending on the electrode backbone (i.e. ion conducting or electron conducting). In most cases the combination of metal and ceramic had shown better performances. The electrode kinetics is very fast at higher temperatures (800-1000°C), however, for the intended low temperature operation of SOFCs, the kinetics of electrocatalyst reactions is slow, necessitating a careful selection of catalyst materials [14]. Exploitation of noble metals metals (Ni, Ir, Pt, Pd, Ru, Rh, etc.) with high catalytic activity for electrocatalyst reactions is quitessential to demonstrate highly efficient SOFC electrodes[15, 12, 16, 17]. The characteristics of cerium oxide, $WO_3$, noble and non-noble catalyst used are discussed in the following sections.

2.2.1 Cerium Oxide

Undoped $CeO_2$ exhibits fluorite type structure. $CeO_2$ is an n-type semiconductor under reducing conditions. An interesting property of $CeO_2$ based ceramics, making it suitable as a catalyst is its ability to release and absorb oxygen during reduction and oxidation cycles[18]. Mixed ionic and electronic conducting (MIEC) ceramic materials based on $CeO_2$ doped with other rare earth elements (Gd, Sm and Y) are widely recognized as electrolyte for intermediate temperature solid oxide fuel cells. For instance, doping $CeO_2$ with lower valence oxide ($Gd_2O_3$) introduces oxide vacancies. Fluorite type structure is retained up to 40 mol % doping with $Gd_2O_3$. A drastic improvement in ionic conduction was achieved by hopping of oxide ions to the vacant sites created. At low $PO_2$, a expansion of $Ce_{0.8}Gd_{0.2}O_2$ occurs due to the charge difference i.e., $Ce^{4+}$ to $Ce^{3+}$ upon reduction[19]. The mechanism for the electrocatalytic activity in $CeO_2$ based ceramics was reviewed in detail by Trovarelli (1996) et al[18].

2.2.2 Tungsten Oxide

$WO_3$ exhibits perovskite–like structure without a B-cation, where W atoms are enclosed by a corner sharing $O_2$ octahedral [20]. The amount of distortion from ideal cubic perovskite –like structure is temperature dependant. In the range of -180 to 900 °C, structural changes from tetragonal-orthorhombic-monoclinic-triclinic-monoclinic during cooling was reported by Salje[20]. At room temperature the most favorable structure for $WO_3$ is monoclinic phase. Under reducing atmosphere, $WO_3$ readily forms sub-stochiometric compounds.
Tungsten and its sub-stoichiometric oxides (\(WO_{3-\delta}\)) have been proven to exhibit adequate catalytic activity for hydrogen oxidation and have good electronic conductivity\([21, 22, 23, 24, 25]\). It is also known that \(WO_3\) has the ability to form tungsten bronzes when incorporated with metals, ammonium ions and \(H_2\). Additionally, sub-stoichiometric oxides of tungsten have been reported to have tolerance to sulfur poisoning \([26, 27]\). Recently, Gorte et. al., reported the electrochemical characterization of SOFC anode based on the infiltration of tungsten bronze into YSZ backbone, which showed moderate catalytic activity and the incorporation of Pd catalyst in to the anode improved the performance\([25, 28]\). Other reports illustrates the doping of Ce in \(WO_3\)[29] and blending YSZ with \(WO_3\) [30] to develop an efficient alternative redox stable electrode materials for various solid state device applications. However, the potential of using \(WO_3\) ceramic as SOFC anode at low temperature is not exclusively reported and are explored in our studies.

2.3 Nanostructured Anodes by Infiltration Technology

Nanostructured electrodes prepared by infiltration of catalyst precursors solutions have been gaining massive importance in the SOFC electrode development. Nanoparticles forming a connected networks in the electrodes lead to considerable improvement in the performance of the ceramic electrodes. The nanoparticulates are introduced to the internal surfaces of the porous electrode through infiltration of metal salt precursor solution followed by heat treatments to decompose the salts leaving the metals. Repeating the infiltration steps provides complete coating on the internal surface of the electrode and enhances connectivity of the nanoparticulates leading to improved electrode performances. Catalytically inactive, porous, electron or oxide ion conducting, (e.g., STN or YSZ, respectively) ceramic electrode is termed backbone. The electrocatalyst like CGO was infiltrated in electron conducting backbone or catalyst such as Ni was infiltrated in ion conducting backbone to form a nanostructured anodes.

2.3.1 Infiltration Process and Metal-ceramic Electro catalyst

The illustration of infiltration process is shown in Figure 2.3. The infiltrations was performed step wise, a single infiltration step corresponds to Infiltration \(\rightarrow\) Vaccum Chamber (1-100 mbar, 10 s) \(\rightarrow\) Heat Treatment (350\(^\circ\)C, 1 h) i.e.,
infiltration on porous ceramic electrodes were performed by adding few drops of the precursor solution in to the backbone. Subsequently, the samples were placed in the vacuum chamber. Vacuum was applied in order to remove the air bubbles and facilitate the liquid precursor to penetrate into the anode. After which, they are heat treated in a furnace, the heat treatment depends on decomposition temperature of the salts used to prepare infiltration solutions e.g., chlorides or nitrates.

Noble metals such as Pt, Ru and Pd are well studied by researchers in the field of heterogeneous catalysis[15, 12, 16, 17]. These catalyst can accommodate large number of \( H_2 \) atoms in its crystal structure making it ideal for \( H_2 \) oxidation and are much suitable for SOFC anode. The infiltration technology allows exploitation of various electrocatalyst in combination, reducing the quantity of noble metals in an anode. Binary catalyst effectively improved the performance of SOFC anode with dual function i.e., metal and ceria electrocatalyst for incorporation of catalytic activity and ionic conductivity, respectively in ceramic anode. A drastic improvement in electrochemical activity of the Ni-YSZ anode with the addition of small quantity of noble metals such as Pt, Pd and Ru[15, 12, 16, 17] had been reported.
3.1 About This Chapter

This chapter concentrates on electrochemical characterization of Ni and Gd-doped $CeO_2$ (CGO) infiltrated $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$ (STN) anodes. STN backbones I (36% porosity) and II (47% porosity) were obtained by sintering STN in air and reducing atmosphere, respectively. The porous microstructures were then infiltrated with Ni-CGO precursor to incorporate the electro catalytically active sites. The electrochemical performance of the anode improved with the increment of Ni-CGO loadings. The gas diffusion impedance was investigated with $He/H_2/H_2O$ and $N_2/H_2/H_2O$ gas mixtures and by varying the $H_2O$ content at $655 \, ^oC$. This study indicated that the total gas diffusion impedance in these infiltrated electrode are influenced by a combination of Knudsen and bulk diffusion.

3.2 Introduction

The electrode performances of two types of STN backbones have been compared before and after infiltration of Ni-CGO. The performances were measured in the low temperature range of 350-650 $^oC$. Two microstructures coarser (backbone-I) and finer (backbone-II) were obtained by sintering conditions in air and in a reducing atmosphere, respectively. The polarization resistance ($R_p$) without infiltration was very high for both backbones. With the infiltration of a small amount of Ni-CGO, the impedance decreased significantly, indicating an improvement in the electrocatalytic activity of the anode.

$^1$Accepted for publication in International Journal of Hydrogen Energy (in press, 2012)
volume percentage of the Ni-CGO electrocatalyst, $R_p$ is reduced considerably. The improvement with increase in Ni-CGO loading is mainly attributed to the increase in electro catalytically active sites for hydrogen oxidation.

The main scope of this chapter is focused on

1. The effect of backbone microstructure and sintering conditions on the electrochemical performance of infiltrated STN anodes

2. To optimize the Ni-CGO electrocatalyst in the STN backbone for an improved anode performance and

3. To verify and determine the gas diffusion impedance from the electrochemical impedance spectra in order to resolve the different electrode processes.

3.3 Experimental

3.3.1 STN Backbone Preparation

STN powders were synthesized by a wet chemical method mentioned in chapter 4. The prepared STN powders were ball milled in ethanol and dried overnight. The STN powders were then formulated into a STN screen printing ink with the necessary organic additives. Symmetrical cells were produced by printing two nominally identical backbones on each side of a dense ScYSZ (10 mol % $Sc_2O_2$, 1 mol % $Y_2O_3$ stabilized $ZrO_2$) electrolyte with an approximate thickness of 120 μm. Backbones I and II were obtained by sintering STN symmetrical cells for 4 h in air and reducing atmosphere ($9\%H_2 – N_2$), respectively at 1200 °C. The sintered STN backbones were cut into squares measuring an area of 0.25 cm$^2$.

3.3.2 Infiltrations and Loading Of Ni-CGO

Nitrates of Ni, Ce and Gd were dissolved in water for the preparation of the infiltration solution [NiO-CGO ($Ce_{0.8}Gd_{0.2}O_2\_d$)] with the concentration of 0.55 and 0.75 M of Ni and CGO percursors, respectively. The NiO-CGO precursor contained 25 wt. % of Ni relative to CGO. A small amount of polymer surfactant was added to enhance the wetting properties. A dropper was used to infiltrate the solution precursors into the backbone. The infiltrated cells were placed in
vacuum (1-100 mbar) at room temperature to remove air bubbles and to obtain an uniform coating all over the backbone. The surface of the backbone was wiped and the sample was calcined at 350 °C to decompose the nitrates in the infiltrate precursor solution. The weight changes from calcinations were determined at each infiltrations step. The NiO-CGO was in-situ reduced in dry hydrogen at 650 °C overnight (12 h) to form Ni-CGO. The volume percentage of the Ni-CGO loading was calculated for a backbone volume of 0.5 × 0.5 × 0.002 cm³ (i.e. an electrode thickness of 20 µm). The loadings of Ni-CGO and the respective porosity corresponding to number of infiltrations are listed in Table 3.1.

<table>
<thead>
<tr>
<th></th>
<th>Backbone-I</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number of Ni-CGO infiltrations</td>
<td>0×</td>
<td>1×</td>
<td>3×</td>
<td>5×</td>
</tr>
<tr>
<td></td>
<td>Loading (Vol.%</td>
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<td>4.4</td>
<td>11.2</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>Porosity (Vol. %)</td>
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<td>31.6</td>
<td>24.8</td>
<td>23.5</td>
</tr>
<tr>
<td></td>
<td>Backbone-II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Number of Ni-CGO infiltrations</td>
<td>0×</td>
<td>1×</td>
<td>3×</td>
<td>5×</td>
</tr>
<tr>
<td></td>
<td>Loading (Vol.%</td>
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<td>5.5</td>
<td>15.7</td>
<td>23.9</td>
</tr>
<tr>
<td></td>
<td>Porosity (Vol. %)</td>
<td>47</td>
<td>41.5</td>
<td>35.8</td>
<td>23.1</td>
</tr>
</tbody>
</table>

Table 3.1: Ni-CGO loading and porosity with each infiltration. ¹Backbone-I - sintered in air at 1200°C, ²Backbone-II -sintered in reducing gas ( 9 % N₂/H₂ at 1200°C )

### 3.3.3 Electrochemical Characterization

The infiltrated STN electrodes were electrochemically tested in the temperature range of 350 to 650 °C in H₂/0.03 H₂O using electrochemical impedance spectroscopy (EIS) on the symmetrical cells with two electrode as described in chapter 3. A Pt paste (Ferro GmbH) was used as the current collector. An oxygen sensor was used to determine the partial pressure of oxygen (pO₂). A pO₂ of 5 × 10⁻²⁶ atm (-1.125 V Vs. air was obtained at 650°C) H₂/0.03 H₂O. Similarly, a pO₂ of 1 × 10⁻²⁶ atm (-1.165 V Vs. air was obtained at 655 °C) for H₂/0.01 H₂O. The impedance measurements were performed using a Solartron SI 1260 frequency response analyzer. An amplitude of 50 mV was set on the Solartron. The frequency range was from 1 MHz to 5 mHz. The gas composition (a) 0.91 N₂/0.08 H₂ / 0.01 H₂O and (b) 0.91 He/0.08 H₂/0.01 H₂O were used to study the impedance arc variations in the low frequency part of the spectra. A 100 ml/min flow rate was used in composition (a) and (b). A constant pO₂ of was maintained in both compositions.
The effective binary diffusion coefficients for the binary gas mixtures in an open volume is considered equal to the binary diffusion coefficient and were determined using the Fuller correlation \[31\] shown in equation 3.1

\[
D_{AB} = 10^{-3}T^{1.75} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} P(\sqrt{V_A} + \sqrt{V_B})
\] (3.1)

where, \(D_{AB} = D_{BA}\), A and B corresponds to any of the three binary pairs in \(N_2/H_2/O\) or \(He/H_2/O\) gas mixtures. \(P\) is the pressure in atmosphere, \(M_A\) and \(M_B\) are the molecular weight of gas A and B, respectively, \(T\) is the temperature in K and \(v_A\) and \(v_B\) is the diffusion volume of gas A and B, respectively. However, the pairs must be either \(H_2/O\) or \(N_2/O\) due to their molecular weight differences and cannot be considered for multicomponent gas mixtures due to the difference in diffusion coefficients between each gas mixture combination. Thus, the ternary diffusion coefficients \[32\] of multicomponent gas mixtures are determined from Equation 3.2, wherein \(D_{A-mix} \neq D_{B-mix}\).

\[
D_{A-mix} = \frac{(1 - y_A) y_B D_{AB} + y_C D_{AC} + \ldots}{y_B D_{AB} + y_C D_{AC} + \ldots}
\] (3.2)

where, \(D_{A-mix}\) is the effective diffusion coefficient of gas A and \(y_A, y_B, y_C\) are the molar fractions in the ternary gas mixture \((A = H_2/O, B = H_2\)and \(C = N_2\) or \(He\)). \(D_{AB}\) and \(D_{AC}\) correspond to the respective effective binary diffusion coefficient determined from Equation 3.1.

The impedance data were corrected for the series inductance arising from the wiring of electrochemical test setup, which was determined at short circuit conditions. The series inductance was in the order of 30-60 nH depending on the cell. The impedance was fitted with an equivalent circuit model.

3.4 Results and Discussions

3.4.1 Microstructural Analysis of backbone and Infiltrated Anodes

Figure 3.1 shows the typical SEM images of the STN backbones after being sintered in air and in reducing conditions. In Figure 3.1a and 3.1b, the cross section image depicts the interface of electrolyte and backbone. Both backbones
Figure 3.1: SEM micrograph of STN backbones.
Figure 3.2: SEM micrograph of Ni-CGO infiltrated STN anodes.

have bonded well with the dense ScYSZ electrolyte without any separation. The backbone-I appeared to have slightly lower porosity with coarse microstructure compared to backbone-II having a finer microstructure. Backbone-I has 36% porosity, while backbone-II has 47% porosity, determined by using simple phase analysis software on the polished SEM images. The thicknesses of both backbones are in the order of 18-20 mm.

Figure 3.2 shows the microstructure of the STN backbone 5× infiltrated with Ni-CGO. Figure 3.2a depicts backbone-I filled up with Ni-CGO electrocatalyst. Figure 3.2b is the magnified image of Ni-CGO infiltrated backbone. Shown in Figure 3.2c is the micrograph of STN backbone-II. The porosity of the backbones corresponding to 5× infiltration of Ni-CGO electrocatalyst is listed in Table 3.1. Figure 3.2d is the magnified image of Figure 3.2c.

3.4.2 Crystallographic Analysis of Electrocatalyst

XRD patterns of the NiO-CGO and CGO electrocatalyst calcined at 350°C for 1 h is shown Figure 3.3. The clear peaks of CGO shown in XRD pattern (a) of Figure 3.3 indicates the formation of $Ce_{0.8}Gd_{0.2}O_{2-δ}$ fluorite type structure at 350 °C. XRD pattern (b) shown in Figure 3.3 is that of NiO-CGO electrocatalyst with differentiable peaks of NiO and CGO showing no reaction between electrocatalyst.
3.4.3 Electrochemical Investigation of Backbone And Infiltrated Anodes

The sum of electrode process resistance and gas diffusion resistance, $R_p$, of the electrode was determined using electrochemical impedance spectroscopy. Figure 3.4 shows the impedance plot of the symmetrical cells with STN backbones-I and II measured at 650 °C in $H_2/0.03H_2O$. The $R_p$ value of both backbones-I and II was very high, 75 and 95 $\Omega \text{cm}^2$, respectively at 600°C, demonstrating their poor catalytic activity and oxide ion conduction. It is expected that $R_p$ of backbone-II should be less, owing to its finer microstructure and higher porosity compared to backbone-I, but in fact, it was high. Backbone-II was sintered in reducing conditions ($N_2/H_2$) and thus, a complete removal of any decomposed binders or organic substances may have been less complete than in the case of backbone-I which was sintered in air. This might have led to impurity segregation at the electrode/electrolyte interfaces and resulted in slightly high $R_p$.

Figure 3.6 a and b presents the impedance spectra of the STN backbone-I and II infiltrated with Ni-CGO electrocatalyst obtained at 650 °C in $H_2/0.03H_2O$. An equivalent circuit containing the electrolyte series resistance, $R_0$ in series with a $(R_1Q_1)$ parallel and a finite length Warburg (O) in series i.e. $R_0(R_1Q_1)(O)$ was used to model the spectra as shown in Figure 3.5.
Figure 3.4: Electrochemical characterization of STN backbones.

Figure 3.5: An equivalent circuit used to analyse the impedance spectra. The element (O) represent the finite length Warburg.
Figure 3.6: Impedance spectra of Ni-CGO infiltrated STN anodes.
However, for the spectra obtained at temperatures below 550 °C and for STN backbones without infiltrations element (O) is negligible. A small variation in $R_0$ possibly originates from the microstructural differences in the electrode/electrolyte interface and also due to current collector-electrode contact. $R_1$ is the electrode process resistance. A constant phase element (Q) as shown in equation 3.3 is used rather than using a pure capacitor due to the distributed catalytic reactivity of the porous microstructure of the anode[33]. The impedance of the CPE is given by equation 3.3,

$$Q = \frac{1}{Y_0(j\omega)^n}$$  \hspace{1cm} (3.3)

where, $Y_0$ is a constant, $\omega$ is the angular frequency and n is the frequency power. The element (O) is used to determine the value of gas diffusion resistance,$R_D$.

(O) represents the finite length Warburg [34] and the complex impedance of this element is given by the equation 3.4.

$$Y(\omega) = \frac{Tanh[B.\sqrt{j\omega}]}{Y_0\sqrt{j\omega}}$$  \hspace{1cm} (3.4)

$$Y_0 = \frac{nFs.\sqrt{D_A-mix}}{V_m} \left| \frac{dE}{dy} \right|^{-1}$$  \hspace{1cm} (3.5)

$Y_0$ is the admittance parameter, in $Ss^{1/2}$ as shown in equation 3.5. Where, s is the interface area; $V_m$ is the molar volume and $\left| \frac{dE}{dy} \right|^{-1}$ is the slope of the electrochemical titration curve relating voltage and concentration [35]. The gas diffusion impedance is given by the equation $R_D = B/Y_0$, where B is the time constant, in $s^{1/2}$. B and $Y_0$ were obtained from the equivalent circuit fittings. In the case of backbone-I, 1× infiltration of Ni-CGO showed $R_p$ of 0.78 $\Omega cm^2$. A very small loading (437 mg/0.25 cm$^2$) of the electrocatalyst containing Ni-CGO reduced $R_p$ by two orders of magnitude. The subsequent increment in loading of Ni-CGO from 1 to 3 decreased the value of $R_p$ considerably. This is attributed to the catalytically active sites for $H_2$ oxidation and oxide ion conduction. An optimum $R_p$ of 0.20 $\Omega cm^2$ at 650 °C corresponding to a loading of 12.5 vol. % was obtained as a result of 5× infiltration, which was almost similar to 3× infiltration.
Figure 3.7: Schematic sketch of Ni-CGO infiltrated STN anodes and the reaction pathways.

At $9 \times$ infiltration depicted in Figure 3.6a, an increase in $R_p$ was observed with 19 vol. % loading of Ni-CGO, indicating that any further addition of electrocatalyst may not be beneficial for improving the electrochemical performances. For backbone-II as shown in Figure 3.6b, $R_p$ gradually decreased with increment in Ni-CGO loadings. $1 \times$ infiltration of Ni-CGO yields a $R_p$ of 6.8 $\Omega \text{cm}^2$, while a $5 \times$ infiltration of Ni-CGO gives a $R_p$ of 0.21 $\Omega \text{cm}^2$ at 650 $^\circ$C corresponding to a loading of 23.9 vol. % and further increment in Ni-CGO tends to decrease $R_p$ further. The best performance of electrode process ($R_1$) was achieved by $9 \times$ infiltration in backbone-II with 36.7 vol. % of Ni-CGO loading. The gradual reduction in $R_1$ with the increase in loading of Ni-CGO is attributed to the extended length of the triple phase boundaries of the nanostructured electrocatalyst. In addition, higher loading of Ni-CGO ensured a good percolation of oxide ion path induced by ceria. Oxide ion and electronic pathways of the Ni-CGO infiltrated STN anodes are depicted in the schematic sketch shown in Figure 3.7. Nano-sized Ni and CGO particles uniformly covered the STN backbone. Ni is a much better catalyst than CGO, so the more plausible site for hydrogen oxidation reaction is Ni. However, ceria can also act as reaction site, apart from its main role of oxide ion conduction in the STN backbone. The STN backbone facilitates electronic conduction in the anode.

To analyze the impedance spectra of the infiltrated electrodes in detail, the effect of porosity in the electrode processes of backbone I and II at 650 $^\circ$C was plotted and shown in Figure 3.8 and 3.9. Figure 3.8 separates the $R_p$ into an electrode process resistance, $R_1$, and gas diffusion resistance, $R_D$. $R_1$ decreased
Figure 3.8: Variation of electrode process resistance ($R_1$ and $R_D$) with porosity in backbone-I.

Figure 3.9: Variation of electrode process resistance ($R_1$ and $R_D$) with porosity in backbone-II.
down to a porosity of 23% for the infiltrated anodes, after which $R_1$ increased at 17% porosity corresponding to a loading of 9× infiltration. The reason for the increase in $R_1$ at 17% porosity is not clear, but we suggest it could be due to the overloading of electrocatalyst. For backbone-II shown in Figure 3.9, $R_1$ gradually decreased down to a porosity of 10% and the value of $R_D$ is not resolvable at a porosity of 35 and 41% corresponding to 3× and 1× infiltrations. The increase in $R_D$ with porosity in both backbones indicates that, apart from the bulk diffusion inside the anode and the stagnant layer outside the infiltrated electrode, Knudsen diffusion inside the electrode plays a role in the total gas diffusion impedance’s as described in the later section.

Figure 3.10 is the Arrhenius plot of backbone-I, while Figure 3.11 is of backbone-II illustrating the increment in Ni-CGO loadings (measured in $H_2$ in 3% $H_2O$). Table 3.2 gives the calculated values of activation energy ($E_a$) for both Ni-CGO infiltrated backbones. The $E_a$ of both backbones before infiltration are in the range of 1.12-1.14 eV. Despite of the increase in loading of Ni-CGO the $E_a$ remains constant.
Figure 3.11: Arrhenius plot of polarization resistance, $R_p$ for backbone-II.

<table>
<thead>
<tr>
<th>Number of CGO infiltrations</th>
<th>0×</th>
<th>1×</th>
<th>3×</th>
<th>5×</th>
<th>9×</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$ Backbone-I</td>
<td>1.12</td>
<td>1.10</td>
<td>1.01</td>
<td>1.06</td>
<td>1.01</td>
</tr>
<tr>
<td>$^2$ Backbone-II</td>
<td>1.14</td>
<td>1.08</td>
<td>1.09</td>
<td>0.99</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 3.2: Activation energy (eV) of backbones-I and II with Ni-CGO infiltrations.

### 3.4.4 Gas diffusion Limitation in Ni-CGO Infiltrated STN Anodes

The gas diffusion impedance in a cermet anode is considered to occur due to the stagnant layer formed outside the electrode and has been studied in detail by previous researchers using an one-dimensional stagnant layer model [31][36]. These studies suitably explain the role of bulk diffusion in the stagnant layer affecting the gas phase impedance. Equation 3.6 represents the model with the inclusion of ternary diffusion coefficient.

$$R_D^1 = \frac{\eta_D}{i} = \left(\frac{RT}{2F}\right)^2 \frac{d_l}{P} \left(\frac{1}{X_{H_2}D_{H_2-mix}} + \frac{1}{X_{H_2O}D_{H_2O-mix}}\right)$$

(3.6)
where, $R_{1D}$ is the diffusion resistance outside the actual electrode, $\eta_D$ diffusion overpotential, $i$ is current density, $d_l$ is the stagnant layer thickness, $X_{H_2}$ and $X_{H_2O}$ are the molar fractions of $H_2$ and $H_2O$, respectively. $D_{H_2-mix}$ and $D_{H_2O-mix}$ are the ternary bulk diffusion coefficients of $H_2$ and $H_2O$ in the inert gas ($N_2$ or He) calculated from equation 3.2. R, T and F are the gas constant, temperature in K and Faraday constant, respectively. For the infiltrated anodes, the pore size is small (<500 nm) and the gas diffusion impedance is expected to have a contribution from Knudsen diffusion and bulk diffusion inside the anode as well. The effective Knudsen diffusivity, $D_{i,K}^{eff}$ [37] can be obtained from equation 3.7, which includes the porosity and tortuosity parameters.

$$D_{i,K}^{eff} = \frac{2r}{3} \sqrt{\frac{8RT \epsilon}{\pi M_i \tau}}$$

(3.7)

where, $r$ is the pore size, $M_i$ is the molecular weight of gas species $i$, $\epsilon$ is porosity and $\tau$ is the tortuosity factor. The molecular diffusion coefficients, $D_{i,mol}$, combining the bulk diffusion coefficient, $D_{A-mix}$ and Knudsen diffusion coefficient, $D_{i,K}$ expressed in equation 3.8.

$$\frac{1}{D_{i,mol}} = \frac{1}{D_{A-mix}} + \frac{1}{D_{i,K}}$$

(3.8)

Adopting the calculation procedures reported in the literature [38] and from equations 3.2 and 3.8, a DC model accounting for gas diffusion impedance inside the electrode of thickness (L) is given by equation 3.9.

$$R_D^2 = \frac{\eta_D}{i} = \left(\frac{RT}{2F}\right)^2 \frac{L\tau}{P\epsilon} \left(\frac{1}{X_{H_2}D_{H_2,mol}} + \frac{1}{X_{H_2O}D_{H_2O,mol}}\right)$$

(3.9)

where, $R_D^2$ the gas diffusion resistance inside the porous electrode. However, equation 3.9 does not consider gas diffusion impedance due to the stagnant gas layer formed outside the electrode. Thus, in our study we have considered the total gas diffusion impedance as the summation of equations 3.6 and 3.9 i.e., $R_D = R_{1D} + R_D^2$, where $R_{1D}$ is the gas diffusion resistance attributed to the structural parameters (inside the porous electrode) and $R_D^2$ is the gas diffusion resistance from outside of the electrode (stagnant layer).
Table 3.4: Anode structural parameter used for gas diffusion analysis.

<table>
<thead>
<tr>
<th>Porosity (ε), Vol. %</th>
<th>Tortuosity Factor (τ)</th>
<th>Pore Size (r), nm</th>
<th>Stagnant Layer Thickness (d₁), mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>9</td>
<td>390</td>
<td>3.5</td>
</tr>
<tr>
<td>23</td>
<td>13</td>
<td>230</td>
<td>3.5</td>
</tr>
<tr>
<td>17</td>
<td>14</td>
<td>120</td>
<td>3.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Porosity (ε), Vol. %</th>
<th>Tortuosity Factor (τ)</th>
<th>Pore Size (r), nm</th>
<th>Stagnant Layer Thickness (d₁), mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>13</td>
<td>150</td>
<td>5.5</td>
</tr>
<tr>
<td>10</td>
<td>14.5</td>
<td>105</td>
<td>5.5</td>
</tr>
</tbody>
</table>

To investigate the porosity dependence of \( R_D \), equations 3.6 and 3.9 are taken into account. The parameters for modeling are listed in Table 3.4; the pore size, \( r \) was estimated from the SEM micrographs. The tortuosity factor, \( s \) and thickness of the stagnant layer, \( d_1 \) were determined by trial and error fits of the experimental \( R_D \) dependence on porosity (shown in Figure 3.12 and 3.13) to the equations 3.6 and 3.9. It is noted that, in the fitting procedure for \( R_D^1 \) is the stagnant layer adds a contribution that does not depend on the porosity, whereas for \( R_D^2 \) the tortuosity factor in the porous electrode determines the slope of the graph. The values of \( ε \) listed in Table 3.4 are certainly higher than the normally expected tortuosity value i.e., 3-6 [39, 40][41], but a tortuosity factor in the range of 9-15 has previously been reported in the literatures and ascribed to the presence of dead-end pores and pore constrictions [37, 42, 43, 44, 45]. On the other hand, the high values of \( d_1 \) probably indicates the formation of a large gas stagnation layer above the electrode [31][36].
Figure 3.12: Arrhenius plot of $R_D$ for backbone-I.

Figure 3.13: Arrhenius plot of $R_D$ for backbone-II.
Figure 3.14: Impedance spectra showing the variation of low frequency arc in the presence of inert gases at 650ºC for backbone-I&II.

3.4.5 Effect of Inert Gas Mixtures on the Gas Diffusion Impedance of an Infiltrated Anode

Two gas compositions described in the experimental section 3.3.3 in this chapter were used to study the gas diffusion impedance of backbone-I and II, infiltrated 5× with Ni-CGO. Figure 3.14 shows the effect of the gas compositions. Two distinguishable arcs were obtained at 650 ºC from high frequency and low frequency range of the impedance spectra. The impedance spectra were fitted using an equivalent circuit $R_0(R_1Q_1)(O)$. The parameters $R_0, R_1, Q_1$ and $(O)$ have the same meaning as discussed before. For backbone-I shown in Figure 3.14a, the value of $R_D$ is 0.3 $\Omega cm^2$ for $N_2/H_2/H_2O$ gas mixtures and 0.15 $\Omega cm^2$ for $He/H_2/H_2O$ gas mixtures. Similarly, in backbone-II as shown in Figure 3.14b, the $R_D$ values are 0.35 and 0.22$\Omega cm^2$ for $N_2$ and He containing gas mixtures, respectively. In both backbones, $R_D$ determined from $N_2/H_2/H_2O$ gas mixtures were nearly 2 times higher than $He/H_2/H_2O$ gas mixtures and are attributed to the low diffusion coefficient of $N_2$ compared to He containing gas mixtures. The effective diffusion coefficients calculated from equation3.2 shows, $D_{A-mix}$ of composition (A = $H_2O$, mix = $N_2$and $H_2$) and (A= $H_2$, mix = $N_2$ and $H_2O$) is $2.02 \times 10^{-4}$ and $5.48 \times 10^{-4}$ $m^2/sec$, respectively. Similarly, $D_{A-mix}$ value of
composition \((A=H_2O, \text{ mix } = N_2 \text{ and } H_2)\) and \((A=H_2, \text{ mix } = N_2 \text{ and } H_2O)\) is \(6.08 \times 10^{-04}\) and \(1.18 \times 10^{-3}\) \(m^2/sec\), respectively.

### 3.4.6 Temperature Dependency of Gas Diffusion Impedance

The Arrhenius plot of \(R_1\) shown in Figure 3.15, \(R_1\) is not much affected by the substitution of \(N_2\) by He. Shown in Figure 3.16b is the temperature dependence of \(R_D\). A weak temperature dependence of gas diffusion resistance \((R_D \alpha T^{0.25})\) was calculated from the temperature dependent parameters of equations 3.1,3.2 and 3.6. For backbone-I, \(R_D\) increased slightly with temperature for both gas compositions (He and \(N_2\) containing \( H_2 \) - \(H_2O\) gas mixtures), suggesting a slight temperature dependency of the gas diffusion impedance. And no noticeable dependence was observed in backbone- II.

### 3.4.7 Effect of \(H_2O\) Content on Gas Diffusion Impedance

Impedance spectra obtained with a \(H_2O\) content of 0.03 and 0.01 molar fraction in \(H_2\) gas at 655 °C are shown in Figure 3.17. 5× infiltrated Ni-CGO
Figure 3.16: Temperature dependency of $R_D$.

Figure 3.17: Impedance spectra showing the effect of water content on gas diffusion impedance.
electrocatalyst in backbone-I was chosen to study the effect of $H_2O$ content on gas diffusion impedance. $R_1$ and $R_D$ determined by fitting an equivalent circuit $R_0(1 + R_1Q_1)(1 + Q_1)$. The experimental $R_D$ values for 0.01 $H_2O$ is 3 times higher than the value obtained for 0.03 $H_2O$. Shown in Table 3.5 are the ratios of experimental $R_D$, contributions from the stagnant layer and the porous electrode as calculated from equations 3.6 and 3.9, respectively. In both cases an increase of close to a factor of 3 is predicted when going from 0.03 to 0.01 $H_2O$ and is in good agreement with the experimental observations.

<table>
<thead>
<tr>
<th>Gas compositions</th>
<th>$R_D$</th>
<th>$\frac{R_{11}}{R_{33}}$ (experiment)</th>
<th>$\frac{R_{11}}{R_{33}}$ (equation 3.6)</th>
<th>$\frac{R_{11}}{R_{33}}$ equation (3.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Backbone-I</td>
<td>0.15</td>
<td>3</td>
<td>2.94</td>
<td>2.83</td>
</tr>
<tr>
<td>2Backbone-II</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.5: Effect of $H_2O$ content on gas diffusion impedance. A comparison between experimental and calculated ratios of gas diffusion impedance.

### 3.5 Summary

STN based perovskite type oxide can be well suited as anode backbone for LT-SOFCs. The polarization resistance of the backbone without electrocatalyst is very high due to the lack in oxide ion conductivity and catalytic activity of STN. The increment in loading of Ni-CGO on STN backbone considerably reduces the polarization resistance. An optimum performance of backbone-I was obtained at a Ni-CGO loading of 13 vol. % (5× infiltrations) and a best performance of backbone-II was achieved at a loading of 37 vol. % (9× infiltrations). The resulting gas diffusion impedance in these infiltrated anodes showed clear dependence on the structural parameters of the electrode (porosity, pore size etc.,) Knudsen and bulk diffusivity inside the porous electrode along with the bulk diffusion contribution from the stagnant layer outside the electrode. The gas diffusion impedance was identified by varying the temperature, inert gases composition ($N_2/He$) containing gas mixtures $H_2/H_2O$ content. The gas diffusion impedance increases almost twice for $N_2$ containing gas mixtures compared to $He$ containing gas mixtures.
Chapter 4

Nanostructured, Binary/Ternary/Quaternary Electro catalysts for Ceramic Anodes

4.1 About This Chapter

In the first part of this chapter, electrocatalyst precursor of various combinations: Pt, Ru, Pd, Ni and Gd-doped $CeO_2$ (CGO) were infiltrated into a porous $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$ (STN) backbone and the electrode performance are investigated. The performance of the binary electrocatalyst infiltrated ceramic backbones are Pt-CGO > Ru-CGO > Pd-CGO > Ni-CGO. Ternary electrocatalyst of Ni-Pd-CGO and Ni-Pt-CGO showed the lowest polarization resistance, 0.31 and 0.11 $\Omega \cdot cm^2$, respectively at 600°C in $H_2/3\%H_2O$. The average particle size of the ternary electrocatalyst was larger than the binary Pd-CGO and Pt-CGO electrocatalyst due to the particle coarsening and growth of Ni nanoparticles. High resolution transmission electron microscopic analysis on the best performing Ni-Pt-CGO electrocatalyst infiltrated anode reveals the formation of Ni-Pt nanocrystalline alloy and a homogenous distribution of nanoparticles in STN backbone.

Synergistic electrochemical performance of Ru-Pd-Ni-CGO electrocatalyst infiltrated $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$(STN) anodes are described in the second part of this chapter. The polarization resistance of 0.28 and 1 $\Omega \cdot cm^2$ at 600 and 500 °C, respectively are achieved in $H_2/3\%H_2O$. The performance of the Ru-Pd-Ni-CGO is two orders of magnitude better than Ni-CGO electrocatalyst at similar loading conditions. The TEM-EDX analysis on the post-tested anode suggests that the enhanced performance of the Ru-Pd-Ni-CGO is due to the synergetic
effect of Ni-Pd and Ru-CGO. The uniform distribution of nano-sized electrocatalyst nanocomposites at the interface of STN and ScYSZ electrolyte contributes for an improvement.

4.2 Introduction

The most commonly studied anodes for LT-SOFCs are based on cermet of nickel and an oxide ion conductor, e.g. Ni-CGO (Gd-doped ceria). Many recent studies on cermet anodes have been focused on controlling the parameters such as, grain size, porosity, Ni and CGO ratio, stoichiometry of CGO etc., to obtain efficient SOFC anodes\cite{46, 47, 48}. However, they have shown a high polarization resistance of $7.2 \, \Omega \, cm^2$ at 600 $^\circ$C and $61.5 \, \Omega \, cm^2$ at 400 $^\circ$C in moisturized $H_2$ fuel. The poor redox stability of Ni and intolerance to hydrocarbon fuels indicates the need for the development of alternative anode materials for LT-SOFCs \cite{49}.

Nanostructured, oxide ion conducting materials based on $CeO_2$ doped with other rare earth elements (Gd, Sm and Y) are widely recognized as mixed ionic and electronic conduction. In addition, these material have catalytic properties for hydrogen oxidation \cite{50}. A few percent (10-20 vol. %) of metallic catalyst such as Ni mixed with Gd-doped cerium oxide (CGO) infiltrated in $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$ (STN) backbone enhanced the SOFC anode performance considerably compared to CGO alone (chapter 3)\cite{51}. A careful control on loading of electrocatalyst in STN helps in tuning the performance. Results reported in literature prompts to explore other catalytic metals for hydrogen oxidation in combination with Ni to further improve the performance\cite{52, 53}. Infiltration technology (see section 2.3.1) significantly contribute to reduce the quantity of noble metals needed to obtain beneficial electrochemical properties and allows the exploration of nanostructured, noble metal-ceramic catalysts in combinations\cite{53}. Although Ni-CGO infiltrated STN has shown reasonably good anode performance (described in chapter 3), further improvements for LT-SOFC anodes can be made by employing a small quantity of noble metals e.g. Pt, Ru, Pd etc., in combination with Ni.

The first part of this chapter concentrates on electrochemical characterization of STN backbones infiltrated with binary electrocatalyst Pt-CGO, Ru-CGO, Pd-CGO, and Ni-CGO at low temperature (< 600 $^\circ$C). Pt-CGO showed the best performance in comparison to all other binary electrocatalyst. Among the ternary electrocatalyst being investigated, Ni-Pt-CGO infiltrated STN an-
odes showed an excellent performance. Emphasis was given to understand the nanocrystalline properties of Ni-Pt alloy in the Ni-Pt-CGO electrocatalyst using a high-resolution transmission electron microscopy. It is observed that the lattice parameter of Ni-Pt alloy is located in between the two individual metals (i.e., Ni and Pt). The observed alloying of the metallic catalyst and nanostructured morphology of the electrocatalyst are believed to be the reason for an improved anode performance.

The second part of this chapter concentrates on electrochemical characterization of STN symmetrical cells infiltrated with multicatalyst (Ru, Pd, Ni and CGO combinations). The polarization resistance, $R_p$ of multicatalyst infiltrated ceramic anodes has been significantly reduced compared to Ni-CGO investigated under similar loading conditions. Chemical and microstructure analysis of the electrocatalyst was investigated using scanning electron microscopy, scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX). The distributions of Pd-Ni catalyst on the backbone, while Ru-CGO covers the rest of the uncovered area. The synergistic effect of the electrocatalyst is created by the performance of the infiltrated electrocatalyst also depends on the loading of the electrocatalyst and the resulted particle size.

4.3 Experimental

4.3.1 STN Synthesis and Characterization

STN perovskite oxide was prepared using a wet chemical synthesis route. Strontium carbonate ($SrCO_3$), titanium (IV) isopropoxide ($Ti\{OCH(CH_3)_2\}_4$) and niobium oxalate ($C_2NbO_4$) were used as starting materials (Sigma Aldrich) to obtain a STN composition of $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$. A 260 ml of titanium (IV) isopropoxide and 160 ml of niobium oxalate was mixed separately in an already prepared 500 ml ethanol and water mixture in a proportion of 1:1.5. The resulted precipitates were filtered, washed in ethanol and dried. Subsequently, the dried solids were dissolved separately in citric acid monohydrate ($HOC(COOH)(CH_2COOH) \cdot 2H_2O$) with the addition of 20 ml hydrogen peroxide ($H_2O_2$) solution. The concentration of niobium and titanium ions containing solutions was 5.7 and 2.1 wt. %. About 13.9 g of $SrCO_3$ powder along with 20 ml of $H_2O_2$ was added slowly into 125.5 g of $TiO_2$ and 63 g of $NbO_2.5$ containing solutions. This mixture was placed in a crucible and heated on a hot plate at 300
$^{90}C$ for 5 h. The resulted solids were heat-treated at 1000 $^\circ$C for 3 h and ground to fine powder. The crystalline peaks of STN were confirmed using XRD for each batch.

4.3.2 Symmetrical Cell Preparation and Infiltrations

STN powder was formulated as a screen printing ink following an in-house preparation procedure using surfactant, plasticizer and a binder and mixed thoroughly by using a mechanical shaker overnight. The screen printed STN on a dense ScYSZ tapes of 120 $\mu$m thick were sintered at for 4 h in a reducing atmosphere (9% $H_2/N_2$). The porous STN anodes were deposited on both sides of the ScYSZ electrolyte. The tape was cut into small squares measuring an area of 0.25 $cm^2$ for use in the electrochemical set-up.

To obtain a CGO composition of $Ce_{0.8}\text{Gd}_{0.2}O_{2-\delta}$, 0.75 M of CGO precursor solution was prepared by dissolving cerium nitrate ($Ce(NO_3)_3\cdot6H_2O$) and gadolinium nitrate($Gd(NO_3)_3\cdot6H_2O$) in $H_2O$ along with polymer surfactants. The precursor solution of Ni-CGO, Pt-CGO contains 25 wt. % of Ni and 25 wt. % of Pt, respectively relative to CGO and was prepared by dissolving 0.6 M nickel nitrate ($Ni(NO_3)_2\cdot6H_2O$) and 0.2 M of tetra ammine platinum (II) nitrate ($H_{12}N_6O_6Pt$) in already prepared CGO precursors. For Pd-CGO, approximately 10 wt. % Pd in the form of palladium nitrate ($Pd(NO_3)_2\cdot6H_2O$) with a concentration of 0.6 M was dissolved in CGO precursors. In case of the Ru-CGO containing infiltrates, 25 wt. % of Ru in the form of ruthenium chloride ($RuCl_3\cdot xH_2O$) with a concentration of 0.3 M was dissolved in CGO precursor. The infiltrated STN anodes were prepared by immersing the symmetrical cells into the precursors, after which they were placed in a vacuum chamber. Vacuum was applied in order to remove air bubbles from the porous STN backbone and to facilitate the liquid precursor to homogeneously coat the surface of the anode.

For binary electrocatalyst (BEC) infiltration, Pt-CGO, Ru-CGO, Pd-CGO and Ni-CGO were infiltrated 3 times to increase the loadings in porous STN; after each infiltration the cells were calcined at 350 $^\circ$C for 1 h. In case of ternary electrocatalyst (TEC) infiltration such as Ni-Pd-CGO and Ni-Pt-CGO, dual infiltrations were carried out. Firstly, Pd-CGO and Pt-CGO were infiltrated two times and followed by infiltration of Ni-CGO 3 times. The heat treatments were performed after each infiltration. The change in weight after calcinations was recorded after each infiltration. The electrocatalyst samples for physico-chemical
and microscopic analysis were prepared under the similar conditions as that of ECs infiltrated in STN backbone.

For quaternary electrocatalyst infiltration, palladium nitrate and ruthenium chloride were used as precursors and are dissolved in CGO as mentioned earlier. A Ru-Pd-CGO precursor solution containing 11 wt % of Ru, 5 wt % of Pd and 84 wt % CGO was prepared. Ru-Pd-Ni-CGO infiltrations were done by infiltrating twice with the Ru-Pd-CGO precursor and calcined at 650 °C for 2 h in air to remove the chloride residues. Afterwards the symmetrical cells were infiltrated 3 times with Ni-CGO using the same procedure. The change in weight after calcinations was recorded after each infiltration. The volume fraction of Ni-CGO is 24.6%, while that of Ru-Pd-Ni-CGO is 24 % in which Ni-CGO and Ru-Pd-CGO is 8.2% and 17.8 %, respectively. The performance of Ru-Pd-CGO infiltrated in STN backbone is also compared to and it has a loading of 16%.

4.3.3 Electrochemical Characterizations

The symmetrical cells were electrically contacted using Pt-paste (Ferro GmbH) and a Pt-grid. The cells were heated to 650 °C in 9% H2/N2, whereafter the gas was changed to dry H2 (EMF = -1.312 V vs. air @650°C). The temperature was kept at 650°C for 12 h. The impedance spectra were recorded by applying an amplitude of 50 mV in the frequency range of 1 MHz to 1 mHz. The impedance was measured in the temperature range 650 to 350 °C in H2 with 3% H2O. The partial pressure of oxygen, (pO2) was measured using an oxygen sensor. The EMF values were -1.125, -1.131, -1.140 and -1.147 V vs. air and the corresponding pO2 were 10^-26, 10^-27, 10^-29, and 10^-31 atm. at 650, 600, 550 and 500 °C, respectively. These values corresponds very well with the intended gas composition of H2/3%H2O. All the obtained impedance spectra were corrected for inductance in the range of 30-60 nH originating from the leads of electrochemical setup depending on the samples position. The impedance spectra were fitted with equivalent circuit model using a complex non-linear least squares fitting routine (CNLS).

During impedance measurements on symmetrical cells, one side of the electrode will function as anode, while the other side functions as cathode. The anode and cathode side changes with the alternating current. Hence, the reactions under investigation when using symmetrical cells are the hydrogen oxidation and

1\(^{(the output voltage of the Solartron varies from 5-50 mV depending on the temperature of measurement and the resulted cell impedance)}\)
the reduction of stream as shown in reaction 4.1 and 4.2, anodic and cathodic current, respectively.

\[ H_2(g) + O^{2-} \rightarrow H_2O(g) + 2e^- \quad (4.1) \]

\[ H_2O(g) + 2e^- \rightarrow H_2(g) + O^{2-} \quad (4.2) \]

4.4 Results And Discussions

4.4.1 Physico-chemical Characterizations

Figure 4.1 shows the XRD of the TECs, Ni-Pd-CGO and Ni-Pt-CGO and are compared to that of Ni-CGO and CGO. The formation of fluorite-like single phase of CGO is evident even at a low calcination temperature of 350°C (1hr, air). No reaction has occurred between the metal and ceramic phase, in other words, metal exists as a separate dispersed phase in a CGO matrix. XRD pattern of both TECs showed (111) reflex of Ni; however Pt and Pd peaks are not identified. The poor detection of X-ray reflections of such catalysts was already reported and is ascribed to its highly dispersed nature[54]. Moreover, a shift towards lower angle in Ni (111) is observed in Ni-Pt-CGO indicating a possible alloying.

The low thermal treatment of electrocatalysts at 650 °C in reducing atmosphere resulted in the nanostructured crystalline phase. The high resolution-transmission electron microscopy (HR-TEM) analysis was performed for the best performing Ni-Pt-CGO and is shown in Figure 4.2. Both CGO and metallic phases were identified. The perpendicular (111) and (2-20) crystal planes of CGO is located on the right side of the figure; two small metallic grains are located on the left. By using EDX quantification (Figure 4.3), the weight percent of Ni/Pt is in the ratio of 95:100 from 15 regions, consistent with the nominal ratio. Furthermore, a close observation on Figure 4.2 illustrates that the lattice parameter of the alloy phase locates is situated in between those of Ni and Pt, indicating the formation of Ni-Pt alloy phase besides the CGO phase. However a small variation in lattice parameter at different area of measurements is envisaged, ascribed to coexistence of Ni and Pt phase apart from the Pt-Ni alloy phase. The Pt-Ni alloy phase adopts the same face-centered-cubic (FCC) structure as Pt and
Figure 4.1: XRD of CGO, Ni-CGO, Pd-Ni-CGO and Pt-Ni-CGO electrocatalyst. The catalysts were heat treated at 650°C for 12 h.

Figure 4.2: HRTEM of Pd-Ni-CGO and Pt-Ni-CGO electrocatalyst.
Figure 4.3: EDX of Pt-Ni-CGO electrocatalyst. TEM image of the Pt-Ni-CGO electrocatalyst is shown in the inset.

Ni phase, which are in good agreement with the XRD data. Additionally, in contrast to the pure Ni, some resultant lattice expansion was observed, e.g., an interplanar spacing of (111) plane is 2.3% larger than that of Ni. The resulted particle size of the infiltrated electrocatalysts were found to be around 5-10 nm and are highly dispersed.

The backbone for infiltration used in this study is Nb-doped, Sr deficient $\text{SrTiO}_3$ cubic perovskite with a composition of $\text{Sr}_{0.94}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ prepared using a wet chemical method (see section 4.3.2). The powder XRD pattern of STN with a heat treatment at 1000°C for 4 h (Figure 4.4a) shows a single perovskite phase without any formation secondary phases. The anodes were characterized using a symmetrical cell configuration of $\text{STN} | \text{ScYSZ} | \text{STN}$ (XRD pattern of this symmetrical cell is shown in Figure 4.4b). The XRD pattern resembles as that of STN powder and few minor secondary phases were also detected. Formation of reduced $\text{TiO}_2$ (rutile) is expected for a STN sintered in reducing atmosphere [55, 11]. However, the intensity of those unidentified peaks was very small to resolve. ScYSZ electrolyte peaks were seen along with STN peaks. The signal from the electrolyte was presumably detected through the porous electrode or could be from the sides of the symmetrical cell, where the electrolyte was exposed.

The scanning electron microscopy (SEM) micrographs of the BEC and TEC infiltrated STN anodes are shown in Figure 4.5. The micrograph of BECs and TECs infiltrated STN shows a uniform distribution of nanostructured CGO.
It has also formed a percolated network in the STN backbone, which facilitates oxide ion conduction throughout the backbone. The nano-sized metal phase is found well dispersed in the CGO matrix and they are expected to act as active sites for hydrogen oxidation. For the Ni-Pd-CGO and Pt-Pd-CGO, the average particle size of the metal phase is larger than Pd-CGO and Pt-CGO, respectively and is attributed to rapid particle growth of Ni nanoparticles.

4.4.2 Electrochemical Performance of Binary and Ternary Electrocatalyst Infiltrated Anodes

Figure 4.6a shows the impedance measurements of STN symmetrical cells infiltrated with Ni-CGO, Pd-CGO, Ru-CGO and Pt-CGO electrocatalyst at 600 °C. The electrolyte ohmic resistance, $R_0$ was in the range of 1.5 to 1.9 Ωcm$^2$ at 600 °C for all the infiltrated anodes. The reason for this variation in ohmic resistance is discussed in the later part of this section. $R_p$ (i.e. summation of $R_1$ and $R_2$) of the STN anode without infiltration shows a high value of 352 Ωcm$^2$; however it reduces to 0.96, 0.57, 0.51 and 0.16 Ωcm$^2$ for Ni-CGO, Pd-CGO, Ru-CGO and Pt-CGO, respectively at 600 °C. The drastic improvements in the electrode performance are due to the catalytic activity of the infiltrated Ni, Pd, Ru, Pt catalyst and CGO[56, 57]. Although CGO exhibits catalytic activity, it cannot be used as a standalone electrocatalyst due to its limited catalytic activity. The volume fraction of electrocatalyst infiltrated in the STN backbone was determined by measuring the change in weight after calcinations and are listed in Table 4.1.

Figure 4.6b shows the Arrhenius plot of $R_p$. STN without infiltration has the highest slope in the Arrhenius plot. The activation energy ($E_a$) of STN anode is 1.14 eV as shown in Table 4.1. The slopes are slightly reduced with
various infiltrates in STN backbone. The $E_a$ of Ni-CGO, Pt-CGO, Ru-CGO and Pd-CGO in STN anodes were 1.09, 0.84, 0.93, and 0.97 eV, respectively. The $E_a$ values are almost same for all the infiltrated STN anodes despite the reduction in $R_p$.

<table>
<thead>
<tr>
<th>Electro catalyst</th>
<th>1^{Metal}</th>
<th>2^{Metal}</th>
<th>CGO</th>
<th>1^{Metal} + CGO</th>
<th>2^{Metal} + CGO</th>
<th>$R_p$ $\Omega cm^2$ at 600 $^\circ$C</th>
<th>$R_p$ $\Omega cm^2$ at 500 $^\circ$C</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1^{Ni-CGO}</td>
<td>3.17</td>
<td>-</td>
<td>9.50</td>
<td>12.66</td>
<td>-</td>
<td>0.96</td>
<td>5.13</td>
<td>1.09</td>
</tr>
<tr>
<td>1^{Pt-CGO}</td>
<td>1.91</td>
<td>-</td>
<td>5.72</td>
<td>7.63</td>
<td>-</td>
<td>0.16</td>
<td>0.64</td>
<td>0.84</td>
</tr>
<tr>
<td>1^{Pd-CGO}</td>
<td>1.30</td>
<td>-</td>
<td>10.56</td>
<td>11.86</td>
<td>-</td>
<td>0.57</td>
<td>2.62</td>
<td>0.93</td>
</tr>
<tr>
<td>1^{Ru-CGO}</td>
<td>4.52</td>
<td>-</td>
<td>13.57</td>
<td>18.09</td>
<td>-</td>
<td>0.51</td>
<td>2.5</td>
<td>0.97</td>
</tr>
<tr>
<td>1^{Ni2Pt-CGO}</td>
<td>2.16</td>
<td>1.14</td>
<td>9.90</td>
<td>4.56</td>
<td>8.64</td>
<td>0.1</td>
<td>0.3</td>
<td>0.85</td>
</tr>
<tr>
<td>1^{Ni2Pd-CGO}</td>
<td>2.15</td>
<td>0.62</td>
<td>11.49</td>
<td>5.67</td>
<td>8.59</td>
<td>0.31</td>
<td>1.62</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 4.1: Performances and loading of various electrocatalyst in STN backbones.
Figure 4.6: Impedance spectra a) binary electrocatalysts measured in 3% $H_2/H_2O$ and b) Arrhenius plot of $R_p$. 
Figure 4.7: Impedance spectra a) Pd-CGO and Ni-Pd-CGO infiltrated STN anodes measured in 3\% $H_2/H_2O$ and b) Arrhenius plot of $R_p$.

Figure 4.7a shows the impedance spectra of STN infiltrated with Ni-Pd-CGO and are compared with Pd-CGO. $R_p$ determined from impedance spectra of Ni-Pd-CGO infiltrated anodes is 0.31 $\Omega cm^2$, while that of Pd-CGO is 0.57 $\Omega cm^2$ at 600 $^\circ$C. The parameters concerning the electrochemical characterization from the impedance spectra of figure 4.7a are listed Table 4.3.

$R_p$ of Pd-CGO infiltrated anodes showed a single arc with a characteristics frequency of 13Hz. The impedance spectra were fitted using the circuit $R_0(R_0Q_0)(R_1Q_1)$ with the number of elements depending on the number of arcs obtained. In case of Ni-Pd-CGO infiltrated anodes, the impedance spectrum showed three distinct electrode processes modeled with sub-circuits, $(R_1Q_1)$, $(R_2Q_2)$ and $(R_3Q_3)$ at high frequency (1 MHz-1000 Hz), middle frequency (1000-10 Hz) and low frequency ranges (10-0.01 Hz), respectively. $R_1$ at high frequency (HF) corresponds to interfacial resistance between the electrode/electrolyte, $R_2$ is associated electrochemical hydrogen oxidation reaction at middle frequencies (MF) and $R_3$ is due to the gas diffusion resistance at low frequency (LF)[16]. A small arc $(R_0Q_0)$ originating at very high frequency of 1 MHz for the impedance spectra are associated with the bulk properties of the electrolyte and is confirmed by observing the impedance spectra measured at low temperatures. For each electrode process the characteristic frequencies are listed in Table 4.3. A reduction in impedance is observed for Ni-Pd-CGO electrocatalyst infiltrated anodes, however it is not possible to determine which electrode process has been significantly reduced. The improvement in electrode performance can be attributed to the synergistic activity of Pd and Ni catalyst as reported in literature[57]. The activation energies of this electrocatalyst infiltrated anodes are calculated from the Arrhenius plot shown in Figure 4.7b. $E_a$ of Ni-Pd-CGO is 0.98 eV and this value is similar to Pd-CGO.
Figure 4.8: Impedance spectra a) Pt-CGO and Ni-Pt-CGO measured in 3% 
$H_2/H_2O$ and b) Arrhenius plot of $R_p$.

<table>
<thead>
<tr>
<th>Electro catalyst</th>
<th>$(R_1Q_1)_{HF}$</th>
<th>$(R_2Q_2)_{MF}$</th>
<th>$(R_3Q_3)_{LF}$</th>
<th>$R_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_1$</td>
<td>$F_{max,HF}$</td>
<td>$R_2$</td>
<td>$F_{max,HF}$</td>
</tr>
<tr>
<td></td>
<td>$\Omega cm^2$</td>
<td>(Hz)</td>
<td>$\Omega cm^2$</td>
<td>(Hz)</td>
</tr>
<tr>
<td>$^{1}$Pd-CGO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>$^{1}$Ni$^2$Pd-CGO</td>
<td>0.2</td>
<td>1940</td>
<td>0.2</td>
<td>144</td>
</tr>
<tr>
<td>$^{1}$Pt-CGO</td>
<td>0.09</td>
<td>2000</td>
<td>0.05</td>
<td>133</td>
</tr>
<tr>
<td>$^{1}$Ni$^2$Pt-CGO</td>
<td>0.07</td>
<td>830</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.3: Electrochemical characterization of the infiltrated STN anodes at 
$600^\circ C$ in $H_2/H_2O$ gas mixtures.

Similarly, the parameters concerning the electrochemical characteriza-
tion of the Ni-Pt-CGO infiltrated anodes are listed in Table 4.3. $R_p$ of Ni-Pt-CGO electrocatalyst infiltrated anode is 0.1 $\Omega \text{cm}^2$ determined from Figure 4.8a. The value of $R_p$ obtained is lowest of anodes that had been tested and is even lower than Pt-CGO infiltrated STN, which is 0.16 $\Omega \text{cm}^2$. For Pt-CGO infiltrated anodes $R_1$, $R_2$ and $R_3$ resistances associated with electrode processes described earlier were observed. The electrode resistance at HF associated with electrode/electrolyte contact is lowered with Ni-Pt-CGO. MF arc associated with electrochemical hydrogen oxidation reaction resistance $R_1$, has been completely disappeared. However, $R_3$ associated with gas diffusion at LF increased slightly. Most of the beneficial electrochemical properties are achieved from the Pt catalyst and nanocrystalline morphology of TEC. $E_a$ of Ni-Pt-CGO anode is 0.85 eV determined from the Arrhenius plot shown in Figure 4.8b. $E_a$ of Pt containing ternary and binary electrocatalyst are almost in the same range and has lower activation energy compared to other catalysts.

A same $R_0$ is expected between the anodes at one particular temperature. This is a good indication in estimation of correct electrode polarization resistance (Figure 4.9 shows the temperature dependence of $R_0$). The solid line indicates the $R_0$ of ScYSZ electrolyte for a thickness of 120 $\mu$m and was calculated based
on the ionic conductivity values reported in literature[58]. $E_a$ obtained for ScYSZ electrolyte is 1.3 eV. The $R_0$ of the anodes infiltrated with various electrocatalyst are almost same and have the same slope as that theoretically calculated ScYSZ. However, the small variations in $R_0$ at high temperatures are probably due to the micro structural variations of the backbone and problems associated with current collector contacts.

4.4.3 Electrochemical Performance of Quaternary Infiltrated Anodes

Figure 4.10a shows the impedance spectra for STN symmetrical cells infiltrated with Ni-CGO and Ru-Pd-Ni-CGO in $H_2$ with 3% $H_2O$ at 600 °C with two distinguishable arcs. The impedance spectra were fitted with the circuit ($R_0Q_0$) ($R_1Q_1$) ($R_2Q_2$). [16]. For the infiltration with Ru-Pd-Ni-CGO a $R_p$ of 0.28 Ω cm$^2$ has been obtained at 600°C. The values of $R_p$ includes the gas diffusion resistance ($R_p = R_1 + R_2$) at 500 and 600 °C are listed in Table 4.4. The metallic catalyst (11% Ru, 5% Pd and 9% Ni) in CGO facilitates significant reduction in $R_1$ compared to Ni-CGO (25% Ni in CGO) electrocatalyst i.e., 0.18 and 0.26 Ω cm$^2$. It is known from our previous experiments [chapter 3] that the gas diffusion resistance, $R_2$ increases with the amount of electrocatalyst loading in STN backbone. As listed in Table 4.4, the loadings of Ni-CGO and Ru-Pd-Ni-CGO were kept constant for comparison of results. Intriguingly, almost similar $R_2$ value of 0.10 and 0.14 Ω cm$^2$ is obtained for Ru-Pd-Ni-CGO and Ni-CGO, respectively and these values imply that the amount of catalyst loaded in STN was the same; however a slight increase in $R_2$ for Ni-CGO is believed to be due to the coarsening of Ni nanoparticles which could hinder the gas access.

<table>
<thead>
<tr>
<th>Infiltrations</th>
<th>$R_p$ at 600 °C[Ω cm$^2$]</th>
<th>$R_p$ at 500 °C [Ω cm$^2$]</th>
<th>Activation Energy (eV)</th>
<th>Infiltrations loadings (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*STN</td>
<td>352</td>
<td>2×10$^2$</td>
<td>1.14</td>
<td>0</td>
</tr>
<tr>
<td>Ni-CGO</td>
<td>0.40</td>
<td>2.28</td>
<td>0.99</td>
<td>25</td>
</tr>
<tr>
<td>Ru-Pd-Ni-CGO</td>
<td>0.28</td>
<td>1.02</td>
<td>0.96</td>
<td>24</td>
</tr>
<tr>
<td>Ru-Pd-CGO</td>
<td>1.30</td>
<td>5.95</td>
<td>0.91</td>
<td>16</td>
</tr>
</tbody>
</table>

Table 4.4: Performance, loading and activation energies of the anodes infiltrated with quaternary electrocatalysts. *STN backbone without infiltrations.

The performance of noble metals containing Ru-Pd-CGO without Ni shows a high $R_p$ of all anodes compared; One possible reason is less loading (16
Figure 4.10: Impedance spectra a) Ni-CGO and quaternary electrocatalysts under equal loading conditions and b) Arrhenius plot of $R_p$. 
Figure 4.11: TEM spectral mapping of quaternary electrocatalyst in STN backbone.

vol. %) of the electrocatalyst in STN backbone or synergistic performance is not achieved in this electrocatalysts combination. The impedance spectrum (not shown) obtained for Ru-Pd-CGO at 600°C have shown two time constants and both $R_1$ and $R_2$ are thermally activated indicating the presence of two different electrode process other than gas diffusion limitations. Figure 4.10b shows the temperature dependence of $R_p$. The activation energies of Ni-CGO, Ru-Pd-CGO and Ru-Pd-Ni-CGO infiltrated STN anodes were almost the same despite the reduction in $R_p$ and are listed in Table 4.4. STN without infiltration had $R_p$ values several orders of magnitudes higher.

Shown in figure 4.11 is the microstructure of STN anodes infiltrated with
Figure 4.12: TEM images of quaternary electrocatalysts in STN backbone (high resolution images).

Ru-Pd-Ni-CGO. A well defined porous STN backbone was covered homogeneously with the infiltrated electrocatalyst as shown in Figure 4.11a. Elements present in the microstructure were mapped using TEM-EDX. The individual elemental mapping of Ce, Ni, Ru and Pd is depicted in Figure 4.11b, which correspond to the microstructure shown in Figure 4.11a. The quantity of Pd and Ru infiltrated in the structure was low and thus, the X-ray signals detected were weak, however the major composition of the electrocatalyst was CGO. Ce and Gd being heavier elements showed a clear X-ray mapping illustrating an uniform nano-coating of STN backbone.

Shown in figure 4.12 and 4.13 are the TEM images with with high magnification illustrating the distribution of electrocatalysts nanoparticles in the STN anode. The line-scan microanalysis was performed across the nanocomposite marked with an arrow as shown in 4.13b for a distance of 115 nm. From the X-ray signals, it appears that Ni formed an alloy with Pd[57] and are illustrated in figure 4.13c. Shown in figure 4.13d are the X-ray signals of Ce, Gd and Ru in the STN. It is suggested from the analysis that the nanocomposites of Ce, Gd and Ru cover the places that are less coated by Ni and Pd (shown in figure 4.13c), which resulted in a synergistic performance of electrocatalysts in the STN anode.
4.5 Summary

Nanostructured electrocatalyst suitable for low temperature solid oxide fuel cells anode were evaluated. Pt-CGO infiltrated STN anodes have showed a low electrode polarization resistance of $0.16 \, \Omega \, \text{cm}^2$ best performance among the binary electrocatalyst, while addition of Ni in Pt-CGO and Pd-CGO by dual infiltrations further lowered the electrode polarization resistance. The morphology of the catalyst showed well dispersed metal nanoparticles distributed in the matrix of CGO. The nanocrystalline alloys of Ni-Pt were formed in Ni-Pt-CGO electrocatalyst along with the coexistence of Ni and Pt nanoparticles as separate phase.

Ru-Pd-Ni-CGO electrocatalyst infiltrated STN anodes have shown better anode performance suitable for low temperature operating SOFCs; particularly the electrode interface resistance has been reduced compared to Ni-CGO electrocatalyst. The major portion of the electrocatalyst was nanostructured CGO uniformly covering the STN backbone. The metal particles distributed on the CGO acts as effective catalytic sites for hydrogen oxidation. The improved performance of the Ru-Pd-Ni-CGO electrocatalyst is attributed to the synergistic effect of Ni, Pd and Ru, CGO electrocatalyst.
Chapter 5

Improved Ceramic Anodes with Metallic Functional Layer at the Electrode/Electrolyte Interface

5.1 About This Chapter

The electrode performance of solid oxide fuel cell anode with Pd nanoparticles at the interface of ScYSZ electrolyte and and $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$ (STN) electrode introduced in the form of metal functional layer have been investigated at temperatures below 600°C. A Pd metal functional layer was deposited by magnetron sputtering technique. Effecting from the heat treatments, Pd nanoparticles with particle sizes in the range 5-20 nm were distributed at the interface, and throughout the backbone. The polarization resistance of the modified STN reduced to $30\Omega cm^2$ at 600°C, which is three times less than an unmodified STN backbone. In order to improve the anode performance further, Pd and Gd-doped $CeO_2$ (CGO) electrocatalysts were infiltrated into the STN backbone. The modified interface with Pd nanoparticles in combination with nanostructured electrocatalyst by infiltration resulted in polarization resistances of $0.35\Omega cm^2$ at 600 °C in $H_2/3\% H_2O$.

5.2 Introduction

When pure electronic material like STN is used as anode, the electrochemical reactions are confined to the electrode/electrolyte interfaces (EEI) [59], where electrode, electrolyte and the fuel gas are in contact forming a three phase bound-
ary (TPB). Incorporation of nanostructured, catalytically active sites and path for oxide ion conduction is necessary in extending the TPBs [60]. TPB length plays a crucial role in improving the performance of SOFC anodes. Moreover, introducing electrocatalyst such as Ni and Gd-doped ceria (CGO) by infiltration is proven to extend the TPB length and to improve the performances [11]. Anode performance can be optimized by adjusting the electrocatalyst loading and particle size.

The main goal of this study is to improve the performance of STN based anodes by introducing catalyst nanoparticles at the EEI i.e., nano-sized Pd catalyst was incorporated in the required site of hydrogen oxidation in the form of a metal functional layer (MFL). The study was made systematic by varying the thickness of MFL deposited at the interface with the aim to increase the loading of catalyst; however the best performance is achieved with a MFL of 20 and 30 nm. The combined beneficial effects of Pd-CGO electrocatalyst infiltration and distributed Pd nanoparticles at the interface have shown a drastic improvement in electrode performance at low temperatures.

5.3 Experimental

5.3.1 Deposition of Metal Functional Layer (MFL) using Magnetron Sputtering

The MFL was deposited by magnetron sputtering system on both sides of presintered ScYSZ (10 mol % $Sc_2O_3$ in 1 mol % $Y_2O_3$ stabilized $ZrO_2$) electrolyte tape to form a symmetrical cell used for electrochemical testing. The magnetron sputtering setup is shown schematically in Figure 5.1. It consists of a vacuum chamber evacuated up to $10^{-6}$ Torr with a set of roughing and turbo molecular pumps. Ar gas was fed using a mass flow controller to create a working pressure ($p$), of tens of mTorr. The magnetron sputtering cathode is produced by Kurt Lesker and uses targets of 50 mm in diameter with indirect water cooling and possibility of both RF excitation and DC bias with respect to the ground (anode). In present experiments, a palladium plate of 0.2 mm in thickness and 50 mm in diameter was bounded with a thermally conductive silver adhesive on a thicker a copper disc. The target was then placed in front of permanent magnets that confine the plasma in to a ring-like structure situated very close to the surface. The target was DC biased ($U_{DC}$) with more than 200 V to ignite the
Figure 5.1: Schematic of sputter deposition technique (magnetron sputtering).
plasma discharge, while measuring the discharge current ($I_D$). Ions produced by electron ionization in the plasma-ring were accelerated towards the target (biased negatively) striking its surface with energies of over 100 eV. The ion impact produces physical sputtering of atoms and clusters from the target that was then transported by diffusion on the substrate forming a film with a certain deposition rate. A ScYSZ electrolyte tape with an area of $6\times 6 \text{ cm}^2$ and $120 \mu\text{m}$ thick was used as a substrate to deposit MFL. Typical parameters were, $p=50 \text{ mTorr}$, $U_{DC} =360 \text{ V}$, $I_D =200 \text{ mA}$ with a deposition rate of 20 nm/min. Deposition times of 60, 90, 300 and 500 s were used to deposit films of thickness 20, 30, 100 and 170 nm, respectively. The thickness of the films was determined using a Veeco stylus profilometer. The initial structure of the symmetrical cells was MFL$|$ScYSZ electrolyte$|$MFL.

### 5.3.2 Symmetrical Cells and Infiltrations

The STN powders synthesized by wet chemical method[61, 62] is mentioned in chapter 3 (section 4.3.1). Backbones of STN was prepared by screen printing an in-house STN ink on both the sides of ScYSZ electrolyte deposited with MFL to form a STN$|$MFL$|$ScYSZ electrolyte$|$MFL$|$STN structure. This raw symmetrical cell was sintered in air for 4 h. Subsequently, the sintered symmetrical was pre-reduced at 1000$^\circ\text{C}$ in $H_2/N_2$ gas for 5 h. These heat treatments resulted in distribution of MFL in EEI. The tape was cut into smaller pieces having an electrode area of $0.25\text{ cm}^2$ for use in the electrochemical set-up. The porosity of the STN backbone was determined by using simple phase analysis software on the polished SEM images.

A $0.75 \text{ M CGO (Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta})$ precursor solution were prepared by dissolving cerium nitrate ($\text{Ce(NO}_3)_3\cdot 6\text{H}_2\text{O}$) and gadolinium nitrate ($\text{Gd(NO}_3)_3\cdot 6\text{H}_2\text{O}$) in water along with a polymer surfactants to improve wetting properties. A precursor solution of Pd-CGO was made by mixing $0.60 \text{ M palladium nitrate (Pd(NO}_3)_2\cdot 6\text{H}_2\text{O})$ in an already prepared CGO solution. Pd-CGO precursor solution contains 10 wt. % of Pd and 90 wt. % of CGO. The STN anodes were prepared by infiltrating few drops of the prepared precursor solution into the symmetrical cell, after which they were placed in a vacuum chamber. Vacuum was applied in order to remove the air bubbles and facilitate the liquid precursor penetrate the anode homogeneously. The cell was infiltrated 3 times with Pd-CGO; after each infiltration the cells were calcined at 350$^\circ\text{C}$ for 1 h in air. The change in weight after calcination was recorded after each infiltration. The volume
fraction of Pd-CGO is 7.6 vol. % in STN|MFL|ScYSZ electrolyte|MFL|STN, while 8.5 vol. % for STN|ScYSZ electrolyte|STN symmetrical cell.

5.4 Results and Discussions

5.4.1 Electrochemical Characterization of Interface Modified STN Anodes

Figure 5.2 is the schematic sketch of anode structure used in this work. Process 1, before sintering portray the raw assembly (one side of the symmetrical cell is shown), wherein MFL is sandwiched between the STN and pre-sintered ScYSZ tape. Process 2 corresponds to distribution of Pd thin film into nanoparticles in the EEI and on an STN backbone after sintering and the process 3 illustrates the infiltrated Pd-CGO electrocatalyst into the STN backbone forming a percolated network of Pd-CGO.

Shown in figure 5.3 are the impedance spectra of STN symmetrical cells with and without MFL measured at 600 °C. The high frequency intercept in the X-axis corresponds to the ohmic resistance of the electrolyte ($R_0$). In the spectra shown, the values of $R_0$ and polarization resistance ($R_p$) were determined from the impedance spectra fitted using the general equivalent circuits $R_0(R_pQ_p)$. The fitted parameters such as resistance (R), admittance parameter ($Y_0$), and frequency power (n) for each (RQ) sub-circuits were used to calculate the characteristic frequency ($F_{max}$) and capacitance (C) using the relations 5.1 and 5.2.
Figure 5.3: Impedance spectra of modified and unmodified STN with Pd nanoparticles at the interface measured in 3% \( H_2/H_2O \).

\[
F_{\text{max}} = \frac{1}{2\pi\tau_{\text{RQ}}}
\]  

(5.1)

\[
C = Q^{\frac{1}{2}} R^{\frac{1}{n+1}}
\]  

(5.2)

The bar chart shown in figure illustrated the reduction in \( R_p \) at 600 °C. The impedance of STN without Pd has shown a high \( R_p \) of 90Ω\( cm^2 \). With a Pd MFL of 170 nm at the EEI, \( R_p \) reduced to 54 Ω\( cm^2 \). A thinner MFL at the interface yields better performance. This can be seen from the impedance spectra for various MFL thicknesses ranging from 20 to 170 nm. For instance, with 100 and 30 nm thick MFL, \( R_p \) reduces to 45 and 33 Ω\( cm^2 \), respectively. For thin films below 100 nm, 40 to 50 % reductions in \( R_p \) was achieved at 600 °C. The performance of 30 nm MFL is similar to that of 20 nm MFL, which is about 30 Ω\( cm^2 \). With a 20 nm thick MFL, \( R_p \) reduction of 70 % is achieved to that of STN without MFL. The enhanced performance of thinner MFL is due to the distribution of Pd MFL into nanoparticles with high surface area at the EEI and by the incorporation of catalytically active sites for hydrogen oxidation. Although a considerable reduction in \( R_p \) is achieved by incorporating MFL, a further reduction in STN anodes are required and could be achieved only with the introduction of electrocatalyst by infiltration into STN backbone.
Figure 5.4: Bar chart of $R_p$ with result of Pd MFL measured at 600 °C in 3% $H_2/H_2O$.

Shown in figure 5.5a is the Arrhenius plot of $R_p$. The activation energy ($E_a$) was determined as 0.95 to 1.00 eV for all anodes, both with or without MFL and irrespective of its thickness, despite the variation in polarization resistance. Figure 5.5b shows the temperature dependence of $R_0$. A random variation in $R_0$ was observed at high temperatures (550 to 650 °C) for all the anodes measured, including an unmodified STN backbone. A comparison of $R_0$ with the ohmic resistance of ScYSZ electrolyte calculated from the literature reported ionic conductivity values corresponding to the thickness 120 µm is shown [58]. The variations in $R_0$ are thought to originate from the differences in current collector contact and microstructures as described earlier.
Figure 5.5: Arrhenius plot of polarization resistance, $R_p$ and electrolyte ohmic resistance $R_0$ measured in 3% $H_2/H_2O$. 
Figure 5.6: Arrhenius plot of polarization resistance, $R_p$ and electrolyte ohmic resistance $R_0$ measured in 3% $H_2/H_2O$. 


<table>
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<tr>
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<th>$R_2 Q_2$</th>
<th>$R_3 Q_3$</th>
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<td>0.5-2.5 µF/cm$^2$</td>
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<th>$F_{\text{max, HF}}$</th>
<th>$R_2$</th>
<th>$F_{\text{max, HF}}$</th>
<th>$R_3$</th>
<th>$F_{\text{max, HF}}$</th>
<th>$R_p$</th>
<th>$\Omega cm^2$</th>
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<td>-</td>
<td>-</td>
<td>0.3</td>
<td>105</td>
<td>0.8</td>
<td>4.3</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>Pd-CGO with MFL</td>
<td>0.1</td>
<td>$2 \times 10^6$</td>
<td>0.35</td>
<td>507</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
<td>-</td>
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</table>

Table 5.2: Electrochemical characteristics of STN backbone with 20 nm MFL and Pd-CGO infiltrations measured at 600°C.

Figure 5.6a shows the impedance spectra of Pd-CGO infiltrated STN backbone with and without MFL of 20 nm thickness measured at 600°C. Equivalent circuits $R'_0(R_0 Q_0)(R_1 Q_1)$ and $R_0(R_1 Q_1)(R_2 Q_2)$ were used to determine $R_s(= R'_0 + R_0)$ and $R_p(= R_1 + R_2)$. The $R_p$ of Pd-CGO electrocatalyst infiltrated STN is 1.1 $\Omega cm^2$ and for an infiltrated backbone with Pd nanoparticles at the EEI, $R_p$ has been reduced to 0.35 $\Omega cm^2$, which is 65% reduction. The performance of these electrodes was compared with almost similar loading (8 vol. %) of Pd-CGO electrocatalyst. The electrochemical properties at 600 °C are listed in Table 5.2. Pd-CGO electrocatalyst infiltrated STN without MFL was fitted with equivalent circuits containing the sub-circuits $(R_1 Q_1)$ and $(R_2 Q_2)$ i.e., $R_0(R_1 Q_1)(R_2 Q_2)$. The former sub-circuit represents high frequency part (100-500Hz) of the spectrum and is associated with the charge transfer resistance at the electrode/electrolyte interface, while the latter sub-circuit at low frequency part (5-10Hz) represents the impedance due to dissociative adsorption in combination with gas diffusion limitations [57]. However, the gas diffusion impedance must be very small compared to the impedance of other electrode processes. In case of Pd-CGO infiltrated with Pd MFL of 20 nm thickness, $(R_0 Q_0)$ and $(R_1 Q_1)$ i.e., $R'_0(R_0 Q_0)(R_1 Q_1)$ equivalent circuit was used to fit the spectrum. $(R_0 Q_0)$ at very high frequency part of spectrum is not an electrode related process and represents the bulk properties of electrolyte. This can be supported from low capacitance (0.8 µF/cm$^2$) and by observing the impedance spectra at low temperatures, where impedance arcs ascribed to grain boundary and grain interior were evolved completely. As suggested earlier, the sub-circuit $(R_2 Q_2)$ is linked to electrode process in combination [57]. A drastic improvement in charge transfer in combination with dissociative adsorption of hydrogen is observed in these modified electrodes. The presence of gas diffusion impedances at low frequencies (10 Hz) slightly appears at this temperature and is more evident at high temperatures.
Figure 5.7: TEM images of the STN symmetrical cells with MFL a) illustrates the Pd nanoparticles in the interface of STN backbone and ScYSZ electrolyte and b) energy dispersive spectroscopy (EDX) analysis on the nanoparticles.

The Arrhenius plot of $R_p$ is shown in Figure 5.6b. The $E_a$ of the Pd-CGO infiltrated STN anode without MFL is 1 eV and for the anode with MFL a similar $E_a$ of 0.9 eV is obtained. Shown in Figure 5.6c are the temperature dependencies of $R_0$. The calculated $E_a$ is 1.3 eV for ScYSZ electrolyte.

### 5.4.2 Role of Metal Functional Layer

The role of the MFL in improving the performance of the STN based anodes was investigated using TEM. Hydrogen oxidation in STN was expected to take place only at the interface and modification at interface with high surface area catalyst is proven beneficial [59]. Figure 5.7 and 5.8 gives an overview of STN electrode with 30 nm Pd MFL in the EEI. Figure 5.7a is the cross section of STN/ScYSZ symmetrical cell. Close examination of the interface of ScYSZ electrolyte and STN backbone reveals dark spots of Pd nanoparticles and they are about 20 nm in size. Furthermore, STN backbone adheres well with the ScYSZ electrolyte. Figure 5.7b shows the presence of Pd peaks at 2.84 and 3.5 keV resulted from an EDX point analysis on these dark spots.

Further elemental analysis on STN/ScYSZ interface shown in Figure 5.8a reveals the nanoparticles of Pd at the interface and on the STN backbone (shown
Figure 5.8: TEM images of the STN backbone showing the distributed nature of MFL after sintering. a) STN/ScYSZ interface with distributed Pd nanoparticles and b) the three images (1, 2 and 3) depicts nanosized Pd in the STN backbone.

Figure 5.9: TEM images a) STN anode showing nanostructured Pd-CGO infilltrations in combination with Pd nanoparticles and b) Higher magnification of figure 5.9a.
in Figure 5.8b. The size of the Pd particles is surprisingly small (< 5 nm) and resulted in a very high surface area. During sintering in air, the Pd MFL is expected to form PdO and re-distribute on the STN backbone. Following sintering, a treatment in $H_2/N_2$ gas conditions at 1000°C would convert the PdO into Pd. Shown in Figure 5.9a and b (high resolution image) is the Pd-CGO infiltrated STN anode in combination with Pd nanoparticles. The image shown in Figure 5.9a clearly reveals the distribution of Pd nanoparticles at the interface and demonstrates that they uniformly cover STN backbone. It is suggested from Figure 5.9b that Pd-CGO has the particle size smaller than the Pd nanoparticles, which may have resulted in better electrode performance.

5.5 Summary

The electrochemical properties of $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$ ceramic backbone as SOFC anodes had been improved by a Pd nanoparticles at the interface of electrode and electrolyte. The catalytic activity is still insufficient to attain a decent SOFC anode performance at low temperatures of SOFC. Hence, the anode is further infiltrated with Pd-CGO electrocatalyst, which resulted in a drastic reduction of electrode polarization resistance. The combination of interface modification with Pd-CGO electrocatalyst infiltrations had shown an improved electrode performance of 0.35 $\Omega cm^2$. The microstructural analysis on the electrode revealed the presence of nanosized electrocatalyst with two different particle size distributions.
Chapter 6

Effect of Ceria Interfacial Layer in The STN Anode

6.1 About This Chapter

Modification of Nb-doped $\text{SrTiO}_3$ with Gd-doped ceria (CGO) exhibits improved electrocatalytic property for low temperature solid oxide fuel cell (SOFC) anodes operating at less than 600°C. CGO was introduced in Nb-doped $\text{SrTiO}_3$ in the form of a thin layer using spin coating technique at the ScYSZ/STN interface. The assembly was then fired at in air, with subsequent heat treatment at 1000°C in reducing gas condition. The TEM-EDX analysis suggests that the dissolution of Ce in Nb-doped $\text{SrTiO}_3$(STN). An anode polarization resistance of 20 $\Omega cm^2$ at 600°C was measured in hydrogen fuel (3% $H_2O/H_2$) for a CGO modified STN. Although this resistance is too high for an efficient SOFC, this value is 80% lower than that of the unmodified STN anode. It is demonstrated that a high performance of 0.1 and 1.5 $\Omega cm^2$ at 600 and 400°C, respectively can be obtained with a CGO modification in STN combined with Pd-CGO electrocatalyst loading of 21 vol. %. Microstructure analysis of the infiltrated Pd-CGO electrocatalyst reveals a nanocrystalline morphology.

6.2 Introduction

It is known that, $\text{SrTiO}_3$ perovskite oxide exhibits electronic conduction resulting from Ce-doping [63]; however the catalytic properties of this ceramic have not been investigated in depth. Marina et al [64, 65] reported on the (Ce, La) doped
SrTiO$_3$ ceramics with excellent electrocatalytic activity to hydrogen oxidation at high temperature. In this chapter, we describe the modification of STN backbone with CGO, introduced in the form of a spin coated layer at the interface of STN and ScYSZ. A drastic reduction in electrode polarization resistance. Transmission electron microscopic characterization reveals a partial dissolution of CGO in STN as result of heat treatments. The CGO-modified STN backbone was further infiltrated with Pd-CGO electrocatalysts. The loading of the electrocatalyst were increased systematically to study the electrochemical properties of the infiltrated anodes. The electrochemical studies revealed that CGO modification in STN backbone significantly contributes to the improvement in electrode performance of the infiltrated anodes.

### 6.3 Experimental

#### 6.3.1 Spin Coating of CGO

CGO precursor gel suitable for spin coating was prepared by dissolving cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) and gadolinium nitrate ($Gd(NO_3)_3 \cdot 6H_2O$) of molar ratio Ce:Gd=0.8:0.2 in ethylene glycol. The detailed characterization of the CGO precursor for spin coating was reported by our group [66]. Pre-sintered ScYSZ (10 mol % $Sc_2O_3$, 1 mol % $Y_2O_3$stabilized $ZrO_2$) tapes of area $6 \times 6 \ cm^2$ were washed with ethanol and heat treated at 300$^\circ$C overnight, to remove organic impurities. A few drops of precursor were added on the tape which was held by a vacuum created by the spin coater (Model: WS-400A-8NPP/LITE, Laurell Technologies Corporation). During the spin process, initial ejection of excess solvent took place was followed by an evaporation of the solvents resulting in a thin film. The thin film deposited on the electrolyte was heat treated at 350$^\circ$C for 1 h in air, which burned away the binders and left a weakly bound CGO layer measuring 400-500 nm in thickness.

#### 6.3.2 Formation of Anodes by Pd-CGO Infiltrations

The STN powders synthesized by wet chemical method[61, 62] as mentioned in chapter 4 (section 4.3.1). Backbones of STN were prepared by screen printing an in-house STN ink on both the sides of CGO coated ScYSZ electrolyte tapes. This raw symmetrical cell was sintered in air for 4 h. Subsequently, the sintered sym-
metrical cell was pre-reduced at 1000°C in H₂/N₂ for 5 h. The cells were cut into smaller squares having an electrode area of 0.25 cm² for use in the electrochemical set-up. An approximate porosity of 42 vol. % was obtained in the STN backbone, as determined by analysis of the SEM images using phase analysis software.

A 0.75 M CGO (Ce₀.₈Gd₀.₂O₂₋₅) precursor solution were prepared by dissolving cerium nitrate and gadolinium nitrate in water along with a polymer surfactant to improve wetting properties. A precursor solution of Pd-CGO was made by mixing 0.60 M palladium nitrate in an already prepared CGO solution. The Pd-CGO precursor solution contains 10 wt. % of Pd and 90 wt. % of CGO. The STN anodes were prepared by infiltrating a few drops of the precursor solution into the symmetrical cell. Vacuum was applied in order to remove the air bubbles in the porous STN backbone and to facilitate the liquid precursor to coat the surface of the anode homogeneously. The cell was infiltrated 1×, 3×, 5× and 9× with Pd-CGO to vary the loadings in the porous STN systematically. After each infiltration, the cells were calcined at 350°C for 1 h in air. The change in weight after calcination steps was recorded; the loading in volume percentage with repetitive cycles of infiltrations is listed in Table 6.1. The procedure for electrochemical characterization are reported in chapter 4 (section 4.3.3).

<table>
<thead>
<tr>
<th>STN backbone</th>
<th>Number of Pd-CGO infiltrations</th>
<th>0×</th>
<th>1×</th>
<th>3×</th>
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<tr>
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<tr>
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<td>R_p(Ωcm²) at 400°C</td>
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<table>
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<tr>
<th>CGO modified STN (CMS) backbone</th>
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<th>1×</th>
<th>3×</th>
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<td>14</td>
<td>21</td>
<td></td>
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<td>21</td>
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<td>R_p(Ωcm²) at 400°C</td>
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<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1: Pd-CGO loading and porosity after each infiltration.

The microstructure of the STN backbone and CGO-modified STN were investigated with a transmission electron microscopy (TEM) at an accelerating voltage of 300 kV (JEM – 3000F, FEGTEM). Energy dispersive X-rays (EDX) spectral mapping was performed on the infiltrated backbone using an Oxford EDX detector. A~ 100 nm thin TEM lamella was prepared by the use of a FIB-TEM H-bar technique in a crossbeam 1540XB dual focused ion beam (FIB)/SEM
6.4 Results and Discussions

6.4.1 Electrochemical Performance of CGO Modified STN Backbone

Impedance spectra of STN backbone and CGO modified STN at 600°C are shown in Figure 6.1a. The STN backbone shows a high $R_p$ of 90 $\Omega \text{cm}^2$ and the CGO modified STN; a reduced $R_p$ of 20 $\Omega \text{cm}^2$ is obtained. Impedance spectra for this electrodes appears to overlap in time constant and fitted using the circuit, i.e. $R_0(R_1Q_1)$. $R_0$ of both anodes is the same 0.9 $\Omega \text{cm}^2$ at 600°C. Despite the decrease in $R_p$ for the CGO-modified STN, there was no significant difference in the activation energies ($E_a=1.2$ eV) of the two backbones as shown in Figure 6.1b.

In order to study the effect of CGO in STN backbone, a small quantity of powders were infiltrated with CGO precursors. A CGO loading of (8.3 mol. %) in STN was obtained. XRD of CGO modified STN, CMS powder at oxidation (1200°C in air, 4h), reduction (1000, 1200 and 1300°C in 9% $N_2/H_2$, 5h) and re-oxidation (1000°C in air, 5 h) was performed and is shown in Figure 6.2. For the composite sintered at 1200°C in air, separate peaks of fluorite CGO and cubic perovskite STN were obtained. This finding is consistent with previous reports suggesting no reactions between these phases in air[67]. The XRD pattern obtained at 1000°C in $N_2/H_2$ shows the low intensity peaks of CGO and this is attributed to the reduction of $Ce^{4+}$ to $Ce^{3+}$. A low intensity peaks are observed up to 1200°C in $N_2/H_2$ gas conditions and the peak intensities are very small. Intriguingly, at 1300°C in $N_2/H_2$ gas conditions, the most of the CGO peaks of very low intensities could not be resolved except the main (111) peak. The presence of (111) ceria peak essentially indicates the presence of a small quantity of Ce on the STN. Furthermore re-oxidation of the CMS at 1000°C in air retained the CGO peaks with broader peaks.

It is to be noted that, no secondary phases are resolved from the XRD. The formation of $SrCeO_3$ and $Sr_2TiO_4$ is possible in Ce-modified $(La, Sr)(Ti, Ce)O_3$ in reducing atmosphere as reported by Marina et al[64]. The XRD pattern showing the strong reflections of ScYSZ and STN electrode limited the detection of secondary phases. Further, XRD pattern of a CGO modified STN backbone had not revealed the peaks corresponding to CGO. Interference of ScYSZ electrolyte...
Figure 6.1: a) Impedance spectra STN and CGO modified STN and b) Arrhenius plot of $R_p$
Figure 6.2: XRD of CMS (CGO modified STN) showing oxidation and reduction characteristics.

peaks of fluorite type structure due to porous nature of the electrode interferes with the resolution of the CGO peaks. The improved electrochemical properties of the CGO modified STN backbone as anode is probably due to the catalytic activity of CGO. Koutcheiko et al[67] investigated the effect of ceria modified Y-doped SrTiO$_3$ (YST) ceramics. In conclusion, the catalytic behavior of YST had been improved with ceria modification, however reduction in electronic conductivity is observed by increasing the ceria content in YST.

The microstructure of the post-tested STN backbone is shown in Figure 6.3(top image) and is compared with CGO modified STN backbone in Figure 6.3(bottom image). No change in grain sizes or other microstructural difference can be seen in the SEM images. The slight differences in these images are due to the detector used, i.e., for STN backbone in-lens detector and for CGO modified STN backbone SE2 detector. TEM investigation was performed on the samples. Figure 6.4a, b show images of the CGO modified STN backbone. The presence of CGO layer or nanoparticles at the interface or on the STN is not observed, however X-ray signals of Ce are detected in STN backbone as shown in Figure 6.4c This TEM-EDX analysis indicates the dissolution of Ce in STN. Cu peaks are from the sample holder and Ga signal appears from the sample preparation. With the expected peaks of ScYSZ (Sc, Y and Zr) and STN (Sr, Ti and Nb), a Si impurity peak is also detected.
Figure 6.3: SEM image of STN and CGO modified STN
6.4.2 Effect of Pd-CGO Infiltration in CGO Modified STN

The CGO modified STN backbone was used as the backbone and Pd-CGO electrocatalyst was incorporated by infiltration to form the anode. Figure 6.5 shows anode formation schematically. Process 1 shows the raw symmetrical cell assembly. Two CGO thin layers were deposited on a pre-sintered ScYSZ tape by spin-coating and calcined at 350°C in air in between each coating. The approximate thickness of the spin coated layers is around 1 µm, which consists mainly of binder. An approximate 25 µm thick STN layer was printed on the CGO coated electrolyte tape. Process-2 shows the CGO modified STN backbone. The most possible site for hydrogen oxidation is at the interface of ScYSZ and STN, since CGO is not present on the surface to facilitate ionic conductivity. The electronic conduction is achieved by the STN backbone. Process-3 illustrates the formation of the anode by infiltration of Pd-CGO electrocatalyst. The most favorable site for hydrogen oxidation reaction is on the Pd nanoparticle, however, the reaction can also take place on the nanostructured ceria distributed over the surface of the STN backbone. CGO further facilitates the oxide ion conduction in the anode with the distribution of three phase boundary.

Figure 6.6 shows the impedance spectra of CGO-modified backbone infiltrated with different amounts of Pd-CGO electrocatalyst. It is well known that,
Figure 6.5: Schematic sketch representing the process involved in the formation of infiltrated electrocatalysts on a CGO modified STN backbone.

Increasing the electrocatalyst loading improves the electrode performances[16]. As shown in Figure 6.6a, even the loading of 1 vol. % Pd-CGO, with one infiltration, reduced the $R_p$ to 0.55 $\Omega \text{cm}^2$, a value requiring at 3 infiltrations in non modified STN backbone. A significant enhancement in electrochemical properties was achieved by CGO modification. Further increase in the loading of Pd-CGO to 14 and 21 vol. % considerably lowers the $R_p$. The impedance spectra shown in Figure 6.6b composed of two arcs. The very high frequency arc at 600 °C indicates the bulk impedance of the electrolyte, which grows further at low temperature measurements and are included in the values of $R_0$ reported. The remaining two arcs essentially relate to the electrode process. The arc ($R_1Q_1$) with the $F_{max}$ range at 600-1000 Hz depending on the electrode indicates the charge-transfer process at the electrode/electrolyte interface [57] and is thermally activated. The low frequency arc ($R_2Q_2$) with $F_{max}$ in the range of 5-10 Hz is due to the gas diffusion impedance (chapter 3), which is almost constant with temperature. Both of these processes vary with increasing loading of Pd-CGO.

The changes in porosity resulting from Pd-CGO loading are listed in Table 6.1. The values of $R_1$ and $R_2$ obtained by fitting the impedance spectra with equivalent circuits are investigated by plotting them as the function of porosity as shown in Figure 6.7. $R_1$ decreased considerably from 45 vol. % down to 23 vol. %, owing to the incorporation of a large number of catalytically active sites for hydrogen oxidation. This type of lowering in $R_1$ with increase in loading of electrocatalyst has been earlier reported by Babaei et al [16] attributing to increase active sites for electrochemical reactions. On the contrary, $R_2$ increases with the porosity changes from 5 vol. % down to 23 vol. %. This is due to filling up of pores with the increment in loading of Pd-CGO. Our earlier study (chapter 3) on gas phase impedance revealed that, $R_2$ arises from the bulk and Knudsen diffusion of the porous anode and from the stagnant layer outside an electrode. The values of $R_p$ are considered to be a summation of electrode process resistance.
Figure 6.6: Impedance spectra of CGO modified STN anode infiltrated with Pd-CGO electrocatalyst

$R_1$ and $R_2$.

Figure 6.8 shows the Arrhenius plot of $R_p$. The activation energy ($E_a$) of the Pd-CGO in STN backbone is 1 eV. $E_a$ gradually decreased from 0.9 eV to 0.7 eV with the increment in loading of Pd-CGO from 1 to 21 vol. %. The lowering of activation energy with the loading of Pd-CGO is due to the major contribution from $R_2$, which has very low temperature dependence of $R_2 \propto T^{0.25}$ [chapter 3]. Separating $R_1$ and $R_2$ contributions is not possible due to the overlapping of time constants.

6.4.3 Ohmic Resistance and Current Collector

The Pt-paste used as the current collector was examined as anode. A very high $R_p$ of 123 \( \Omega cm^2 \) was obtained at 650°C in $H_2/3\%H_2O$, owing to its coarse microstructure. In high performing anodes, most of the beneficial electrochemical properties happen only at the few microns from the interface [68]. Thus, the contribution from Pt current collector is negligible in our electrodes and the same current collector was used for all the anodes to compare the results. Moreover, the interference of Pt and Au current collector on the electrochemical properties of the anode was investigated by Mueke et al [48]. The study by Mueke et. al. revealed no significant difference in using Pt and Au current collector.
Figure 6.7: The variations of electrode process resistance with porosity in Pd-CGO infiltrated anodes.

Figure 6.8: Arrhenius plot of $R_p$ for CGO modified STN anode infiltrated with Pd-CGO electrocatalyst.
Monitoring the ohmic resistance of the anodes is quite important for correct estimation of an electrode process impedance. Figure 6.9 shows the dependence of $R_0$ with temperature. $R_0$ of ScYSZ electrolyte measuring a thickness of 120 $\mu$m is plotted as a reference from the conductivity values reported in the literature [58]. The values of $R_0$ estimated using the equivalent circuits on these spectra obtained for infiltrated electrode vary from ScYSZ electrolyte resistance at high temperature (650 to 500°C), but are almost the same for the entire electrodes investigated. The slight variation in $R_0$ originates from microstructural differences at the interface of electrode/electrolyte and from the current collector contact.

6.4.4 Microstructural Characterization of The Infiltrated Anodes

Shown in Figure 6.10a and b are the SEM micrographs of the infiltrated anodes with a Pd-CGO of 14 vol. %. Figure 10a shows the fractured cross-sectional view of the CGO-modified STN infiltrated with Pd-CGO electrocatalyst. A good connectivity is seen with the Pd-CGO electrocatalyst, which facilitates oxide ion conduction over the STN backbone. A close inspection of this image shown in
Figure 6.10: SEM images of CGO modified STN anode infiltrated with Pd-CGO electrocatalyst.
Figure 6.11: TEM image of Pd-CGO electrocatalyst in CMS backbone.

Figure 6.12: TEM-EDX spectral imaging of Pd-CGO electrocatalyst in CMS backbone.
Figure 6.10b illustrates the uniform distribution of nano-sized Pd particles all over the backbone.

TEM micrographs shown in Figure 6.11, illustrates the three phase boundary created by infiltration. STN backbone with a pore radius of 200 nm facilitates electronic conduction and the pores shown provides gas access to the anode, while the Pd-CGO acts as the transport medium for oxide ion (apart from its main function as hydrogen oxidation catalyst). Owing to the well dispersed nature of Pd-CGO, X-ray signals detected were weak as reported by Tanksale et al [54]. Thus, EDX spectral imaging was performed on the infiltrated anode. The EDX elemental mapping analysis shown in Figure 6.12 identified the elements (Sr, Ti) and (Pd, Ce and Gd) corresponding to STN and Pd-CGO, respectively. Figure 6.13 shows the HR TEM image of the Pd-CGO electrocatalyst infiltrated in STN backbone. The CGO phases can be identified for the two grains, where the characteristic crystal planes of (111) and (200) are labeled. This analysis clearly confirms the presence of nanocrystalline Pd and CGO even at the low calcinations temperature of 350°C in air.
6.5 Summary

The effect of CGO in STN backbone was studied. Dissolution of Ce in STN backbone was investigated. CGO modified STN backbone has shown a beneficial electrochemical properties under anode measurement conditions. An anode was formed by infiltrating Pd-CGO electrocatalyst to a CGO modified STN backbone, which resulted in high performance SOFC anodes suitable for low temperatures. Increasing the loading of Pd-CGO decreased the charge transfer resistance of the electrode and increased the gas diffusion impedance as a result reduction in porosity. A high performance is achieved with Pd-CGO electrocatalyst loading 21 vol. % in CGO modified STN backbone. Pd-CGO showed nanocrystalline morphology and Pd nanoparticles were dispersed in CGO nanoparticulates.
Chapter 7

Physico-chemical and Electrochemical Properties of Tungsten Oxide Infiltrated SOFC Anodes

7.1 About This Chapter

Preparation and electrochemical characterization of $WO_3$-infiltrated W-Cu-ScYSZ (WCS) anode for solid oxide fuel cell are reported. The DC conductivity measurements on $WO_3$ ceramic revealed 1200 and 24 S/cm in reducing and oxidizing atmospheres, respectively at 650 °C. WCS porous backbones in the form of symmetric cells were prepared by screen printing of $WO_3$-CuO-ScYSZ ink and subsequent sintering at 1300°C for 1 h in 9% $H_2/N_2$. Phase analysis of the sintered backbone by X-ray diffraction showed metallic W and Cu reflections. Precursor solution of $WO_3$ or CuO was infiltrated into the porous WCS backbones to form the anode. The electrochemical performance measured on these anodes by impedance spectroscopy showed a polarization resistance values of 11 and 6.5 $\Omega cm^2$ for $WO_3$ and CuO infiltrated anodes respectively at 600°C in humidified hydrogen. Activation energy values of 0.9 and 1 eV were obtained for $WO_3$ and CuO infiltrated WCS anodes respectively. The microstructure of the tested anodes showed well-dispersed sub-micron particles of $WO_3$ in the WCS backbone, whereas CuO infiltration resulted in a dense microstructure.
7.2 Introduction

One extensively studied anode (fuel electrode) for SOFC is the Ni-YSZ cermet [69, 70]. Although Ni exhibits an excellent catalytic activity and electronic conductivity, it has the drawback of carbon and sulphur poisoning in hydrocarbon fuels and poor redox stability[71]. Various non-nickel based materials have been investigated in order to explore new anodes for SOFCs[72, 73, 74, 75]. For example Cr-Fe-YSZ [74], CeO$_2$-YSZ and La$\text{0.75}$Sr$\text{0.25}$Cr$\text{0.5}$Mn$\text{0.5}$O$_3$ $-$ $x$ [75] composites were reported as SOFC anodes operating at intermediate temperature range of 600-750°C. Similarly, perovskite type oxides such as La-doped $SrTiO_3$ and Nb-doped $SrTiO_3$ were reported as stable backbones (skeletal porous microstructure into which electrocatalyst materials are infiltrated) for SOFC anodes. Backbones are ionic or electronic conductors (e.g. Nb-doped $SrTiO_3$ and YSZ, respectively) and catalytic activity into these materials has been introduced by infiltration of electrocatalyst [51, 76, 77, 11].

In this present work, a preliminary investigation was made on WO$_3$-infiltrated 0.48W-0.52Cu-ScYSZ (WCS) composite material in order to explore its potential as low temperature (< 600 °C) SOFC anode operating in $H_2$ fuel. The WCS composite by itself has been examined as an anode and the results showed poor percolation of W and Cu along with disrupted electronic paths. This necessitated the infiltration of WO$_3$ and CuO into the WCS composite for hydrogen oxidation. Investigation on the electrochemical performance was performed on WO$_3$ and CuO infiltrated WCS anode and the results were compared.

7.3 Experimental

7.3.1 Symmetrical Cells Preparation and Infiltrations

WO$_3$ powder (Aldrich) was blended with CuO (Fluka) in a ratio of 70:30 by volume. This mixture was ball milled with 10 mm zirconia balls for 24 h in ethanol medium. The prepared mixture was added with ScYSZ (10 mol % $Sc_2O_3$ in 1 mol % $Y_2O_3$ stabilized $ZrO_2$) powder at a ratio of 50:50 by volume and ball milled for 24 h in ethanol medium. The resulting mixture (WO$_3$/CuO/ScYSZ) was dried overnight to remove ethanol and was then grounded to obtain a fine powder.
Symmetrical cells consisting of $\text{WCS/ScYSZ/WCS}$ for electrochemical impedance spectroscopy (EIS) measurements were prepared as follows. The $\text{WO}_3/\text{CuO/ScYSZ}$ powder mixtures were used to prepare screen printing ink by adding organic solvent, binder, plasticizers in a measured quantity. The ink was homogeneously mixed in a mechanical shaker for 12 h. The prepared ink was printed on both sides of the pre-sintered ScYSZ electrolyte tape of thickness 120 $\mu$m to fabricate the electrodes and sintered at 1300°C in 9% $\text{H}_2/\text{N}_2$ gas for 1 h. The sintered backbone has the thickness of 12-15 $\mu$m. The sintered symmetric cell was cut into small pieces with an area of 0.3 $cm^2$. The porosity of the resulting WCS backbone was 28%, as determined from SEM images of polished cross-sections of the symmetrical cells. The porosity of the symmetrical cells and pellets for electrical characterization was determined using a simple phase analyzing software developed in-house.

The $\text{WO}_3$ infiltration solution was prepared using ammonium metatungstate, (H.C. Starck). About 0.75 M of $\text{WO}_3$ precursor was prepared by dissolving ammonium tungstate in water along with 2 wt. % of polymer surfactant to enhance the wetting properties of the infiltration solution. The infiltrated WCS anodes were prepared by dropping few drops of the prepared precursor solution on to the symmetrical cells, after which they were placed in a vacuum chamber. Vacuum (100 mbar for 10 s) was applied in order to remove the air bubbles in the porous backbone and to facilitate the liquid precursor to homogeneously coat the surface of the anode with the capillary forces. In between each infiltration the electrodes were heat treated at 650°C for 2 h in air to form $\text{WO}_3$ and the weight changes were monitored. At the final loading (3rd infiltration) of $\text{WO}_3$ precursor in the WCS backbone, a 19 vol. % of $\text{WO}_3$ is achieved with respect to the electrode volume of $5.1 \times 10^{-4} \text{ cm}^3$.

Similarly CuO infiltration solution was prepared with copper nitrate (Alfa Aesar) as starting chemical. The concentration of the precursor was 0.42 M and was prepared by dissolving the copper(III) nitrate salt in water. About 2 wt. % of polymer surfactant was added. The same infiltration procedure stated for $\text{WO}_3$ was used. After each infiltration step, the electrodes were heat treated at 350°C for 1 h in air. The symmetrical cells were reduced in dry $\text{H}_2$ ($pO_2$ of $8.5 \times 10^{-30} \text{ atm}$) at 650°C for 12h before the electrochemical measurements were carried out.
7.3.2 Electrical Characterization of Porous $WO_3$

The samples for DC conductivity measurements were fabricated by uniaxially compacting the $WO_3$ powder using a die ($0.5 \text{ cm} \times 0.5 \text{ cm} \times 5 \text{ cm}$) at 40 MPa followed by isostatic compaction at 250 MPa. Subsequently, the pellets were sintered in air at 850°C for 10 h. The edges of the pellets were painted with Pt-paste for current collection and heat treated at 700°C in air. The conductivity measurements were performed under controlled oxygen partial pressure ($pO_2$). The $pO_2$ values were determined using an in-situ oxygen sensor. The measurement was initiated in air and the temperature was raised from 30 to 650 °C. Then the gas atmosphere was changed from air to reducing mixture (9% $H_2 / N_2 / 3% H_2O$ gas mixture) with the purging of $N_2$ gas in between. Redox stability was investigated by alternating the gas conditions between oxidizing and reducing gas while measuring the conductivity. For safety reasons, the rig was purged with nitrogen between the oxidation and reduction treatments.

7.3.3 Electrochemical Characterization of Anodes

The symmetrical cells were electrically contacted using Pt-paste (Ferro GmbH) and a Pt-grid. The electrochemical impedance measurements were performed using a Solartron (SI) 1260 frequency response analyzer. Amplitude of 50 mV was set on the SI resulting in a voltage of 5-50 mV across the symmetrical cell depending on the cell impedance. EIS measurement was performed with a temperature interval of 50 °C in the range from 650 to 400 °C. The frequency range was from 1 MHz to 5 mHz. The $pO_2$ values were determined by using an in-situ oxygen sensor in the test rig setup. A $pO_2$ of $5 \times 10^{-26}$ atm (-1124 mV vs air is obtained at 650 °C) was measured corresponding to 97 % $H_2$ in 3 % $H_2O$. The impedance data was corrected for a serial inductance in the order of 30-60 nH and modeled with equivalent circuits. The electrode polarization resistance ($R_p$) was divided by two considering the symmetrical cell and multiplied by area to obtain area specific resistances.

7.3.4 Microstructure and Physico-chemical Analysis

In order to observe the microstructure of the porous $WO_3$ pellets and to analyze the elemental composition of sintered pellets and fabricated WCS/SCYSZ/WCS symmetrical cells, they were mounted in epoxy resin under vacuum, polished and
carbon coated. A high resolution Zeiss Supra 35 scanning electron microscope (SEM) was used to observe the microstructure and energy dispersive spectroscopy (EDX) was used to analyze the elemental composition. The crystalline nature and phase analysis of WCS backbone was analyzed using Bruker D8 Bragg-Brentano X-ray diffractometer (XRD) with a step size of 0.05 and 2 s/step.

The weight loss of \( \text{WO}_3 \) in reducing atmosphere was determined using thermo gravimetric analyzer, TGA (NETZSCH, STA 409 PC/PG). A few milligrams of the \( \text{WO}_3 \) powder was heated to 1000 °C at a rate of 5 °C/min with a dwell time of 2 h and then cooled down to 30 °C at the same rate in 9 % \( \text{H}_2/\text{Ar} \) gas mixtures.

7.4 Results And Discussion

7.4.1 Characterization of \( \text{WO}_3 \)

SEM images of the pellets in oxidized and reduced state is shown in Figure 7.1a and b, respectively. For the micrograph shown in Figure 7.1a, \( \text{WO}_3 \) pellet was sintered at 850°C for 10 h in air. A density of 6.3 g/cm\(^3\) determined by Archimedes principle, which is 88% of the theoretical density. The SEM observation on this polished pellet evidently shows the presence of pores. Complete densification of \( \text{WO}_3 \) ceramic is difficult to achieve for pellets sintered in air ascribed to the \( \text{N}_2 \) insolubility, which hinders the densification process [78]. Heat treating the pellet in reducing gas (9% \( \text{H}_2/\text{N}_2 \)) at 650 °C leads to the microstructure shown in Figure 7.1b. No evidence of grain growth was observed after reduction. A rough estimation of porosity from the SEM images was 35% and 46 % for as-sintered in air and reduced samples respectively. It is to be noted that, the porosity determination by identifying dark (pores) and bright (grains) pixels on polished SEM images is not accurate; however this method can be used for relative comparison of porosity. An increase in porosity was observed in reduced pellets due to formation of sub-stoichiometric tungsten oxides and loss of \( \text{O}_2 \). In order to quantify the loss of oxygen, thermogravimetry analysis was carried out on \( \text{WO}_3 \) powders in 9% \( \text{H}_2/\text{Ar} \) gas mixture and the loss of weight as a function of temperature is shown in Figure 7.2. The weight loss at 650 °C is attributed to the loss of \( \text{O}_2 \) and at temperatures above 900 °C; the weight loss is attributed to sublimation of \( \text{WO}_3 \) as well as further loss of oxygen. The kinetics of the reduction is continuous and is dependent on the temperature and duration of exposure. Hence, the data
Figure 7.1: SEM microstructure of WO$_3$ pellets in reduced and oxidized state.

Figure 7.2: TGA of WO$_3$ powders determined in air.

from Figure 7.2 should be taken as a qualitative reference to the range of oxygen loss and cannot be read as absolute values of oxygen loss.

The DC conductivity measurements were carried out on a porous pellet of WO$_3$ over a period of 75 h at a temperature of 650°C in the reducing atmosphere (9%H$_2$ / N$_2$ / 3% H$_2$O ). The calculated conductivity values in different atmospheres are shown in Figure 7.3. At a $pO_2$ of $10^{-23}$ atm, a conductivity of 1200 S/cm was obtained for the WO$_3$ pellets and the conductivity value was stable for around 20 h. After the initial measurement, the redox stability of the porous pellets was studied by changing the reducing gas to increasing the $pO_2$ conditions. A conductivity of 24 S/cm was obtained for WO$_{3-\delta}$ pellet at a $pO_2$ of 0.21 atm. Further, changing from air to reducing gas, the initial conductivity was regained. WO$_3$ exhibited good stability under redox conditions.
7.4.2 Characterization of W-Cu-ScYSZ Anode

In general, the $WO_3$ crystal exhibits perovskite-like structure (i.e., without a B-cation in $ABO_3$ perovskite structure), where W atoms are enclosed by a corner sharing $O_2$ octahedral [20]. The amount of distortion from ideal cubic perovskite-like structure is temperature dependent in $WO_3$. In the range of -180 to 900°C, structural changes from tetragonal-orthorhombic-monoclinic-triclinic-monoclinic during cooling were reported by Salje [20]. At room temperature the most favorable structure for $WO_3$ is monoclinic phase. Under reducing atmosphere, $WO_3$ readily forms sub-stochiometric compounds. Figure 7.4 and 7.5 shows the XRD of the powder mixture of $WO_3$/CuO/ScYSZ and after sintering the powder mixture at 1300°C for 1 h in 9% $H_2/N_2$. Figure 7.4 shows the monoclinic peaks of $WO_3$ and CuO along with the cubic peaks of ScYSZ as separate phases as expected from the powder mixture. Figure 7.5 shows the XRD of the powder mixture after sintering in reducing gas, and clearly shows the peaks of W (BCC), Cu (FCC) and ScYSZ without the formation of any secondary phases. The sintering in reducing gas at 1300°C resulted in the reduction of $WO_3$ and CuO to their metallic states, W and Cu, respectively. Shown in Figure 7.6 is the compositional analysis spectrum from EDX along with the SEM micrograph of the WCS symmetrical cell cross section (shown in Figure 7.6).
Figure 7.4: XRD of $\text{WO}_3/\text{CuO/ScYSZ}$ powder mixtures.

Figure 7.5: XRD of W-Cu-ScYSZ powder mixtures in reduced state.
It is believed that at the electrode sintering temperature of 1300°C molten Cu re-arranged the nanoparticles/microparticles of W and resulted in agglomeration [79]. This resulted in a poor percolation of W and Cu in ScYSZ, which hinders current collection by disruption of the electron conducting paths, as depicted in Figure 7.7a. Thus, the backbone mainly provides an ion conduction path via ScYSZ. In order to compensate for an unintended rearrangement of Cu and W in ScYSZ, it is necessary to introduce electronic conducting paths. This can be done by the infiltration of electrocatalytic materials or possibly by optimizing the ratios of W, Cu and ScYSZ in the WCS composite. In this work, more electron conduction path was incorporated by the infiltration of WO$_3$ or CuO into the WCS backbone. The schematic sketch of the WO$_3$-infiltrated WCS anode is shown in Figure 7.7b. The infiltration step was repeated 3 times to increase the loading of CuO or WO$_3$ as shown in Figure 7.8. An approximate infiltration loading of 16 and 19 vol. % of the electrode is achieved for CuO and WO$_3$, respectively.

### 7.5 Electrochemical performance of WO$_3$-Infiltrated W-Cu-ScYSZ

Shown in Figure 7.9 are the electrochemical impedance measurements on WO$_3$ and CuO-infiltrated WCS anode at 600°C. The impedance was determined using a two electrode symmetrical cell configuration at the temperature range of 400 to 650 °C in H$_2$ / 3% H$_2$O. The impedance spectra shown were corrected for the series inductance, which arises from the wiring of the electrochemical test rig setup and from the measuring equipment. Impedance spectra were modeled with
Figure 7.7: Schematic of W-Cu-ScYSZ backbone infiltrated with $WO_3$.

Figure 7.8: Infiltration and corresponding loadings of $WO_3$. 

![Diagram showing infiltration process and corresponding loadings](image)
an equivalent circuit $R_0(R_1Q_1)(R_2Q_2)$. $R_0$ corresponds to the electrolyte series resistance. $R_1$ and $R_2$ are the resistances associated with the electrode processes, while $Q_1$ and $Q_2$ are the constant phase element (CPE). The admittance of the CPE is expressed by $Q = Y(j\omega)^n$, where $Y_0$ is an admittance parameter, $\omega$ is the angular frequency and $n$ is the frequency power. The polarization resistance of the electrode, $R_p$ is the summation of $R_1$ and $R_2$. $R_p$ of 11 $\Omega cm^2$ was measured for WO$_3$-infiltrated WCS symmetrical cell at 600°C from the impedance spectra shown in Figure 7.9a. Figure 7.9b shows the impedance spectra of CuO-infiltrated WCS symmetrical cell with $R_p$ of 6.5 $\Omega cm^2$ at 600°C. Bode plot of the impedance data is shown in Figure 7.9c. The peaks obtained at around 10 Hz for two infiltrated anodes indicate the characteristic frequency at low frequency region and the contribution at high frequency region of the impedance is not seen in Bode plot.

The electrochemical parameters resulted from an equivalent circuit fitting are listed in Table 7.1. The values of $n_1$ and $n_2$ are listed for both infiltrated anodes for the sub-circuits, $(R_1Q_1)$ and $(R_2Q_2)$, respectively. The fitted parameters $R$, $Y_0$ and $n$ values for each (RQ) sub-circuits were used to calculate the characteristic/summit frequency ($F_{max}$) and quasi-equivalent capacitance (C) using the relations 5.1 and 5.2.

<table>
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<tr>
<th>Electrocatalyst</th>
<th>$R_0(\Omega cm^2)$</th>
<th>$R_1(\Omega cm^2)$</th>
<th>$Q_1(s^{n_1}Ω^{-1})$</th>
<th>$n_1$</th>
<th>$F_{max,1}$</th>
<th>Act. energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$</td>
<td>1.64</td>
<td>6.7</td>
<td>0.00014</td>
<td>0.6</td>
<td>28</td>
<td>1.2</td>
</tr>
<tr>
<td>CuO</td>
<td>1.65</td>
<td>2.8</td>
<td>0.00021</td>
<td>0.5</td>
<td>45</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>$R_2(\Omega cm^2)$</td>
<td>$Q_2(s^{n_2}Ω^{-1})$</td>
<td>$n_2$</td>
<td>$F_{max,2}$</td>
<td>Act. energy (eV)</td>
<td></td>
</tr>
<tr>
<td>WO$_3$</td>
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<td>0.0009</td>
<td>0.9</td>
<td>7.5</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>3.6</td>
<td>0.00127</td>
<td>0.8</td>
<td>7.5</td>
<td>0.94</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.1: Electrochemical properties of infiltrated anodes resulted from the fitting procedures at 600°C.
Figure 7.10: Arrhenius plot, $R_1$ of $WO_3$ and CuO infiltrated anodes.

Figure 7.11: Arrhenius plot, $R_2$ of $WO_3$ and CuO infiltrated anodes.
Figure 7.12: Arrhenius plot, $R_p$ of $WO_3$ and CuO infiltrated anodes.

In both infiltrated anodes a single depressed semicircle was obtained. The sub-circuit ($R_1Q_1$) at high frequencies is thermally activated electrode process. Fig 7.10 shows the Arrhenius plot of $R_1$. The activation energy ($E_a$) of $R_1$ is 1.2 eV for both anodes indicating a common electrode process for $WO_3$ and CuO-infiltrated WCS anodes. The electrode process at high frequency is known to be linked to ionic conduction limitation/ charge transfer at the interface [38]; however, it proved impossible, in this case, to resolve the individual electrode processes ($F_{\text{max}}$ in the range of 30-50 Hz). The sub-circuit ($R_2Q_2$) at low frequencies possibly indicates the dissociative adsorption of hydrogen on the electrode surface [38]. Figure 7.11 is Arrhenius plot of $R_2$. $E_a$ of $WO_3$-infiltrated anode is 0.9 and 0.94 eV for CuO-infiltrated anode. $F_{\text{max}}$ obtained was approximately 10 Hz as listed in Table-1. Gas diffusion impedance contribution is believed to co-exist in both electrodes, but those values are too small and can be neglected due to high impedance values. The Arrhenius plot of $R_p$ (i.e., $R_1 + R_2$) is shown in Figure 7.12. The calculated $E_a$ for $WO_3$ is 0.9 eV. $E_a$ obtained for CuO as infiltrate in WCS backbone is 1 eV.

Certainly the values of $R_p$ obtained for $WO_3$-infiltrated anode is very high compared to the state-of-art Ni-YSZ anode and this is due to the insufficient catalytic activity of $WO_3$ as reported by Gorte et al [28]. It is to be noted that
the studies on the applicability of $WO_3$ as SOFC anodes are relatively new and is not completely explored in literature. This preliminary finding from our study on $WO_3$ infiltrated anodes indicates the potential of this material as SOFC anode, only by lowering of the polarization resistance. Existing reports on this material as electrode suggests that, the improvement in performance of $WO_3$ based ceramic materials as electrocatalyst could be achieved by loading a small amount of Pt or Pd, which reduces the $R_p$ drastically\cite{27, 28}. On the other hand, the electrode performance can be improved by increasing the loading of $WO_3$; however, the present study is aimed at exploring the initial electrochemical properties of $WO_3$ and not concentrated on optimizing the performance.

The values of $R_0$ are expected to be the same for different types of electrodes as they are mainly originating from the electrolyte, but a small variation is often observed due to microstructural differences at the electrode/electrolyte interface and the current collector contacts. Figure 7.13 shows $R_0$ and its temperature dependencies for $WO_3$ and CuO infiltrated WCS backbone. These are consistent with the ScYSZ electrolyte resistance calculated for a thickness of 120 µm from ionic conductivity values reported\cite{58}, indicating that a good current collection is achieved by infiltration. The electrochemical performance of the Pt
Figure 7.14: SEM image of $WO_3$ and CuO infiltrated anodes (fractured cross section).

The $R_0$ of WCS backbone without infiltrations is several orders of magnitude higher than that of ScYSZ electrolyte, implying no percolation of W and Cu in the ScYSZ matrix, which in turn limits the current collection and increases the $R_0$. These high values demonstrate that the current collection in WCS backbone is achieved only through Pt current collector. Moreover, the total impedance contribution of the backbone $R_p$ is mainly associated with the ionic conduction limitation of the backbone and other processes contributing to impedance is negligible.

The SEM micrograph portraying the fractured cross section of the post-tested WCS backbone with and without the infiltration of $WO_3$ and CuO is shown in Figure 7.14. The backbone without infiltration has disrupted electronic conduction paths and tungsten particles are dispersed. The heat treatment of the infiltrated electrodes was at 650°C for 12 h in dry hydrogen initially and then shifted to 3% moisturized $H_2$ (after 36 h) and this yielded a nano/microstructured morphology for $WO_3$-infiltrated anodes. In case of CuO-infiltration similar protocol for heat treatment resulted in the dense microstructure and complete reduction of CuO to Cu. Moreover, the large grain growth could also be due to exposing the anode for 50 h to $H_2$ at 650 °C. Further exposure might result in deactivation of Cu. Similar kind of poor microstructure of Cu was observed in CuO-infiltrated YSZ backbone due to its low thermal stability [80], when exposed
to $H_2$ based fuel for 2 h at high temperature.

### 7.6 Summary

Sub-stoichiometric $WO_3$ has shown good redox stability and electrical conductivity at 650 °C. Microstructural observation of W-Cu-ScYSZ composite showed poor percolation of W and Cu in ScYSZ matrix and cannot be used as an anode. As a result anodes were fabricated by the infiltration of $WO_3$ or CuO into W-Cu-ScYSZ backbone. The electrochemical performance of the $WO_3$-infiltrated W-Cu-ScYSZ backbones was comparable to that of CuO-infiltrated W-Cu-ScYSZ backbone determined in $H_2/3\% H_2O$. $WO_3$ infiltrated anodes showed nano/micro structured microstructure compared to the more coarser CuO infiltrated anodes. The initial investigation indicated the potential of these materials as SOFC anodes at low temperatures. Further studies are required to understand and improve the performance of $WO_3$ based anodes.
Chapter 8

Effect of Strong Cathodic Polarization in Ni-YSZ Anodes - A Brief Review

8.1 About This Chapter

Researchers have observed a considerable enhancement in hydrogen oxidation rate in metal point-contacts on yttria-stabilized zirconia (YSZ) electrolyte with an application of cathodic bias. A recent report further documented, that performance of already degraded SOFCs can be recovered by the application of reverse polarization. In this chapter, cathodic polarization experiments in a Ni-YSZ anode deposited on a three-electrode pellet are presented. A 40 % reduction in polarization resistance of the anode in a dry $H_2$ atmosphere, at $400^\circ C$ has been obtained with the application of cathodic bias. This chapter also provides an overview of the experiments carried out so far to understand the mechanism behind the improvement in performance of Ni-YSZ anode after a strong cathodic polarization.

8.2 Introduction

SOFCs traditionally use yttrium-stabilized zirconia (YSZ) as solid electrolyte, a material which has dominated the field for many years[81]. During the past three decades, researchers have examined the phenomenon of electrochemical blackening, or discoloration, in YSZ due to the application of a high cathodic bias under reducing conditions [82]. As an outcome, an enhancement of the
reaction rate for hydrogen oxidation was achieved for a metal in contact with YSZ electrolyte[83]. The improvement in performance was observed in Ni, Pt, and Au etc [82]. While this phenomenon has been recognised as having practical importance in improving the performance of SOFCs, the underlying reason has not been fully understood or clarified yet. Several work groups have reported the same phenomenon in different contexts and with different names, such as electrochemical blackening due to cathodic processes [84, 85], reverse current treatment (RCT) [86] etc. In this chapter, the concept is referred as strong cathodic polarization (SCP).

Several workers have investigated the mechanism behind SCP application [87]. Morphological studies using scanning and transmission electron microscopes [88, 89], crystallographic and structural studies using X-ray photo electron spectroscopy and X-ray diffraction [89], conductivity measurements, optical absorption studies [90, 91] were carried out. The explanations offered for the phenomenon are listed below:

- The formation of metallic zirconia on the surface of the YSZ[92].
- Reduction of $\text{ZrO}_2$ to its sub oxide ($\text{ZrO}_{2-x}$)[88].
- Increase in electrocatalytic activity[93, 94]

Experiments carried out in our own group have revealed improved electrode kinetics with the application of SCP on Ni point electrodes in contact with YSZ electrolyte[95]. Furthermore Cu, Pd and Pt point electrodes on YSZ electrolyte had been investigated with an applied SCP. A factor of 20 to 40 % reduction in polarization resistance was achieved [96]. All these results are encouraging to implement this concept on a full cell level, but the SCP parameters (application duration, gas conditions etc.,) need to be optimized in order to achieve desired improvements. Moreover, the polarization resistance obtained in point electrodes was very high due to the small contact area and is difficult to compare with a practical anode. Thus, SCP experiments in a Ni-YSZ cermet anode deposited on YSZ electrolyte was considered in order to gain further knowledge on this concept.

Point-contact metal electrodes are used to study the electrochemistry of the interface of cermet anodes and electrolyte. Point-contacts have a well-defined geometry, in contrast to the complex microstructure of cermet anodes. Ni point-contact electrodes were produced by pressing Ni wire on to YSZ, as shown in
An initial polarization resistance of these electrodes is 19 $k\Omega cm^2$ falling to 0.3 $k\Omega cm^2$ with the application of SCP. However, after 15 h, the polarization resistance increased to 0.6 $k\Omega cm^2$. These experiments were carried out in $H_2/0.08 H_2O$. The amount of charge applied was 3.9 – 4.6 $C/cm^2$, sufficient to reduce the YSZ to a depth of ~ 2 $\mu$m. After application of SCP, the activation energy fell from 1.3 to 0.6 eV. The impedance arc from two semi-circles was changed to one semi-circle by the treatment, suggesting that the number of rate limiting steps was reduced due to the surface changes. As observed in another study [96], the series resistance of the YSZ was not affected by this treatment. The point-contact electrode of Cu, Pd and Pt were studied in a similar set up, under the same conditions. With the application of a cathodic bias of -1000 mV between RE and WE, a 20 to 40 % decrease in polarization resistance was observed, when this was measured at open circuit voltage (OCV). All three metals showed a similar response, namely a reduction in the activation energy [96]. This improvement was ascribed to the reduction of impurities segregated at the TPB.

The present study concentrates on the investigation of anode performance with the application of SCP to the Ni-YSZ cermet anode at a low temperature of 400°C. A reduction in polarization resistance of the anode is achieved with the application of SCP-1 and 2. The reason for improved performance reported in
literatures have been reviewed in this work, however, the underlying mechanism is not experimentally proven to support our results.

The polarization experiments were carried out on Ni-YSZ cermet anodes deposited on a 3-electrode pellet of in-house design, made of 8YSZ[13, 97, 98], and shown in Figure 8.2. For measuring under anodic conditions, current is passed between the counter electrodes (CE) and working electrode (WE) and the voltage difference between the WE and the reference electrode (RE1) was measured. The WE in this experiment was Ni-YSZ. The potential of the WE is monitored using another reference electrode (RE2). The reactions under investigation, when using 3-electrode pellet were the $H_2$ oxidation reaction and reduction of $H_2O$ as shown in reaction shown in equation 4.1 and 4.2 in chapter 4. The $H_2$ oxidation takes place in WE and the reduction of $H_2O$ takes place in CE in SOFC mode. In a 3-electrode pellet a) a single electrode can be characterized under DC loading b) The interference of the current electrode can be avoided c) the reference electrode can be fixed with a small contact area as possible[99].
8.2.1 Electrochemcial Characterization

For electrochemical characterization on Ni/YSZ cermet anode, current collector slurry constituting of Ni with 10% of YSZ was sprayed on the Ni-YSZ anode. The anode and the current collection layer were sintered at 1300 °C for 1 h. A point contact of Pt was made as a reference electrode and the Pt paste was painted to function as the counter electrode. The set up was heated up in reducing gas (9% \( N_2/\text{H}_2 \)) and then changed to \( \text{H}_2 \). The anode was allowed to reduce completely at 1000 °C in \( \text{H}_2 \) for 1 h. The electrochemical impedance spectrum (EIS) measurements were carried out at different temperatures 1000, 850, 650 and 400 °C. The frequency range of the measurement was 64 kHz to 3 mHz. The SCP experiments were carried out at 400 °C using Solartron SI 1250.

8.3 Application of Strong Cathodic Polarization on Ni-YSZ Cermet

SCP experiments in Ni-YSZ cermet anodes were performed in 0.99 \( \text{H}_2/\text{0.01 H}_2\text{O} \) gas mixture. The amount of coulombs required to reduce 3\( \mu \)m of \( \text{ZrO}_2 \) to Zr metal as shown in equation 8.1 was calculated using the equation 8.2\[95\]. The number of moles of \( \text{ZrO}_2(n_{\text{ZrO}_2}) \) is calculated from the equation 8.3,

\[
\text{ZrO}_2 + 4e^- \rightarrow \text{Zr} + 2O^{2-}
\]  

(8.1)

\[
\eta_{\text{coloumb}} = n_{\text{ZrO}_2} \times n_{e^-} \times F = (6 \times 10^{-6})\text{mol} \times 4 \times 96485 \text{C/mol}
\]  

(8.2)

\[
n_{\text{ZrO}_2} = \frac{dx A \rho_{\text{ZrO}_2}}{M_{\text{ZrO}_2}} = 6 \times 10^{-6}\text{mol}
\]  

(8.3)

where, \( d = 3 \text{ } \mu\text{m} \) is the thickness of the \( \text{ZrO}_2 \) expected to reduce, area of the anode, \( A = 0.44 \text{ cm}^2 \), \( \rho_{\text{ZrO}_2} = 5.6 \text{ g/cm}^2 \) and \( M_{\text{ZrO}_2} = 123\text{g/mol} \) is the density and molar mass of \( \text{ZrO}_2 \), respectively.

In the present experiments two SCP steps (SCP-1 and SCP-2) were car-
Figure 8.3: Chronoamperometry measurements on Ni-YSZ electrode. SCP-1 indicates strong cathodic polarization and SCP-2 indicates strong cathodic polarization a) current as a function of time and b) a variation in cathodic bias of -3V with time.

Carried out using chronoamperometry. Current and potential plot as a function of time is shown in Figure 8.3. For SCP-1, a cathodic bias of -3V between WE and RE was applied for 9 minute duration. The charge density ($\rho_c$) was calculated by integrating the area under the curve (current vs time shown in Figure 8.3a.) and is 2.4 C/cm$^2$. EIS was measured immediately after SCP-1 (0 minute) and after 8 h at OCV. For SCP-2, a cathodic bias of -3V is applied for 15 minute resulted in a $\rho_c$ of 4.4 C/cm$^2$. EIS was measured immediately after SCP-2 (0 minute) and after 8 h. A voltage drop was observed during the chronoamperometry measurements, the variation of applied cathodic bias -3V as a function of time is shown in Figure 8.3b.

Shown in Figure 8.4 are the impedance spectra of the Ni-YSZ at 400 °C measured at OCV after the application of SCP. With the application of cathodic bias of -3V for 9 minute., the polarization resistance ($R_p$) decreased from 2300 to 1500Ωcm$^2$, indicating a start of reduction of ZrO$_2$ in YSZ. However, the EIS measured after a long period of time 8 h indicates that the polarization resistance slightly increased to 1800 Ωcm$^2$. This could be due to the oxidation of ZrO$_{2-x}$ over the period of time. The reduction of ZrO$_2$ requires several steps attributed
Figure 8.4: Impedance spectra of Ni-YSZ anode measured at 400 °C in OCV with the application of strong cathodic polarization in $H_2/O.1H_2O$ gas. 

To the multivalent nature of Zr. Further application of SCP-2 of -3V for 15 minute, the polarization resistance reduced to 1400 $\Omega cm^2$. Interestingly, for an impedance spectrum measured after 8 h, the resistance further decreased reaching 1200 $\Omega cm^2$. The improvement in polarization resistance is depicted in Figure 8.5 as a bar chart. It is noted that, the extrapolated $R_p$ of Ni-YSZ electrode reported in literature is 550 $\Omega cm^2$ at 400°C[100], which is low compared to our Ni-YSZ anode measured in a 3-electrode pellet. The reason for a higher $R_p$ for our unmodified Ni-YSZ anode (before SCP) is unclear; however the initial value of 2300 $\Omega cm^2$ is considered as reference to study the SCP effect.

With the application of SCP for longer duration, a stronger reduction of $ZrO_2$ is expected, but that could also decrease the electrolyte resistance ($R_s$). In the current experiments, the SCP is carefully controlled and no change in $R_s$ was observed. $R_s$ for the EIS measured at 400°C is estimated to be 1200$\Omega cm^2$. The serial resistance measured at OCV and the electrolyte resistance calculated from the cell geometry and the ionic conductivity of 8YSZ in the literature [48],
are compared in Figure 8.6 and found to agree well. The activation energy is approximately 0.9 eV.

The reduced $R_p$ is attributed to the surface treatment of the YSZ/Ni-YSZ anode interface, which resulted in breakage of impurity layer. A schematic sketch of Ni/YSZ interface is shown in Figure 8.7. Additionally, modification of $\text{ZrO}_2$/Ni interface within the Ni-YSZ anode is believed to increase the TPB, which in turn increase the performance. The formation of electro active sites may also contribute to this effect[85, 96, 95].

### 8.3.1 Uncontrolled Application of Strong Cathodic Polarization

The effect of uncontrolled application of SCP resulted in deep reduction of YSZ 3-electrode pellets. Shown in Figure 8.8 (right) is the three electrode pellets before and after application of SCP of -30V for more than one hour. This resulted in an abrupt color change and distorted EIS, which cannot be resolved or analyzed. Pellets were almost crumbled due to the application of high voltage. One of those pellets was polished and placed in the epoxy stub, coated with carbon for
Figure 8.6: Arrhenius plot of electrolyte resistance at OCV before strong cathodic polarization.

Figure 8.7: Schematic sketch showing the interface of Ni and YSZ with the application of strong cathodic polarization.
scanning electron microscopy (SEM) imaging. The analysis revealed that the cracks were formed along the grain boundaries of YSZ as depicted in Figure 8.8 (left).

### 8.4 Strong Cathodic Polarization Experiments on a SOFC

An anode supported SOFC with Ni/8YSZ anode and LSCF cathode was subjected to SCP at regular intervals (four times) [86]. The impedance spectra was measured before and after SCP, a 40% reduction in polarization resistance was observed. The interesting part of their finding was a) the electrolyte resistance remains unchanged as reported by previous authors b) The gas diffusion loss remains unchanged and c) The performance for an already degraded SOFC showed a significant recovery. The authors speculated that the improved performance was due to the enhancement in ionic conductivity of the Ni-YSZ anode and reduction of YSZ electrolyte; but the speculations have not been proved experimentally.

### 8.5 Summary

The experiments on strong cathodic polarization to achieve beneficial electrochemical properties on electrode/YSZ electrolyte have been reported earlier in literature. In recent years, very few researchers were focused experiments on
this concept. This concept has practical significance in performance recovery of
 degraded cells. A 20 to 40 % reduction in polarization resistance of the SOFC
 anodes was reported in the literature, which are measured on point-contact elec-
 trode. The SCP experiments reported in this paper on a Ni-YSZ anode measured
 using a 3-electrode pellet had also shown an improvement in anode performance. A
 40 % reduction in polarization resistance was achieved with a cathodic bias
 of -3V in two steps (SCP-1 and 2). The proposed reason for the improvement
 in anode performance was breakage of impurity layer on the electrode/electrode
 interface resulting in enhanced triple phase boundary. The charge applied, du-
 ration, temperature were the critical parameters needed to control the desired
 degree of reduction in YSZ for beneficial electrochemical properties. Experimen-
tal evidences are required to support the obtained results.
Incorporation of ionic conductivity in strontium titanates ($SrTiO_3$) would greatly facilitate for the production of high performance anodes for low temperature SOFCs. Particularly, doping $SrTiO_3$ with $CeO_2$ has a greater significance and requires attention. The number of repetitive steps involved in infiltration should be reduced by optimizing the concentrations of precursor solutions, eventually; this would help in rapid reduction of gas diffusion impedances arising from infiltrated porous electrodes. The catalytic activity of the Pt, Pd, Ru, Ni and CGO and its combinations needs DFT (density functional theory) calculations to understand the synergistic performance of the electrocatalyst for hydrogen oxidation. The CGO modification at the interface of electrode/electrolyte mentioned in this studies has shown dissolution of CGO in STN. The aspect of this work needs more attention as the modification resulted in drastic reduction in the electrode polarization resistances. It is demonstrated that the electrochemical performance of tungsten oxide can be improved by adding a small quantity of noble metals such as Pt or Pd.
References


