Convertible solid oxide fuel cell/electrolyser cell with optimised composite electrodes and bi-layer electrolyte

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CONVERTIBLE SOLID OXIDE FUEL
CELL/ELECTROLYSER CELL WITH
OPTIMISED COMPOSITE ELECTRODES
AND BI-LAYER ELECTROLYTE**

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To My Lovely Parents

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Abstract

Fuel cells are electrochemical and efficient energy conversion devices that directly convert a fuel's chemical energy into electrical energy. They have environmental advantages in reduced pollution and high energy conversion efficiency when compared with the conventional power generation systems such as internal combustion engines and gas turbines fired with fossil fuels. Among all fuel cell types, the Solid Oxide Fuel Cell (SOFC) produces high quality waste heat, which can be utilised to increase the overall energy conversion efficiency. When operating in a reverse manner, a SOFC becomes a Solid Oxide Electrolyser Cell (SOEC), which works well with the intermittent renewable energy such as solar PV and wind turbine as it converts the electrical energy generated by the renewable energy into hydrogen through electrolysis of water, thus serving as energy storage. The objective of this study is to propose a Solid Oxide Cell (SOC) system, which is optimised to operate in both SOFC and SOEC modes.

In order to explore electrolytes with improved conductivity, ceria based electrolytes including gadolinia doped ceria (GDC), $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$, and samaria doped ceria (SDC), $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$, are synthesised and characterised. Samples sintered at 1400°C-1500°C possess relative densities as high as 97.7% suggesting that this temperature range leads to improved densification of electrolyte as reflected by the high open circuit voltages. The Arrhenius plots of GDC and SDC conductivities show that SDC electrolyte presents higher conductivity compared to GDC, especially those sintered at 1400°C and 1500°C. Moreover, Ni-GDC/GDC/ $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and Ni-SDC/SDC/BSCF cells were fabricated and polarisation curves were obtained. The thickness of the SDC and GDC electrolytes were identical and about 7.5 μm . Based on polarisation results, open-circuit voltages (OCVs) of 0.829 V, 0.817 V and, 0.792 V and maximum power densities of 0.368 $\text{W}\cdot\text{cm}^{-2}$, 0.619 $\text{W}\cdot\text{cm}^{-2}$ and, 0.790 $\text{W}\cdot\text{cm}^{-2}$ were recorded at 500°C, 550°C, and 600°C, respectively, for the Ni-GDC/GDC/BSCF cell. With humidified hydrogen (3 vol% water vapour) as fuel and air as oxidant, the Ni-SDC/SDC/BSCF cell generates OCVs at 500°C, 550°C, and 600°C as 0.848 V, 0.815 V, and 0.797 V, and maximum power densities of 0.398 $\text{W}\cdot\text{cm}^{-2}$, 0.810 $\text{W}\cdot\text{cm}^{-2}$ and, 1.1 $\text{W}\cdot\text{cm}^{-2}$, respectively.

ABSTRACT

There is a potential for a bi-layer electrolyte to render high ionic conductivity without a remarkable sacrifice of open circuit voltage and lowering the operating temperature of the cell. Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 7 wt.% of graphite as the pore former in the Ni-YSZ structure, dense YSZ-SDC as the electrolyte and porous 20 wt.%SDC-80 wt.% BSCF as the air electrode were the three distinguishable layers well adhered to each other in order to study the effect of blocking layer in the electrochemical performance of the SOFCs and SOECs. In order to dominate the OCV loss and enhance the chemical stability of doped ceria electrolyte in reducing atmospheres, SDC was coated with a very thin layer of YSZ film (1.5 μm , 2.5 μm , 3.5 μm , 3.8 μm , and 4.4 μm) to form a bi-layer electrolyte. In both the fuel cell and electrolyser cell mode, the blocking of electrons takes significant effect when the blocking layer is increased to 3.5 μm .

Although the porosity of the Ni-YSZ anode increases by in-situ reduction of NiO available in the primary anode material, the final value of the anode porosity of the cell with Ni-YSZ structure is not high enough to provide an easy flow of the gases during the cell operation. Hence, adding a pore former enhances the gas accessibility to the anode active three-phase boundary. So, the porous structures of fuel electrodes have been proposed to fulfil the anodic and cathodic functions of SOFC and SOEC, respectively, for further improvement of the performance of the cells. The ohmic and polarisation resistances of the fuel cells and electrolyser cells were characterised over the temperature range of 650°C to 800°C.

To make BSCF more thermo-mechanically compatible with the SDC electrolyte, the formation of a composite electrode by introducing SDC as the compositing material is proposed in order to decrease the mismatch of the TECs of electrode and electrolyte, hence improve the cell performance. In this study, after successfully synthesising the BSCF-SDC/YSZ-SDC/Ni-YSZ single cell with 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.%, and 50 wt.% of commercial SDC powder mixed with BSCF powder to make the composite air electrode, the electrochemical study was evaluated over the temperature range of 650°C to 800°C for both SOFCs and SOECs. Furthermore, for all the samples of this PhD study, the effect of 10%, 30%, 50%, and 70% hydrogen humidity levels on the performance of the electrolyser cells tested at 800°C were evaluated.

ABSTRACT

As an overall conclusion, for both the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell and electrolyser cell, 3.5 μm of YSZ as the blocking layer for the electrolyte, 7 wt.% graphite pore former for the fuel electrode, and the 20% SDC- 80% BSCF for the air electrode composition led to an optimised desired performance.

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Table of Nomenclatures

Abbreviations	Meaning
SOFC	Solid oxide fuel cell
SOEC	Solid oxide electrolyser cell
SOC	Solid oxide cell
ITSOFC	Intermediate temperature solid oxide fuel cell
ITSOEC	Intermediate temperature solid oxide electrolyser cell
LTSOFC	Low temperature solid oxide fuel cell
LTSOEC	Low temperature solid oxide electrolyser cell
PEMFC	Polymer electrolyte membrane fuel cell
PAFC	Phosphoric acid fuel cell
MCFC	Molten carbonate fuel cell
AFC	Alkaline fuel cell
FESEM	Field emission scanning electron microscopy
HRTEM	High resolution transmission electron microscopy
EFTEM	Energy-filtered transmission electron microscopy
XRD	X-ray diffraction
HT-XRD	High temperature X-ray diffraction
TGA	Thermogravimetric analysis
DTA	Differential thermal analysis
OCV	Open-circuit voltage
I-V	Current-Voltage
I-P	Current-Power
MPD	Maximum power density
CD	Current density
TEC	Thermal expansion coefficient
SCCM	Standard cubic centimeters per minute
TPB	Triple phase boundary
LHV	Lower heating value
TPD	Temperature programmed desorption
ORR	Oxygen reduction reaction
ASR	Area-specific resistance
MIEC	Mixed ionic electronic conductor
PLD	Pulsed laser deposition
3DOM	Three-dimensionally ordered macroporous
DFT	Density functional theory
ERZ	Effective reaction zone
EIS	Electrochemical impedance spectroscopy
FRA	Frequency response analyser
GPES	General Purpose Electrochemical System
GNP	Glycine–nitrate process

TABLE OF NOMENCLATURES

APU	Auxiliary Power Unit	
PMMA	Polymethyl methacrylate	
TEA	Triethanolamine	
BBP	Benzyl butyl phthalate	
PG	Propylene glycol	
PVB	Polyvinyl butyral	
EDTA	Ethylenediaminetetraacetic acid	
YSZ	Yttria-stabilised zirconia	
YDC	Yttria doped ceria	
Ni–ScSZ	Nickel–scandia stabilised zirconia	
GDC	Gadolinia doped ceria, $Gd_{0.2}Ce_{0.8}O_{1.9}$	
SDC	Samaria doped ceria, $Sm_{0.2}Ce_{0.8}O_{1.9}$	
BSCF	$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	
LSGM	$La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$	
LSM	$La_{1-x}Sr_xMnO_3$	
LSC	$La_{0.70}Sr_{0.30}CoO_{3-\delta}$	
LSCF	$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$	
LSCN	$La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4.08}$	
LSF	$La_{0.8}Sr_{0.2}FeO_3$	
SFM	$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$	
LCMO	$La_{0.7}Ca_{0.3}MnO_3$	
BCY	$BaCe_{0.9}Y_{0.1}O_{2.95}$	
BCS	$BaCe_{0.9}Sm_{0.1}O_{2.95}$	
BZCY	$BaZr_{0.1}Ce_{0.7}Y_{0.2}O_3$	
LC	$LaCoO_3$	
BSSCF	$(Ba_{0.5}Sr_{0.5})_{1-x}Sm_xCo_{0.8}Fe_{0.2}O_{3-\delta}$	
BSCT	$Ba_{0.6}Sr_{0.4}Co_{1-y}Ti_yO_{3-\delta}$	
BSZF	$Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-\delta}$	
Symbol	Meaning	Usual Units
A	Area	cm^2
h	Time	h
I	Current density	$A.cm^{-2}$
P	Power density	$W.cm^{-2}$
R_s	Ohmic resistance	Ω
T	Temperature	$^{\circ}C$
t	Thickness of the electrolyte	μm
V	Potential	v
Z_I	Imaginary part of the impedance	$\Omega.cm^2$
Z_R	Real part of the impedance	$\Omega.cm^2$
ρ	Material's density	$g.cm^{-3}$
	Electrical resistivity	$\Omega.cm$
σ	Conductivity	$S.cm^{-1}$

CHAPTER 1. Introduction

1.1. Introduction on fuel cell and electrolyser cell

Over 160 years ago, in 1839, Sir William Grove introduced the fuel cell concept and developed it all over the world (Grove 1839). Since the last four decades, fuel cells have been representing their new applications by increased reliability, enhanced performance, and reduced cost. They are gaining commercial appeal because of the continuous pursuit of human beings for appropriate energy and the low-carbon economy.

Fuel cells have environmental advantages in reduced pollution and high energy conversion efficiency when compared with conventional power generation systems such as internal combustion engines and gas turbines fired with fossil fuels (Granovskii et al. 2006). Fuel cells are electrochemical and efficient energy conversion devices that directly convert fuel's chemical energy into electrical energy. Based on the type of the electrolyte used in the fuel cells they are classified into five types: 1) polymer electrolyte membrane fuel cell (PEMFC), 2) phosphoric acid fuel cell (PAFC), 3) molten carbonate fuel cell (MCFC), 4) alkaline fuel cell (AFC), and 5) solid oxide fuel cell (SOFC). More information about these five types of fuel cell technology can be found in Table 1. Among all, SOFCs have the advantages of the excellent fuel flexibility and the highest energy conversion efficiency because of their high quality waste heat, which can be recovered rather efficiently. A single SOFC consists of a dense, oxygen-ion conducting electrolyte sandwiched by two porous electrodes. The electrolyte is an ion-conducting electronic insulating ceramic that allows only the oxygen ion or proton to pass through. On the air electrode side, oxygen is reduced to oxygen ions which are then pumped through the oxygen ion conducting electrolyte. On the fuel electrode side, fuels are oxidised by the pumped oxygen ions to release the electrons. The Gibbs free energy difference between the fuel electrode and air electrode forces the released electrons to flow through an external electrical circuit to the air electrode to complete the circuit and to perform electrical work (McIntosh and Gorte 2004). The efficiency of this process is influenced by the internal losses in the cell, including the interfacial resistances of the electrodes and the ohmic loss caused by the electrolyte.

CHAPTER 1

Table 1 Characteristics of different types of fuel cells (Energy Nexus group, USA (*Technology Characterization: Fuel Cells* 2008))

Type	Polymer electrolyte membrane fuel cell	Alkaline fuel cell	Phosphoric acid fuel cell	Molten carbonate fuel cell	Solid oxide fuel cell
Type of electrolyte	H ⁺ ions (with anions bound in polymer membrane)	OH ⁻ ions typically aqueous KOH solution	H ⁺ ions (H ₃ PO ₄)	CO ₃ ²⁻ ions (typically molten Li ₂ CO ₃ /K ₂ CO ₃ mixture)	O ²⁻ ions (stabilised ceramic matrix with free oxide ions)
Typical construction	Plastic, metal or carbon	Plastic, metal	Carbon, porous ceramics	High temperature metals, porous ceramics	Ceramics, High temperature metals
Internal reforming	No	No	No	Yes, good temperature match	Yes, good temperature match
Oxidant	Air to O ₂	Purified air to O ₂	Air to enriched air	Air	Air
Operational temperature	65°C-85°C	90°C-260°C	190°C-210°C	650°C-700°C	600°C-1000°C
Fuels	H ₂ , natural gas, methanol, LPG, naphtha, kerosene	H ₂ , methanol, ethanol, sodium boro hydride	H ₂ , natural gas, methanol, LPG, naphtha, kerosene	H ₂ , natural gas, methanol, LPG, naphtha, kerosene, coal	H ₂ , natural gas, methanol, LPG, naphtha, kerosene, coal, hydrocarbons
Power generation efficiency (%)	30-36	30-40	35-42	40-60	40-60

A SOFC's efficiency is not limited by the Carnot principle and is as high as 40%-60% because it does not include thermal and mechanical steps and is not a heat engine (Onda et al. 2003). During past decades, R&D activities have been focused on low-cost processing methods and cheap materials (Menzler et al. 2003; Gaudon et al. 2004; Neagu et al. 2006; Rossignol et al. 2011). One of their main goals has been lowering

the operating temperature by employing those oxygen ion conductors which are highly conductive (Boulc'h and Djurado 2003). By using advanced SOFC fabrication techniques they have been able to fabricate cells with low resistance, enabling SOFCs to operate at lower temperatures (down to 500°C) (Nesaraj 2010). Although the ideal operating temperature for SOFCs is still controversial, intermediate-temperature SOFC (IT-SOFC, 600°C < T < 800°C) has been demonstrated successfully with reduced capital costs, while high-temperature SOFCs (HT-SOFCs, 800°C < T < 1000°C) show increased efficiency. Besides, HT-SOFCs can recuperate high quality waste heat for heating the inlet fuels. They can also be coupled to traditional gas turbines in order to improve the overall energy efficiency. There is a close relation between SOFCs and other technologies, such as ceramic electrochemical reactors, ceramic ion-conducting membranes, and oxygen generators. Such collaboration lowers investment risk and increases entrepreneurial efforts on developing SOFC devices for stationary and distributed power generation, auxiliary power units (APUs) and vehicle motive power (Ge 2012).

The operation of SOFCs can be in a reverse manner, for example when applying electrical power to the cell, H₂ and CO are produced by electrolysing a mixture of CO₂ and steam. This is referred to as a solid oxide electrolyser cell (SOEC). The produced H₂ and CO gas mixture is actually known as the synthetic fuel. The SOEC technology was under progress as an interesting alternative to ordinary alkaline electrolysis during the 1980's (Dönitz and Erdle 1985). The progress of SOECs was stopped around 1990 due to low cost of fossil fuels.

1.2. Operating principle of SOC

Basically a fuel cell consists of a air electrode, at which the reduction reaction happens, an ion conducting electrolyte and an fuel electrode, at which the oxidation reaction takes place. A SOC is built up of a ceramic oxide ion conducting electronic insulating electrolyte, which is sandwiched between a porous electron conducting air electrode and fuel electrode. This three components arrangement is shown in Figure 1.

When the cell is working in the fuel cell mode, specific gases such as methane, hydrogen, or even ammonia can be used as the fuel. As shown in Figure 1 (A) in the

SOFC mode, the hydrogen electrode works as the fuel electrode where H_2 is oxidised to H_2O . The oxygen electrode is exposed to O_2 or ambient air. At the air electrode /electrolyte interface oxygen molecules reduce to oxide ions and these oxide ions travel through the electrolyte. So when hydrogen is the fuel, the total reaction of the fuel cell is: $2H_2 + O_2 \rightarrow 2H_2O + \text{heat} + \text{electrical energy}$. The electrolyte is polarised in anodic current load (fuel cell mode) while having more positive potential in the direction of the hydrogen electrode.

Figure 1 Basic working principle for a Solid Oxide Cell (SOC) operated as a A) SOFC or B) SOEC

When the cell operates in electrolyser mode, it requires an external power supply and the processes are reversed in comparison with the fuel cell operation of the SOC. The steam electrolysis reaction is: $2H_2O + \text{heat} + \text{electrical energy} \rightarrow 2H_2 + O_2$. In an electrolyser cell, the hydrogen electrode works as the cathode and the oxygen electrode works as the anode (Figure 1 (B)). The electrolyte in cathodic current load (electrolysis mode) has more positive potential in the indirection of the oxygen electrode.

The operating temperature of SOC is typically in a range of 600°C to 1000°C . The most extensively used materials are: a nickel-YSZ cermet for the hydrogen electrode, yttria stabilised zirconia (YSZ) as the electrolyte and a composite of YSZ and strontium doped lanthanum manganite (LSM) as the oxygen electrode. The porous Ni-YSZ electrode should have sufficient electronic and ionic conductivities. The structure of YSZ electrolyte is fluorite; it is ion conducting, electron insulating, and gastight. ZrO_2 doped with 8 mol% Y_2O_3 has found to have the maximum ion conductivity for which $\sigma = 0.1 \text{ S.cm}^{-1}$ at 1000°C (Badwal and Foger 1996). The LSM is electron

conducting and stable in oxidising atmosphere. The strontium doping of the LaMnO_3 perovskite improves the electronic conductivity and modifies the thermal expansion coefficient (TEC) (Minh and Takahashi 1995). Apart from these specific requirements for the different major components of the cell, there are also requirements regarding degree of purities, match of TEC, durability, undesirable reactions, sintering, and material costs etc. that needs to be paid attention in the choice of materials and processing techniques.

1.3. Advantages of SOC technology

SOC technology has appeared as a better high temperature fuel/ electrolyser cell technology due to its advantages (Stambouli and Traversa 2002) such as high conversion efficiency (60% for SOFC and higher than 60% for SOEC) which makes it more appropriate for applications in stationary power, having no issues with electrolyte management, extremely low emissions, potential long life expectancy (40000-80000 h), not containing less resourceful metals and last but, not least, high operating temperature of SOCs would lead to high quality heat by-products that can be used for cogeneration.

Even though there are many advantages, the use of SOC is limited due to very high operating temperature and high system cost (Santin et al. 2009). By contrast, reducing the operating temperature of the SOCs to an intermediate-temperature range, especially lower than 650°C , would have some advantages (Maric et al. 2003) like more rapid start-up and shut-down procedures, decreasing the solid-state reaction between the cell components, simpler design and material requirements of the balance-of-plant and having the choice of cheaper metallic materials, such as stainless steels.

However, it also causes a significant enhancement in electrochemical resistance of main cell components, including electrodes and electrolyte. One way to lower the ohmic loss of the cell is to use a thin-film electrolyte. Due to decrease in the thickness of the membrane, the mechanical strength of the thin-film electrolyte becomes poorer, so it should be supported on a substrate. Recently, air electrode or fuel electrode-supported SOCs have been widely tested, and some great electrochemical performances have been achieved (Bao et al. 2005a; Bellino et al. 2006; Gu et al.

2007; Lin et al. 2008a). Also some materials with higher ionic conductivity are exploited as the electrolytes for lower temperature SOCs as an alternative way to lower the ohmic resistance (Kharton et al. 2001).

1.4. SOC development

A strongly increased encouragement in the use of hydrogen energy sources alternative to oil and coal, and CO₂ neutral energy production have been aroused over the last few decades. This had also led to R&D activities and an increased interest within the SOC community. By evaluating the performance of single cells, it is easier to give a perspective on the development of SOCs. Basically, SOCs have three typical designs such as the metal hydrogen electrode supported, ceramic hydrogen electrode supported and electrolyte supported. The electrolyte supported cells have 10 µm-30 µm thick electrodes and an electrolyte of 100 µm-300 µm thickness -typically YSZ- (Kendall et al. 2003; Singhal and Kendall 2003). As the YSZ ion conductivity decreases with decreasing the operating temperature, the electrolyte supported cells are designed to operate at ~ 1000°C (Appel et al. 2001). By decreasing the operating temperature, cheaper materials for accessories can be used. This has led to develop the hydrogen electrode supported cells, which have an active hydrogen electrode supported a 200 µm-300 µm thick support of material similar to the hydrogen electrode, and a thin (10 µm-30 µm) oxygen electrode and electrolyte (De Jonghe et al. 2003). The operating temperature of the hydrogen electrode supported cell is typically 650°C-850°C. This is at the moment the most prevalent type of SOCs. The third and most recently developed type of cells is metal supported cell, which operates at lower operating temperatures of about 600°C. It also leads to lower cost of raw materials as well as materials for interconnects and manifolds (Villarreal et al. 2003).

With decreasing the operating temperature of SOCs from typically 1000°C to an intermediate temperature range of 600°C to 800°C, many benefits such as, shorter start-up time, higher system reliability, longer cell lifespan, lower material degradation, and substantial decreases in material demand and fabrication costs are achievable. During the past decades, remarkable efforts have been made to lower the operating temperature of SOCs (Tsai and Barnett 1997; Hibino et al. 2002; Yan et al. 2002; Nguyen et al. 2004; Liu et al. 2006b). Three approaches have been adopted; 1)

employing new electrolyte materials with high ionic conductivity at intermediate temperatures, 2) reducing the electrolyte thickness, and 3) lowering the electrode polarisation resistance. In this frame, doped ceria is considered as one of the most promising electrolyte options for intermediate temperature SOCs due to its much higher ionic conductivity than the YSZ conventional electrolyte at intermediate temperatures (Steele 2000b). Many research groups have reported the improvement of intermediate-temperature SOCs based on a thin-film doped ceria electrolyte, which has been fabricated by different processes such as dry pressing (Rifau et al. 2006; Zhu et al. 2011; Xia and Liu 2001), multi-layer tape casting (Doshi et al. 1999), spray coating (Zheng et al. 1996; Leng et al. 2004), screen printing (Xia et al. 2001; Peng et al. 2002), and spin coating (Hibino et al. 2002).

The reduction of ceria from Ce^{4+} to Ce^{3+} would lead to electronic conduction in the electrolyte, thus causing a non-negligible drop in the OCV of the cell. It will also cause ceria electrolyte lattice expansion at the fuel side, and hence the cell will face some mechanical stability problems (Liu et al. 2006b; Badwal et al. 1999). In order to reduce the OCV loss and enhance the chemical stability of doped ceria electrolytes in reducing atmospheres, it is proposed to coat doped ceria with a very thin layer of YSZ film to form a bi-layer electrolyte. In this electrolyte, the YSZ layer acts as an electronic blocking layer since YSZ is pretty stable under reducing atmosphere conditions.

Due to the low ionic conductivity of YSZ at intermediate temperatures, the YSZ film as an electronic blocking layer should be thin enough in order to minimise its contribution to the overall resistance of the bi-layer electrolyte. From the thermodynamic point of view, when the oxygen partial pressure across the ceria electrolyte at an operating temperature is more than the equilibrium value of the $\text{Ce}_2\text{O}_3/\text{CeO}_2$ redox reaction, the ceria electrolyte should be chemically stable. Hence, the stability of the bi-layer electrolyte can be defined by the interfacial oxygen partial pressure between the ceria substrate and the YSZ film. Theoretical investigations have illustrated (Virkar 1991; Chan et al. 2003; Marques and Navarro 1997) that the interfacial oxygen partial pressure is determined by the ratio of the two electrolyte layers thickness and that, generally, a few μm thick YSZ film should be sufficient to prevent the reduction of ceria electrolyte and thus overcome the OCV drop due to

ceria reduction (Virkar 1991; Chan et al. 2003; Marques and Navarro 1997). Towards this end, many techniques such as ion plating (Inoue et al. 1989; Eguchi et al. 1992), electrochemical vapour deposition (EVD) (Van Dieten et al. 1992; Schoonman et al. 1991), Pulsed laser deposition (PLD) (Lu et al. 2012), Radio frequency (RF) sputtering (Yahiro et al. 1988; Mehta et al. 1993), DC sputtering (Tsai et al. 1997), metal-organic chemical vapour deposition (MOCVD) (Chour et al. 1997), sol-gel coating (Mehta et al. 1998; Kim et al. 2002; Jang et al. 2002) and recently, spin coating (Plonczak et al. 2011) have been utilised to deposit a thin film of YSZ onto doped-ceria electrolyte. In this work, spin coating is used for depositing the YSZ film.

1.5. Introduction on SOC components materials used in this project

In this study, Samarium Doped Ceria (SDC) ($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$) and Gadolinium Doped Ceria (GDC) ($\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{2-\delta}$) were chosen and compared and the one with higher performance was selected as the electrolyte material for further study. So for these samples which were tested only in the fuel cell mode, Ni-SDC and Ni-GDC were chosen as the fuel electrode material, respectively. The air electrode was a pure BSCF ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$).

There is a potential for a bi-layer electrolyte to render a high ionic conductivity without a remarkable sacrifice of open circuit voltage due to very low thickness in compare with the main electrolyte thickness and lowering the operating temperature of the SOFC (Shen et al. 2013; Wachsman and Lee 2011). A thin layer of YSZ sandwiched between the fuel electrode and a doped ceria electrolyte can protect the SDC from reduction and increase the open circuit potential of SOFCs (Yahiro et al. 1988; Cho et al. 2011). So, for the second step, YSZ thin film was applied to the SDC electrolyte as the blocking layer and the optimisation of its thickness was studied. As for the appropriate matching of thermal expansion coefficients (TECs) of fuel electrode with the blocking layer of the bi-layer electrolyte (YSZ), Ni-YSZ was chosen for which the effect of amount of graphite pore former on the cell performance was investigated. As for the oxygen electrode, BSCF-SDC composite material was selected for which the effect of SDC amount (weight percentage) composed into the BSCF structure and its optimisation was studied. Here a brief introduction on each of these materials is presented.

1.5.1. Ceria based electrolytes

Basically, at low additive concentrations, rare earth oxides are soluble in fluorite lattice of ceria. As the electrical conductivity of these systems depends on ionic radii of the added cation, research has shown that samarium and gadolinium-added ceria have the highest electrical conductivity because of the close ionic radius of Ce^{4+} to the radii of Sm^{3+} and Gd^{3+} (Yahiro et al. 1989).

1.5.2. YSZ-SDC bi-layer electrolyte

A thin layer of YSZ sandwiched between the fuel electrode and an Yttria Doped Ceria (YDC) electrolyte can protect the SDC from reduction and increase the open circuit potential of SOFCs (Yahiro et al. 1988; Cho et al. 2011). When the thickness ratio of YSZ/SDC decreases, the interfacial oxygen partial pressure increases linearly, which results in a reduction in the n-type conductivity of the SDC at the YSZ/SDC interface, an increase in the OCV, and a decrease in the electronic current penetration through the bi-layer electrolyte (Chan et al. 2003; Tsai and Barnett 1998). Chour *et al.* (Chour et al. 1997), Tsai *et al.* (1997), Mehta *et al.* (1998), and Cho *et al.* (2011) fabricated such bi-layer electrolytes and studied the effect of thin YSZ layer on blocking of electronic current and protection of the internal electrolyte.

1.5.3. Ni-YSZ cermet as the hydrogen electrode material

Among all the components of SOC, the fuel electrode plays an important role in the oxidation of fuel to produce electrons (SOFC mode) and reduction of H_2O and CO_2 to produce H_2 and CO (SOEC mode) (Kim et al. 2008). It acts as the main site for the reaction products removal through the whole fuel electrode to avoid concentration polarisation as well as provide essential electrical conductivity to decrease ohmic polarisation (Cho and Choi 2008). SOFC and SOEC fuel electrode need long triple phase boundaries (TPBs) and adequate gas diffusion for the quick transport of both fuel and exhaust gases. Very much attention is paid to the pore former's effect on the TPB areas which produces additional porosity. However, the area where gas diffusion passes is especially needed and would be different from the anodic and cathodic area appropriate for electrochemical reaction. Then the porous structures of fuel electrodes have been proposed to fulfil the anodic and cathodic functions of SOFC and SOEC, respectively, for further improvement of the performance of the cells (Jono et al.

2007). Indeed, not only the porosity but also sintering shrinkage caused by difference in thermal expansion coefficients (TEC) of fuel electrode and electrolyte are important and effective to the overall performance of a fuel electrode-supported SOC. If the sintering shrinkage and difference between the TECs of the fuel electrode and electrolyte film are close to each other, the stress between them will decrease. This inclement stress may produce cracks in the electrolyte, distort the fuel cell and in turn decrease the cell performance (Bao et al. 2005a). When additional pores are present in the structure of the composite, the doped material can expand into the pores, and hence lower the TEC of the composite (Clemmer and Corbin 2004).

The most commonly used fuel electrode material is nickel–yttria stabilised zirconia (Ni/YSZ) cermet (Kim 1999; Haslam et al. 2005; Sanson et al. 2008; Talebi et al. 2010; Bao et al. 2005b). In the Ni-YSZ composite, Ni plays the catalytic role for the hydrogen oxidation, while YSZ provides an extended reaction zone with the porous ceramic network created. YSZ also adapts the thermal and mechanical properties of the fuel electrode side to those of the other components of the cell. Even if the ratios of NiO and YSZ are kept constant in the fuel electrode samples, the TEC is still varied with the amount of pore formers. It shows that not only the size of the pore, but also the interfaces between NiO and YSZ particles are influenced by the pore former (Hu et al. 2008).

The gas permeability, the electrical conductivity and hence, the cell performance are highly dependent on the microstructure of the supporting fuel electrode. The network of the porous fuel electrode plays two roles: providing 1) the mechanical strength for the entire cell, and 2) a facile gas flow to and from the electrolyte (Sumi et al. 2013). On the other hand, Ni particles which enhance the fuel electrode's catalytic activity must form a well-distributed and homogenous matrix.

The porosity, distribution of phases and particle size affect the cell performance significantly (Andersen et al. 2011; He et al. 2009; Yoon et al. 2007). Therefore, optimisation of the microstructure of the cell components is essential in order to achieve the optimum fuel cell performance. Although the porosity of the Ni-YSZ fuel electrode increases by in-situ reduction of NiO available in the primary fuel electrode material, the final value of the fuel electrode porosity of the cell with Ni-YSZ structure is not high enough to provide an easy access of the gases during the cell operation

(Qiang et al. 2009; Fu et al. 2012). Hence, adding a pore former enhances the gas accessibility to the fuel electrode's active site, i.e., the three-phase boundary (Fu et al. 2012; Liang et al. 2012; Liu et al. 2010a).

1.5.4. BSCF-SDC composite air electrode

As it was found that in the intermediate operating temperature range, the performance of the oxygen electrode of the cell tends to limit the cell's performance. Thus, it is necessary to optimise the oxygen electrode material and performance (Li et al. 2008b; Endo et al. 2000; Ioroi et al. 1997; Lee et al. 2003; Maguire et al. 2000; Minh 1993). Conventional SOCs are composed of YSZ electrolyte, NiO-YSZ cermet fuel electrode and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) oxygen electrode, and they operate at around 1000°C (Hibino et al. 1999; Kamata et al. 1998). The high operating temperature is beneficial for decreasing the electrolyte ohmic resistance and increasing the electrode reaction kinetics. However, it also brings up severe difficulties, such as increasing electrode sintering rate, increasing the issues of cell sealing and interconnection, and increasing the interfacial reaction between cell components (Steele and Heinzel 2001). High operating/materials costs and inadequate operational stability are the two major factors hindering the widespread application of high-temperature SOCs. Presently, it is generally agreeable that the reduction of SOC operating temperature to the intermediate temperature range of 500°C-800°C can greatly speed up the commercialisation of the technology (Gong et al. 2006; Xia et al. 2002), as this can effectively lower the operational and materials costs and extend the operating lifetime. However, based on conventional cell materials and configurations with decrease in testing temperature, new challenges turn up for SOCs, such as a significant increase in both the cathodic (SOFC) and anodic (SOEC) polarisation resistance and electrolyte ohmic resistance (Brant and Dessemond 2000; Baumann et al. 2006; Doshi et al. 1999; Kenjo et al. 2003).

Cobalt-based mixed-conducting oxides specifically in combination with doped-ceria electrolytes have been widely used as oxygen electrode materials in IT-SOFCs (Adler 1998; Aguadero et al. 2007; Chang et al. 2006; Kumar et al. 2004; Liu et al. 2006a; Shao and Halle 2004).

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) is a mixed conductor with super high oxygen ionic conductivity, which had been proven to be a high-performance oxygen electrode for SOC based on oxygen-ion conducting electrolyte (An et al. 2010; Guo et al. 2009; Hirabayashi et al. 2005; Tomita et al. 2006; Zhang et al. 2006c; Zhu et al. 2006b). The cell performance is closely relevant to the phase reaction between the oxygen electrode and the electrolyte layers (Lin et al. 2008b).

One of the main problems of cobalt-based perovskite oxygen electrodes is their high TEC, typically higher than $19.7 \times 10^{-6} \text{ K}^{-1}$ in air between room temperature and 900°C (Jacobson 2010; Wang et al. 2003). SDC is indicated to have a TEC $\sim 12.2 \times 10^{-6} \text{ K}^{-1}$ (Yahiro et al. 1988). Due to the big difference between the TECs of SDC and BSCF, there is a high possibility of crack formation due to this mismatch of TECs of the cell components (Singhal and Kendall 2003). To make BSCF more thermo-mechanically compatible with the SDC electrolyte, the formation of a composite electrode by introducing SDC as the compositing material is proposed in order to decrease the mismatch of the TECs of electrode and electrolyte, and hence, improve the cell performance. However, one drawback of SDC is its low electrical conductivity and so the formation of a composite electrode with SDC will reduced the electrical conductivity. Inadequate electronic conductivity can produce a large contact or charge-transfer resistance. However, SDC has a high ionic conductivity. Good electrodes should have high ionic and electronic conductivity in addition to sufficient porosity to improve the triple-phase boundary (TPB) and hence, improve the performance of the cell.

1.6. Objectives, scope and lay-out of the thesis

The microstructure and composition of the SOC components materials have a large effect on the performance of cells. For further improvement in the performance of the cell, the microstructure should be optimised in order to extend the triple-phase boundaries (TPBs). Raw materials and the sintering condition in the sample preparation have important effects on the electrical conductivity. Hence, the objectives of this PhD research project are as follows:

- ✓ To study the electrolyte microstructure and its modification by adding a blocking layer in order to enhance the performance of the fuel cell and electrolyser cell and also optimisation of the thickness of this blocking layer in order to render a high ionic conductivity without a remarkable sacrifice of open circuit voltage and lowering the operating temperature.
- ✓ To investigate the porosity effects in fuel electrode on enhancing the performance of the single cell in both fuel cell and electrolyser cell systems.
- ✓ To modify the air electrode composition and promoting the composition in order to tailor air electrode material and microstructure in such a way that higher performance of the cell operating in both fuel cell and electrolyser cell modes and hence, lower cost and less complexity would be achieved.

The main scope of this work is on Ni-YSZ as the fuel electrode, YSZ-SDC as the electrolyte and BSCF-SDC as the air electrode and their reaction mechanism in a single fuel cell and electrolyser cell. Humidified hydrogen (3 vol% water vapour) was used as the fuel of the cell and the air electrode was exposed to the ambient air. Also a comparison between SDC and GDC electrolyte and their effect in the performance of the whole cell was done. Meanwhile, the effect of hydrogen humidity percentage on the performance of the SOEC was explored in the studies of all the three components. Hence, performance optimisation, from the fuel electrode, electrolyte, and air electrode point of view, for SOFC and SOEC are performed in this work.

A literature survey of solid oxide fuel cell and solid oxide electrolyser cell component materials with an emphasis on the potentials that may improve the reaction mechanism of the components and hence the performance of the cell is presented in Chapter 2.

Studies on optimisation and enhancement of the fuel cell and electrolyser cell performance as a function of blocking layer thickness in the electrolyte microstructure, porosity in hydrogen electrode microstructure, and composite air electrode composition are presented in Chapters 4, 5, and 6, respectively. The experimental procedure including sample preparation, electrochemical measurement, characterisation techniques such as Field Emission Scanning Electron Microscopy

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(FESEM), Electrochemical Impedance Spectroscopy (EIS), High Resolution Transmission Electron Microscopy (HRTEM) and X-ray Photoelectron Spectroscopy, used in the investigations and studies of all the investigated samples together with their results and discussions are presented in each of the Chapters from 3 to 6. Finally, conclusion and recommendations for future work are drawn in Chapter 7, followed by references.

To achieve trustable and repeatable raw data presented in this thesis, for each and every experiment, many samples were fabricated and tested carefully. In order to fabricate uniformly even cells, same raw materials, same calcination and sintering furnace, and oven were used. One of the main issues in testing which was causing errors in data was the hydrogen gas leakage. This leakage could be from two sources; first, from crack formation in cell sealing paste and second, from crack formation in the cell due to the pressure on the surface of those cells which were not flat after the sintering process. These issues were solved in time and by gaining more experience and skills in cell fabrication and testing techniques and only repeatable data are presented.

CHAPTER 2. Literature review

2.1. Solid oxide fuel cells

2.1.1. Trends in novel alternate electrolyte materials for SOFCs

Normally SOFCs are based on YSZ, especially, 8 mol% YSZ, electrolyte and operate at $\sim 1000^\circ\text{C}$ (Badwal and Foger 1996). The benefit of high operating temperature is the reduction in ohmic loss of electrolyte and enhancement in reaction kinetics of the electrode. However, it leads to some drawbacks, such as possibility of crack formation due to mismatch of TEC of the main components of the cell, electrode film densification due to elevated temperature sintering, high possibility of formation of interfacial reaction between the electrolyte and electrode to yield insulating phase(s), and the need of expensive LaCrO_3 as the interconnect material (Singhal and Kendall 2003). By chemical interactions between LaMnO_3 based air electrode and YSZ, insulating phases interface such as $\text{La}_2\text{Zr}_2\text{O}_7$ and SrZrO_3 are produced at high operating temperature (Kuscer et al. 1995). Hence, it is more preferable that SOFCs be operated at lower temperatures. The most promising solid electrolytes are doped CeO_2 and doped LaGaO_3 (Song et al. 2003) due to their higher ionic conductivity than the state-of-art YSZ (Shiono et al. 2004) for ITSOFCs (600°C - 800°C). Some other alternative materials tried as electrolytes for ITSOFCs are salt-oxide composite materials (Zhu 1999). For low temperature SOFCs, nanocomposite based electrolyte materials are developed (Ma et al. 2010).

2.1.1.1. *LaGaO₃ based electrolyte materials*

In order to achieve great ionic conductivity in Mg and Sr-doped LaGaO_3 compounds (solid solutions of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$, LSGM) as electrolytes for ITSOFCs, perovskite materials are evaluated (Ishihara et al. 1994). For $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.85}$ sintered at 1430°C at 800°C , highest conductivity of 0.14 S.cm^{-1} was achieved (Huang et al. 1996). For $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ derived from sol-gel technique at 800°C , lower conductivity of 0.11 S.cm^{-1} was obtained by Huang *et al.* (Huang et al. 1998). These data are compatible to those represented by YSZ at operating temperatures above 1000°C (Chandrasekaran and Azad 2001). Phase diagram study of Ga_2O_3 - La_2O_3 - MgO - SrO system is available in detail (Rozumek et al. 2003). Inagaki *et al.*

(2000) reported the conductivities of thin film $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ electrolyte to be 0.113 S.cm^{-1} and 0.054 S.cm^{-1} at 800°C and 700°C , respectively. SOFC based on LSGM electrolyte with Ni-SDC as the fuel electrode, and $\text{La}(\text{Sr})\text{CoO}_3$ as the air electrode, showed power density over 0.7 W.cm^{-2} and 0.4 W.cm^{-2} at 800°C and 700°C , respectively. For the LaGaO_3 based oxide electrolyte single cell at 500°C , Ishihara *et al.* (2009) reported that the maximum power density (MPD) was as high as 0.6 W.cm^{-2} .

2.1.1.2. *CeO₂ based electrolyte materials*

Studies during the last 20 years, have been focused on new doped ceria material systems which have lower valence cation such as Ca^{2+} , Y^{3+} (Hibino *et al.* 2000; Yamamoto 2000). At high temperatures, Ce^{3+} has higher oxygen deficiency, phase changes and *n*-type conductivity. Gadolinia (GDC) or samaria-doped ceria (SDC) are interesting electrolyte materials for IT-SOFCs. G_2O_3 and Sm_2O_3 are well acknowledged additives which minimise changes in the lattice parameters of CeO_2 oxide (Kim 1989; Veranitisagul *et al.* 2012; Dudek and Mosialek 2013; Tamm *et al.* 2013). Low additive concentrations of rare earth oxides are soluble in ceria fluorite lattice. The ionic radii of the added cation have a significant effect on the electrical conductivity of ceria-rare earth oxides. Gadolinium and samarium-added ceria electrolytes show the highest electrical conductivity. The close ionic radii of Sm^{3+} and Gd^{3+} to the radius of Ce^{4+} cause this behaviour (Yahiro *et al.* 1989; Kim 1989).

2.1.1.2.1. Bi-layer ceria based electrolyte

One of the main problems with research in the SOFC field is the high operating temperature which needs to be reduced (Jung *et al.* 2007; Prasad *et al.* 2008; Suzuki *et al.* 2010; Zha *et al.* 2003). Technically, it is very important to decrease the operating temperature of the SOFCs to ensure their cost-effectiveness and reliability in order to commercialise the cell systems (Lee *et al.* 2007; Prasad *et al.* 2008). It would also simplify the thermal management, leading to smaller system size (Kwon *et al.* 2011a; Noh *et al.* 2011). From the electrolyte point-of-view, there are two main approaches for decreasing the operating temperature of the SOFCs. One is decreasing the physical thickness of the electrolyte material to ensure that the desired conductivity value of the electrolyte is achieved (Noh *et al.* 2011; Noh *et al.* 2009; Steele and Heinzl 2001).

The other approach is to apply an alternative electrolyte material which has a higher ionic conductivity than the conventional electrolyte material (YSZ) (Ding et al. 2010a; Ding et al. 2010b; Duncan et al. 2011; Ishihara et al. 2011; Lee et al. 2007; Lee et al. 2010; Prasad et al. 2008; Zha et al. 2003; Zhang et al. 2010).

Doped ceria materials such as GDC and SDC are alternative materials due to their matched TEC with Ni-cermet fuel electrodes, chemical stability with co-containing air electrodes, and high ionic conductivity at intermediate temperature range (Zhang et al. 2010; Zhang et al. 2007). However, due to partial reduction of Ce^{4+} to Ce^{3+} , which induces cell voltage and efficiency loss because of internal short circuiting, ceria based electrolytes act as mixed conductors in the reducing condition (Duncan et al. 2011; Lee et al. 2010; Zhang et al. 2007). As the thickness of the ceria layer has a significant effect on the OCV (Duncan et al. 2011; Duncan and Wachsman 2009), studies revealed that with the decrease in ceria layer thickness, the OCV drops (Duncan et al. 2011). So in order to suppress the additional drop in OCV value, a thick layer (theoretically 30 μm -40 μm) of ceria electrolyte is employed (Ding et al. 2010a; Duncan et al. 2011; Duncan and Wachsman 2009). This results in a difficult situation for achieving the optimum performance for the SOFC with a single layer electrolyte. With increase in electrolyte thickness, the ohmic loss increases and hence reduced cell power output despite there is an improvement in OCV. for reducing the ohmic loss, the electrolyte thickness should be reduced (Duncan et al. 2011). To solve this problem it is proposed to use a thin layer of doped ceria-base as the electrolyte and in order to avoid the electronic conduction of the electrolyte film, a thin layer of pure ionic conductor like YSZ to be coated on the electrolyte, at the interface of fuel electrode and ceria electrolyte, named as “bi-layer electrolyte” (Kwon et al. 2011b; Liu et al. 2006b; Tsai et al. 1997; Zhang et al. 2006b). However, in some cases the power density of the bi-layer electrolyte SOFC has been lower than that of the single layer electrolyte SOFC (Zhang et al. 2006b). To overcome this problem the thickness of the YSZ blocking layer should be minimised due to higher resistance of the YSZ in compare with ceria based electrolyte (~5 times higher at 600°C) (Zhang et al. 2006b). So to achieve an improved and desired performance for the SOFC, a thin and dense blocking layer between the fuel electrode and ceria electrolyte is necessary.

2.1.1.3. Nanocomposite based materials

The CGO-YSZ electrolyte has been proven to be an efficient and good alternative composite material for applications in ITSOFC (Tsoga et al. 1998) while yttria-doped ceria-yttria stabilised zirconia (YDC-YSZ) composite based has shown the peak power density of 0.122 W.cm^{-2} at current density of 0.285 A.cm^{-2} at 800°C , which is comparable to that of a YSZ single cell (0.144 W.cm^{-2} at 0.33 A.cm^{-2}) with the same thickness at 1000°C (Kim et al. 2002). Composite electrolyte material made from SDC and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ (LSGM) has delivered higher electrical conductivity as compared to SDC at 500°C - 700°C . I-V curves of single cell have exhibited the maximum power density of 0.25 W.cm^{-2} and maximum current density of 1.06 A.cm^{-2} at 800°C . OCV was higher than the cell with single SDC electrolyte at 600°C - 800°C (Xu et al. 2007). Nanocomposite based electrolyte materials may also be used for LTSOFCs to operate at 500°C (Figure 2).

Figure 2 Temperature dependence of electrical conductivity for oxide ion conductors (high temperature range) (Yamamoto 2000)

2.1.2. Trends in novel alternate fuel electrode materials for SOFC

The most commonly used fuel electrode material is nickel–yttria stabilised zirconia (Ni/YSZ) cermet (Kim 1999; Haslam et al. 2005; Sanson et al. 2008; Talebi et al.

2010; Bao et al. 2005b) which is considered as state-of-the-art fuel electrode material for SOFC systems. It shows good current collection and great electro catalytic activity for fuel oxidation, however it causes carbon deposition, redox instability, Ni-grain agglomeration, sulfur poisoning, and Ni toxicity. Attempts are being made to investigate on new alternative fuel electrode materials for SOFCs to overcome the Ni-based fuel electrode material drawbacks (Ringuedé et al. 2002). For this purpose, Petrovsky *et al.* (2005) developed a novel Y-doped ZrO_2 fuel electrode material for application in ITSOFC. Also by using $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC) electrolyte, Wang *et al.* (2008a) presented Ag-CGO porous cermets as the new fuel electrode materials for ITSOFCs. Using co-precipitation process, Ding et al. (2009) presented a novel $\text{Ni-Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ nanocomposite fuel electrode for LTSOFC. In the Ni-YSZ composite, Ni plays the catalyst role for the hydrogen oxidation, while YSZ provides an extended reaction zone with the porous ceramic network created. YSZ also adapts the thermal and mechanical properties of the fuel electrode side to those of the other components of the cell. Even if the ratios of NiO and YSZ are kept constant in the fuel electrode samples, the TEC still varies with the amount of pore formers. It shows that not only the size of the pore, but also the interfaces between NiO and YSZ particles are influenced by the pore former (Hu et al. 2008).

2.1.3. Trends in novel alternate air electrode materials for SOFC

Due to elevated operating temperature of SOFCs, only electronic conducting oxides or noble metals can be used as the air electrode material. Noble metals are not suitable due to insufficient long-term stability and high cost (Minh 1993). $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) has been considered as state-of-the-art air electrode for HTSOFC. Although the traditional LSM air electrode shows a good performance at 1000°C , its poor oxygen ion conductivity increases the electrode resistance at lower operating temperatures. By mixing an electrically conducting material with an ionically conducting material, a two-phase air electrode (LSM-YSZ) is created which results in improved mixed conductivity in air electrode materials can be replaced with perovskites presenting high mix conductivity on B-site of Fe, Co and Ni, etc (Kharton et al. 1998). For LTSOFCs, $\text{La}_{0.70}\text{Sr}_{0.30}\text{CoO}_{3-\delta}$ (LSC) is an appropriate air electrode material candidate, which has excellent ionic and electronic conductivity over a wide temperature range (Mizusaki et al. 1989). However, due to the reaction of LSC with ZrO_2 electrolytes

and formation of Sr_2ZrO_4 and $\text{La}_2\text{Zr}_2\text{O}_7$, the ohmic resistance increases. It was reported that for prevention of reaction between YSZ and LSC air electrode, CeO_2 based material has been introduced as an interlayer (Gödicke and Gauckler 1998). Qiu *et al.* (2003) reported a new air electrode material based on $\text{Ln}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ for ITSOFC application, which has electrical conductivity of 200 S.cm^{-1} at 800°C . $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}/\text{Co}_3\text{O}_4$ composite air electrode reported to have excellent performance in ITSOFC which leads to a maximum power density of 1.092 W.cm^{-2} with air oxidant and humidified hydrogen fuel at 600°C (Zhang *et al.* 2008). Li *et al.* (2008a) investigated the electrochemical performance of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Er}_2\text{O}_3)_x\text{-Ag}$ composite material for ITSOFC air electrode on SSZ $[(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.1}(\text{CeO}_2)_{0.01}]$ electrolyte.

2.1.3.1. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) air electrode

$\text{SrCoO}_{3-\delta}$ perovskite is the origination of BSCF formation. For the progress of a series of functional materials, strontium cobaltite is a significant perovskite-type parent compound. Depending on the synthesis methods, oxygen partial pressure of the atmosphere, thermal history, and operating temperature, $\text{SrCoO}_{3-\delta}$ may display rhombohedral perovskite, 2-H type hexagonal perovskite, cubic perovskite structure, or oxygen vacancy-ordered brownmillerite (Deng *et al.* 2006; Ito *et al.* 2002). Vashook *et al.* (1997) reported that oxygen content in the composite has a great effect on the electrical conductivity and phase structure of $\text{SrCoO}_{3-\delta}$ oxide. Among the different phase structures of $\text{SrCoO}_{3-\delta}$, at $\sim 950^\circ\text{C}$ the oxide with the cubic phase represents the highest oxygen ionic and electronic conductivity, with a total electrical conductivity of $\sim 160 \text{ S.cm}^{-1}$ (Deng *et al.* 2006). In order to stabilise the cubic lattice structure of $\text{SrCoO}_{3-\delta}$ the method of substitution, via the A- or B-site, has been extensively applied (Zeng *et al.* 2008).

In 1991, Teraoka *et al.* (1991) reported on the general trend of oxygen penetration through ceramic membranes that closely relates to the oxygen electronic and ionic conductivities of the oxides. The ceramic membranes were based on doped $\text{SrCoO}_{3-\delta}$ oxides with the composition of $\text{Ln}_{1-x}\text{A}_x\text{Co}_{1-y}\text{B}_y\text{O}_{3-\delta}$ ($\text{Ln}=\text{La, Pr, Nd, Sm, Gd}$; $\text{A}=\text{Sr, Ca, Ba}$; $\text{B}=\text{Mn, Cr, Fe, Co, Ni, Cu}$). When La^{+3} ion is completely replaced by Sr^{+2} ion, $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ perovskite would achieve the highest oxygen permeation flux (Pei *et*

al. 1995). A summary of the perovskite-type oxide materials used in SOFCs with their TECs, ionic and electronic conductivities is presented in Table 2.

Table 2 Perovskite-type oxide materials: thermal expansion coefficient (TEC), electronic (σ_e), and ionic conductivities (σ_i) in air

Composition	TEC ($\times 10^{-6} \text{K}^{-1}$)	T (°C)	σ_e (S.cm^{-1})	σ_i (S.cm^{-1})	Reference
$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	11.8	900	300	5.9×10^{-7}	(Jiang 2002)
$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$	11.7	800	240	-	(Yamamoto et al. 1987; Kharton et al. 2003)
$\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	13	800	130	-	(Kenjo and Nishiya 1992; Ishihara et al. 1995)
$\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	12	950	220	-	(Ishihara et al. 1995)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$	19.1	800	1220	-	(Tietz et al. 2006; Tietz et al. 2007)
$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$	20.5	800	1600	0.22	(Teraoka et al. 1988)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$	12.2	750	155	-	(Tietz et al. 2006; Simner et al. 2002)
$\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$	-	550	352	-	(Bongio et al. 2005)
	-	800	369	0.205	(Patrakeev et al. 2003)
$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$	16.3	800	129	5.6×10^{-3}	(Ullmann et al. 2000; Kindermann et al. 1998)
$\text{Pr}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$	13.2	550	300	-	(Piao et al. 2007)
$\text{Pr}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$	12.1	800	78	-	(Piao et al. 2007)
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$	13.7	750	290	-	(Simner et al. 2002)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	20.1	600	1050	-	(Piao et al. 2007)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	15.4	600	125	-	(Tai et al. 1995a)
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_3$	18.1	500	1400	-	(Chen et al. 2003)
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	21.4	800	269	0.058	(Petric et al. 2000; Teraoka et al. 1991)
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	15.3	600	330	8×10^{-3}	(Ullmann et al. 2000; Tai et al. 1995b)
$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	16.8	600	-	-	(Tai et al. 1995b)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	19.3	800	1000	4×10^{-2}	(Ullmann et al. 2000; Petric et al. 2000)
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.9}\text{Cu}_{0.1}\text{O}_3$	19.2	700	1400	-	(Yasumoto et al. 2002)
$\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	19.69	550	950	-	(Meng et al. 2008)
$\text{Pr}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Cu}_{0.1}\text{O}_3$	-	700	1236	-	(Zhu et al. 2008)
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	20	500	30	-	(Wei et al. 2006b)
$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$	20.5	700~900	>1000	-	(Ishihara et al. 1998; Xia et al. 2002)
$\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$	11.4	800	580	-	(Chiba et al. 1999)
$\text{Sr}_{0.9}\text{Ce}_{0.1}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$	18.9	800	87	0.04	(Ullmann et al. 2000)

By using different analysing systems such as temperature programmed desorption, neutron diffraction, differential thermal analysis, high temperature XRD, and thermogravimetric analysis, McIntosh *et al.* (2006) determined the oxygen stoichiometry and structure of SCF and BSCF up to 1273K in the oxygen partial pressure range of 1 to 10^{-5} atm. They found that the concentration of oxygen vacancy in BSCF structure was interestingly higher than that of SCF and considerably higher than that of the vacancy-ordered brownmillerite phase. The mixture of the absence of the ordering phase and a high vacancy concentration resulted in the higher oxygen penetration fluxes through BSCF membranes in comparison to SCF. Some investigations, both theoretically and experimentally, have shown that BSCF is an optimal material in the $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ family as a air electrode for ITSOFCs (Wei et al. 2006b).

2.1.3.1.1. BSCF composite air electrode

Generally a composite air electrode, which includes a mixture of an electronic and oxygen ionic conducting material, with an ionic conductor, shows higher performance in compare with a sample having single-phase air electrode. In many studies composite air electrodes such as LSM-YSZ (Marinković et al. 2004; Murray et al. 1998), LSCF-GDC (Dusastre and Kilner 1999; Esquirol et al. 2004), and SSC-SDC (Xia et al. 2002), have proven to exhibit an excellent electrochemical performance. So some other groups have studied other composite air electrodes such as BSCF- $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_3$ (BZCY) (Lin et al. 2009), BSCF-LSGM (Liu et al. 2008), and BSCF-SDC (Li et al. 2008b; Wang et al. 2008b; Wei et al. 2006a). Wang *et al.* (2008b) tested the performance of the composite BSCF-SDC (70:30 in weight ratio) air electrode which was prepared by mechanical mixing for ITSOFC. The results showed that this composite air electrode presented a better performance in compare with the pure BSCF air electrode fired at 1000°C. But it demonstrated lower performance than pure BSCF air electrode at other operating temperatures. The obtained ASR values were $0.099 \text{ } \Omega \cdot \text{cm}^2$ and $0.064 \text{ } \Omega \cdot \text{cm}^2$ for the samples with pure BSCF air electrode and with BSCF-SDC composite air electrode, respectively. For other air electrode materials such as LSM, SSC, and LSCF by introducing an ionic conducting phase to form the composite air electrode, improved performance with

more than one order of magnitude has been achieved (Dusastre and Kilner 1999; Esquirol et al. 2004; Marinković et al. 2004; Xia et al. 2002).

2.2. Solid oxide electrolyser cells

Electrolysis of water is a well-known established process, which produces oxygen and hydrogen and so water and direct current electricity are converted into gaseous oxygen and hydrogen. This process is the reverse of a hydrogen fuel cell, which back in 1800 Carlisle and Nicholson demonstrated the process and in the 1820s, the principles were clarified by Faraday who introduced the word “electrolysis” in 1834. The commercialisation of hydrogen production by electrolysis process started in 1902 by an engineering company named Oerlikon. At the same time the basis of SOFC and SOEC, which was a high-temperature electrolyte ZrO_2 with 15% Y_2O_3 , was developed by Nernst. In 1951, Lurgi introduced the first commercially available electrolyser, which was working under high pressure (30 bars). These days, electrolysis technology operating at low temperatures is available from at least 13 manufacturers. However, the technology of SOEC is still under development. Studies done in 1980s by Donitz and Erdle (Dönitz and Erdle 1985) attracted a lot of interest to this technology. Using electrolyte supported tubular SOEC, they reported the results of single cells which operated in long-hour at current densities of -0.3 A.cm^{-2} and 100% Faraday efficiency, as well as a low voltage of 1.07 V, within the HotElly project from Dornier System GmbH. In addition, Area Specific Resistance (ASR) of about $0.6 \text{ } \Omega\text{.cm}^2$ per cell was reported for a seven-cell stack at 1003°C (Isenberg 1981). In recent years, there has been a significant increase in research on high temperature electrolysis. Basically the common materials used in SOEC are similar to those typically used in SOFC (Laguna-Bercero 2012).

2.2.1. Oxygen ion conducting electrolyte materials for SOECs

2.2.1.1. *LaGaO₃ based electrolyte materials*

One of the most promising oxide ion conducting materials for ITSOFCs is LaGaO_3 based oxide electrolyte, which is normally doped with Sr on the La site and Mg on the Ga site (LSGM). For a SOEC application using $\text{Ni}_{1-x}\text{Mg}_x\text{O}$ -ceria composite as the fuel electrode and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ (LSC) as the air electrode, LSGM is proposed to be the

electrolyte material (Elangovan et al. 2007). The measured ASR at 800°C and using 56% relative humidity was $0.6 \Omega \cdot \text{cm}^2$.

2.2.1.2. *Scandia doped zirconia electrolytes*

YSZ has good chemical stability and high ionic conductivity and so is the most popular electrolyte material for SOFC applications. However, in recent years, some other materials such as Scandia-stabilised zirconia (ScSZ) are proposed which demonstrated higher ionic conductivity than the standard YSZ. Therefore, they help to decrease the system's operating temperature requirement. At Imperial College London, researchers studied ScSZ cells in which they used electrolyte supported Scandia (10 mol%) and ceria (1 mol%) stabilised zirconia (10Sc1CeSZ), Ni-YSZ for the fuel electrode, and platinum for the air electrode (Laguna-Bercero et al. 2009). They obtained $-450 \text{ mA} \cdot \text{cm}^{-2}$ current density at 1.5 V and $0.99 \Omega \cdot \text{cm}^2$ ASR at 900°C and using 80% relative humidity of the steam at the fuel electrode side.

2.2.1.3. *Ceria based electrolytes*

The most promising electrolyte for ITSOFC is ceria electrolyte. Cerium oxide is normally doped with SDC or GDC in order to produce higher ionic conductivity than YSZ. Investigations on planar SDC based cell in compare with the YSZ based cell under electrolysis mode have shown that although using ceria based cell leads to lower both air electrode and hydrogen electrode overvoltage in compare with the YSZ based cells, the high applied voltages results in reduction of Ce^{4+} to Ce^{3+} and decreasing the ionic transference number (Eguchi et al. 1996).

Some studies have reported the performance of the cells with ceria based composite (CBCs) electrolytes (Zhu et al. 2006a; Kim-Lohsoontorn et al. 2011). Kim-Lohsoontorn *et al.* (2011) used a bi-layered GDC-YSZ and compared it with a GDC and YSZ electrolyte using LSM-YSZ for the air electrode and Ni-GDC for the hydrogen electrode. As shown in Figure 3, the cell with bi-layer YSZ-GDC electrolyte has significantly demonstrated higher performance compared to the cell with GDC or YSZ single layer electrolyte.

Figure 3 I-V curves of the cells having different electrolytes (YSZ, GDC, and bi-layered GDC-YSZ electrolyte) in the steam electrolysis and SOFC modes measured at 800°C (Kim-Lohsoontorn et al. 2011)

A summary of the reported ceria based electrolytes with the ionic conductivities at typical temperatures used in SOECs is presented in Table 3. It can be seen that SDC and GDC show good ionic conductivity at intermediate temperatures compared with conventional YSZ.

Table 3 Reported ionic conductivities of different ceria-based electrolytes for SOECs

Material	Conductivity (S.cm ⁻¹)	Temperature (°C)	Remarks	Reference
15GDC(Ce _{0.85} Gd _{0.15} O _{2-δ})	4.07×10^{-2}	700	High purity CeO ₂ and Gd ₂ O ₃ powders were used as the starting materials	(Zhang et al. 2006a)
25GDC(Ce _{0.75} Gd _{0.25} O _{1.875})	1.01×10^{-2}	600	Prepared by the flame spray pyrolysis method	(Seo et al. 2006)
25GDC(Ce _{0.75} Gd _{0.25} O _{1.875})	7.5×10^{-3}	600	Prepared by hydrothermal method	(Dikmen et al. 2002)
20GDC	9.0×10^{-2}	800	Prepared by oxalate coprecipitation method	(Van Herle et al. 1996)
	4.2×10^{-2}	700		
20SDC	8.8×10^{-2}	800	Prepared by oxalate coprecipitation method	(Van Herle et al. 1996)
	4.1×10^{-2}	700		
20YDC	7.7×10^{-2}	800	Prepared by oxalate coprecipitation method	(Van Herle et al. 1996)
	3.5×10^{-2}	700		
17SDC(Ce _{0.83} Sm _{0.17} O _{1.95})	5.7×10^{-3}	600	Prepared by hydrothermal method	(Huang et al. 1997)
20YDC(Ce _{0.8} Y _{0.2} O _{1.9})	3.4×10^{-2}	700	Prepared by citric acid-nitrate low-temperature combustion process	(Xu et al. 2006)

2.2.2. Fuel electrode materials for SOEC

The fuel electrode of a SOEC is the electrode that supports the diffusion of hydrogen gas and steam and also provides active sites for the steam to be reduced. As well as in SOFCs and SOFCs applications, Ni-YSZ is commonly used under electrolysis mode and for electrolysis applications (Hauch et al. 2008; Hauch et al. 2007; Matsui et al. 2010; Zhu et al. 2006a). During an electrolysis process, small amounts of hydrogen are needed on the fuel electrode side for preventing the oxidation of Ni to NiO. Novel materials are being proposed as the fuel electrode material candidates in SOECs. Marina *et al.* have studied the performance of the cell with lanthanum-substituted strontium titanate/ceria composite as the fuel electrode material. They reported that for steam analysis applications, titanate/ceria composite electrodes are more active than the Ni-YSZ standard composite. Particularly, they reported that under low hydrogen but high steam partial pressures, the Ni-YSZ suffers the irreversible degradation (Marina et al. 2007).

Researchers in Japan found that the ionic conductivity of the zirconia electrolyte increases by increase in the Ni-dispersed SDC fuel electrode activity (Osada et al. 2006; Uchida et al. 2004). They reported that by decreasing the electronic resistance and increasing the active reaction sites, the reaction rate improves. Recently, novel perovskite material $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_3$ (LSCM) is proposed as the fuel electrode material for steam electrolysis cells (Yang and Irvine 2008). Yang *et al.* (2008) fabricated a porous YSZ impregnated LSCM electrode as the fuel electrode, porous YSZ impregnated LSF as the air electrode, and dense YSZ as the electrolyte and concluded that LSCM can be an alternative candidate to Ni-YSZ for SOEC applications. They also observed chemical changes which are possibly due to the LSCM perovskite phase reduction.

2.2.3. Air electrode materials for SOEC

Long term degradation rate in SOEC occurs faster than in SOFC, and this fact is possibly related to the air electrode (Laguna-Bercero 2012). Delamination of air electrodes is a main problem of degradation in SOECs which happens during the steam analysis and is due to high oxygen partial pressure at the electrolyte-electrode interface (Sharma and Yildiz 2010; Sohal et al. 2009). In several studies, Hauch *et al.*

(2008) have tried to optimise the performance of the air electrode in SOECs. The most common air electrode in SOFC is LSM-YSZ (Hauch et al. 2008). A study on LSM-YSZ material operating as the air electrode in SOEC showed that the anodic current treatment of the SOEC enhanced the electrochemical performance of the electrodes (Liang et al. 2009). The same behaviour is seen in the cathodic polarisation of SOFC, which improves the performance of the LSM electrode (Wang and Jiang 2006). Based on these experiments, a model was developed to introduce the possible mechanisms for this behaviour (Backhaus-Ricoult et al. 2008). Several authors reported the acceptable performance of the LSM-YSZ in SOEC mode (Yang et al. 2010; Laguna-Bercero et al. 2010a; Hauch et al. 2006).

GDC impregnated LSM air electrodes are recently developed for SOEC by Chen *et al.* (2010). The addition of GDC particles improves the electrochemical performance for the O₂ evolution in both SOFC and SOEC (Gorte and Vohs 2003; Jiang et al. 2004). GDC addition also prevents the delamination of the air electrode from the YSZ electrolyte. Other authors have investigated the effect of composite air electrodes of YSZ with La_{0.8}Sr_{0.2}FeO₃ (LSF), and La_{0.8}Sr_{0.2}CoO₃ (LSCo) on the performance of the SOEC (Kong et al. 2009; Wang et al. 2006). LSCF (Schiller et al. 2009; Hashimoto et al. 2009; Laguna-Bercero et al. 2010b, 2011a), La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4.08} (LSCN) (Laguna-Bercero et al. 2011b), and Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ} (SFM) (Liu et al. 2010b) are also other alternative air electrodes for SOEC applications.

Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) is a mixed conductor with super high oxygen ionic conductivity, which is proven to be a high-performance air electrode for SOEC based on oxygen-ion conducting electrolyte (An et al. 2010; Guo et al. 2009; Hirabayashi et al. 2005; Tomita et al. 2006; Zhang et al. 2006c; Zhu et al. 2006b). The cell performance is closely relevant to the phase reaction between the air electrode and the electrolyte layers (Lin et al. 2008b). BSCF has been used as the air electrode material in SOFCs and is now being considered for SOECs (Bo et al. 2008). Bo *et al.* (2008) reported that the ASR value for BSCF-YSZ composite air electrode is 0.077 Ω.cm⁻² at 850°C operating temperature and also presented better performance in compare with the standard LSM material in both SOEC and SOFC modes. However, Kim-Lohsoontorn *et al.* (2010) reported a lower performance in compare to the stable LSM-YSZ cell when operating in electrolysis mode. As an appropriate air electrode should have

sufficient ionic and electronic conductivity, thus making a composite air electrode with SDC will improve the performance of the cell.

2.3. Overpotential types in solid oxide cells

In electrochemistry, overpotential is the potential difference (voltage) between a half-reaction's thermodynamically determined reduction potential and the potential at which the redox event is experimentally observed (Bard and Faulkner 2001). The term is directly related to a cell's voltage efficiency. In an electrolytic cell the overpotential requires more energy than thermodynamically expected to drive a reaction. Overpotential is specific to each cell design and varies across cells and operational conditions, even for the same reaction. It is used more practically to define the current density (typically small) at which the overpotential is measured.

The overall overpotential is the summation of many individual losses. Voltage efficiency describes the fraction of energy lost through overpotential. For an electrolytic cell this is the ratio of a cell's thermodynamic potential divided by the cell's experimental potential converted to a percentile. Voltage efficiency should not be confused with Faraday efficiency. Both terms refer to a mode through which electrochemical systems can lose energy. Losses in the potential term through overpotentials are described by voltage efficiency. Losses in the current term through misdirected electrons are described by Faraday efficiency.

The reason that the voltage is so important is that it is a good measure of the electrical efficiency of the cell. The higher the voltage the higher the electrical efficiency and the less loss of energy as heat. Overpotential losses within the active layer can be grouped into four categories (Srinivasan 2006):

- Activation overpotential for the charge transfer reaction; this is a result of the usage of a catalyst. It is the amount of energy that it loss as a result of energy required to initiate the reaction. So if the fuel cell has a good catalyst there would be less loss through activation energy.
- Mass transport overpotential, more so for the diffusion of the reactants to the active site than for the products to diffuse away from the active site; this is

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when the fuel crosses over from the fuel electrode to the air electrode and contaminates the electrolyte. There is a loss in voltage here because there are no electrons being released to the external circuit.

- Ohmic overpotential within the active layer, which is predominantly due to the transport to or from the active site to the bulk electrolyte layer. The ohmic overpotential, due to electron transport within the electrode and to or from the current collector is generally negligible.
- Concentration overpotentials; these losses result when there is a decrease in the concentration of the gases at the electrode. For the fuel cell to continually produce energy the gases must be at the electrode without interference.

CHAPTER 3. Ceria based electrolytes for SOFCs

3.1. GDC and SDC electrolytes preference

Studies during the last 20 years, have concentrated on new doped ceria material systems which have lower valence cation such as Ca^{2+} , and Y^{3+} (Hibino et al. 2000; Yamamoto 2000). At high temperatures, Ce^{3+} has higher oxygen deficiency, phase changes and n -type conductivity. Gadolinia (GDC) or samaria-doped ceria (SDC) are interesting electrolyte materials for IT-SOFCs. Gd_2O_3 and Sm_2O_3 are well acknowledged additives which minimise changes in lattice parameters of CeO_2 oxide (Kim 1989; Veranitisagul et al. 2012; Dudek and Mosiałek 2013; Tamm et al. 2013). Low additive concentrations of rare earth oxides are soluble in ceria fluorite lattice. The ionic radii of the added cation have a significant effect on the electrical conductivity of ceria-rare earth oxides. Gadolinium and samarium-added ceria electrolytes show the highest electrical conductivity. The close ionic radii of Sm^{3+} and Gd^{3+} to the radius of Ce^{4+} cause this behaviour (Yahiro et al. 1989; Kim 1989). GDC Conductivity at 800°C was 0.10 S.cm^{-1} , which in compare with YSZ is one order of magnitude higher (Sammes et al. 1998). For $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) at 700°C , a conductivity of 0.042 S.cm^{-1} was reported (Inaba and Tagawa 1996). Gd-doped ceria based SOFC was reported to have power density of 0.49 W.cm^{-2} at 550°C (Suzuki et al. 2009). Hence, ceria based electrolyte can be considered for intermediate temperature SOFCs operating at temperatures below 800°C since it has shown reasonably high ionic conductivity, in spite of lower open circuit voltage.

High resolution transmission electron microscopy (HRTEM) (JEM, 2010) was used to study the crystallinity and crystal size of the SDC powder. Figure 4 shows the HRTEM images of SDC powder. Uniform single crystals of less than 20 nm size and also isolation of particles can be seen in Figure 4 (a). In all images, in one particle, all lines are in one direction which means that the powder is of a single crystal. Furthermore, uniformity in particle size (20 nm), equiaxial cubic crystals (not elongated) and almost defect-free particles show that the material processing has been successful and it was fully crystalline.

Figure 4 HRTEM images of SDC powder

3.2. Experimental work on electrolyte button cell preparation

SDC ($\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$) and GDC ($\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$) button cells were fabricated for conductivity measurements of the electrolytes using commercial powder (SIGMA-ALDRICH), with 99.9% purity and particle size of 0.1 μm -0.4 μm . The samples were prepared by die-pressing the powder, followed by sintering at 1200°C, 1300°C, 1400°C and 1500°C for 4 hours in the air. The surface of the electrolyte pellets was roughened by grinding with sandpaper in order to increase the contact between silver paste and electrolyte. After measuring the dimensions, silver paste was applied to both sides of the electrolyte, one by one, followed by the drying process at 800°C for 30 minutes. For impedance test, a short Pt-wire was attached to each side of the sample, by silver paste, followed by the same drying process of the silver paste.

To prepare the electrolyte button cells for the microstructural study, after dry polishing with different sand papers, they were polished with diamond cloth, using diamond paste, followed by thermal etching at 25°C lower than the related sintering temperature of the sample.

3.3. Characterisation and impedance study on the electrolyte button cells

The sintering temperature of the electrolytes plays an important role in the whole process. The electrolyte must be almost fully dense, without any open pores. Therefore the microstructure of each sample was studied by FESEM (JEOL, JSM 6340F) for possible pin holes. For simplicity purpose, the sintering temperature was used for identifying the sample number, for example the SDC sample, sintered at 1300°C is named as SDC-3 and GDC-5 is the GDC sample sintered at 1500°C. The micrographs were in two different magnifications, one low and one high (X-3000 and X-19000), which were the same for all samples to make the comparison easier and logical. The measured diameter, thickness, weight, density and relative density ($\rho/7.12$) of GDC button cells before the impedance test, sintered at 1200°C -1500°C, are presented in Table 4.

Table 4 Dimensional and density measurements of SDC and GDC electrolyte samples

Sample	Diameter (mm)	Thickness (mm)	Weight (g)	Density (g.cm ⁻³)	Relative density
SDC-2	9.485	2.140	0.970	6.420	0.902
SDC-3	9.260	2.130	0.980	6.830	0.959
SDC-4	9.200	2.125	0.977	6.920	0.972
SDC-5	9.215	2.180	1.011	6.954	0.977
GDC-2	10.365	2.425	1.065	5.210	0.732
GDC-3	9.22	2.370	1.070	6.765	0.950
GDC-4	9.160	2.335	1.065	6.924	0.972
GDC-5	9.17	2.340	1.063	6.890	0.968

As much as the relative density is closer to 1, the electrolyte will be the densest and the sintering temperature is much appropriate. As it can be seen in Figure 5, the relative density increases with increasing of the sintering temperature and so the highest relative density can be achieved at 1500°C. In a comparison between GDC and

SDC electrolyte, it obviously can be seen that SDC is a better choice for electrolyte material as it has higher relative density at all sintering temperatures.

Figure 5 Relative density versus temperature for GDC and SDC electrolyte

3.3.1. Characterisation and impedance study on GDC button cell

3.3.1.1. Characterisation study

Figure 6, Figure 7, Figure 8, and Figure 9, show the microstructures of samples GDC-2, GDC-3, GDC-4 and GDC-5, respectively. The increasing trend of grain size with increasing the sintering temperature can be seen in these figures. The grain size of the electrolytes, sintered at 1200°C, 1300°C, 1400°C, and 1500°C, were ~130 nm-280 nm, ~320 nm-780 nm, ~500 nm-1.8 μm , and ~1.3 μm -2.8 μm , respectively.

In Figure 6, many pores can be seen on the surface of the electrolyte which means that 1200°C is not an appropriate sintering temperature. The same result is shown for the sample sintered at 1300°C in Figure 7.

Figure 6 FESEM micrographs of GDC electrolyte sintered at 1200°C (GDC-2)

Figure 7 FESEM micrographs of GDC electrolyte sintered at 1300°C (GDC-3)

By increasing the sintering temperature to 1400°C, the grains grow and so the pores get closed and the electrolyte becomes denser (Figure 8). There is almost no pore on the surface of the electrolyte sintered at 1500°C and it is fully dense (Figure 9), which means from microstructure point of view, this temperature is the best sintering temperature, but by studying the results of the impedance test of the electrolytes, one can make the final decision whether 1400°C is the appropriate sintering temperature for GDC or 1500°C.

Figure 8 FESEM micrographs of GDC electrolyte sintered at 1400°C (GDC-4)

Figure 9 FESEM micrographs of GDC electrolyte sintered at 1500°C (GDC-5)

3.3.1.2. Impedance study

Impedance measurements were done on button cells using MultiStat machine. From the impedance spectra, ohmic resistance, R_s , was achieved and conductivity was calculated, using Equation 1.

$$\sigma = \frac{1}{\rho} \quad \text{Equation 1}$$

where ρ , electrical resistivity, was calculated by Equation 2, in which R_s is ohmic resistance, A is the area of the electrolyte and t is the thickness of the electrolytes.

$$\rho = \frac{R_s \times A}{t} \quad \text{Equation 2}$$

R_s is the interceptor point of impedance spectra with 0-line of y-axis for high temperatures and the minimum point between the two overlapping arcs (depressed semicircles) for low temperatures, shown in few graphs of Figure 10. To prevent duplication, only one impedance spectra, related to GDC-5, is presented. The data of impedance test at 1200°C sintering temperatures is presented in

Table 5.

Table 5 Data achieved from impedance spectra of GDC electrolyte sintered at 1200°C (GDC-2), from 300°C-850°C

Temperature (°C)	R_s (Ω)	ρ ($\Omega.cm$)	σ ($S.cm^{-1}$)
850	4.6	15.9	0.063
800	5.7	19.8	0.05
750	7.4	25.8	0.039
700	10.2	35.4	0.028
650	14.9	51.9	0.019
600	23.5	81.7	0.012
550	40.7	141.5	0.007
500	77.4	269.2	0.004
450	171.9	598.2	0.002
400	453.1	1576.6	0.0006
350	1450.5	5047.0	0.0002
300	6066.1	21106.7	0.00005

Figure 10 Impedance spectra of GDC electrolyte sintered at 1500°C (GDC-5), from 300°C-850°C

It can be seen that with increasing the temperature, resistance decreases and conductivity increases. Hence, at higher temperatures the electrical properties are much desired. The same results were achieved for GDC-3, GDC-4, and GDC-5 in Table 6, Table 7, and Table 8 respectively, i.e., with increase in the temperature, resistance decreases and conductivity increases. When the conductivities of samples of different sintering temperatures are compared, one can find out that the conductivities are almost the same. Although GDC-3 and GDC-5 have achieved almost the same highest conductivity, the sintering temperature does not have a significant effect on the conductivity of GDC, and according to FESEM micrographs (Figure 7), GDC-3 had

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many pores on the surface and was not dense, so the appropriate sintering temperature for GDC electrolyte was chosen to be 1500°C.

Table 6 Data achieved from impedance spectra of GDC electrolyte sintered at 1300°C (GDC-3), from 300°C-850°C

Temperature (°C)	R_s (Ω)	ρ ($\Omega.cm$)	σ ($S.cm^{-1}$)
850	4.5	12.7	0.079
800	5.5	15.5	0.064
750	7.2	20.2	0.049
700	9.8	27.7	0.036
650	14.2	39.9	0.025
600	22.0	62.0	0.016
550	38.0	107.1	0.009
500	72.5	204.3	0.005
450	158.5	446.5	0.002
400	433.0	1219.8	0.001
350	1387.0	3907.3	0.0002
300	6041.9	17020.7	0.00006

Table 7 Data achieved from impedance spectra of GDC electrolyte sintered at 1400°C (GDC-4), from 300°C-850°C

Temperature (°C)	R_s (Ω)	ρ ($\Omega.cm$)	σ ($S.cm^{-1}$)
850	5.7	16.1	0.062
800	7.3	20.5	0.049
750	9.7	27.3	0.037
700	13.4	37.9	0.026
650	20.1	56.7	0.018
600	31.9	90.2	0.011
550	56.4	159.2	0.006
500	108.8	307.1	0.003
450	246.6	695.9	0.001
400	671.8	1895.9	0.0005
350	2210.0	6237.1	0.0002
300	9487.0	26774.5	0.00004

Table 8 Data achieved from impedance spectra of GDC electrolyte sintered at 1500°C (GDC-5), from 300°C-850°C

Temperature (°C)	R_s (Ω)	ρ ($\Omega.cm$)	σ ($S.cm^{-1}$)
850	4.4	12.5	0.08
800	5.5	15.6	0.064
750	7.2	20.4	0.049
700	9.9	27.9	0.036
650	14.5	40.9	0.024
600	22.8	64.4	0.015
550	39.7	112.1	0.009
500	77.3	218.1	0.005
450	168.3	475.1	0.002
400	457.0	1289.8	0.0008
350	1490.1	4205.6	0.0002
300	6442.0	18181.6	0.00005

3.3.2. Characterisation and impedance study on SDC button cell

3.3.2.1. Characterisation study

The FESEM micrographs of SDC electrolytes sintered at 1200°C, 1300°C, 1400°C, and 1500°C, with the grain sizes of ~140 nm-360 nm, ~270 nm-670 nm, ~650 nm-1.3 μm , and ~1.2 μm -2.2 μm are shown in Figure 11, Figure 12, Figure 13, and Figure 14, respectively.

At low sintering temperatures many pores can be seen on the surface of the SDC button cells (Figure 11 and Figure 12). As the electrolyte in a full cell has only few micrometers thickness, these pores may contain some open pores in the electrolyte, and so the gas will leak through the electrolyte. Therefore 1200°C and 1300°C are not appropriate sintering temperatures for the SDC electrolyte.

Figure 11 FESEM micrographs of SDC electrolyte sintered at 1200°C (SDC-2)

Figure 12 FESEM micrographs of SDC electrolyte sintered at 1300°C (SDC-3)

Similar to GDC electrolyte, when SDC electrolyte is sintered at 1400°C, only some defects can be seen on the surface of the button cell and the pores are closed. By increasing the sintering temperature to 1500°C, very few pores can be seen on the surface, which means from microstructure point of view, this temperature is the best sintering temperature for SDC, but only by studying the results of the impedance test of the electrolytes, can one make the final decision whether 1400°C is the appropriate sintering temperature or 1500°C.

Figure 13 FESEM micrographs of SDC electrolyte sintered at 1400°C (SDC-4)

Figure 14 FESEM micrographs of SDC electrolyte sintered at 1500°C (SDC-5)

3.3.2.2. *Impedance study*

To prevent duplication, only one impedance spectra, related to SDC-4 (Figure 15) and the data of impedance test at 1200°C sintering temperatures (Table 9) are presented.

CHAPTER 3

Table 9 Data achieved from impedance spectra of SDC electrolyte sintered at 1200°C (SDC-2), from 300°C-850°C

Temperature (°C)	R_s (Ω)	ρ ($\Omega.cm$)	σ ($S.cm^{-1}$)
850	4.5	14.8	0.068
800	4.5	14.9	0.067
750	6.9	22.9	0.044
700	8.2	27.1	0.037
650	12.4	41.0	0.024
600	19.6	64.8	0.015
550	34.7	114.7	0.009
500	68.4	226.0	0.004
450	153.8	507.8	0.002
400	407.1	1344.0	0.0007
350	1275.0	4209.8	0.0002
300	5250.0	17334.4	0.00006

It can be seen that with increasing the temperature, resistance decreases and conductivity increases, so at higher temperatures the electrical properties are much desired. The same results are achieved for SDC-3, SDC-4, and SDC-5 Table 10, Table 11, and Table 12, respectively.

Figure 15 Impedance spectra of SDC electrolyte sintered at 1400°C (SDC-4), from 300°C-850°C

Table 10 Data achieved from impedance spectra of SDC electrolyte sintered at 1300°C (SDC-3), from 300°C-850°C

Temperature (°C)	R_s (Ω)	ρ (Ω.cm)	σ (S.cm ⁻¹)
850	3.2	10.1	0.099
800	3.9	12.5	0.08
750	5.2	16.4	0.061
700	7.2	22.7	0.044
650	10.8	34.1	0.029
600	17.6	55.8	0.018
550	31.9	100.8	0.01
500	62.8	198.7	0.005
450	143.5	453.8	0.002
400	385.4	1218.7	0.0008
350	1259.0	3980.7	0.0002
300	5162.0	16321.1	0.00006

Table 11 Data achieved from impedance spectra of SDC electrolyte sintered at 1400°C (SDC-4), from 300°C-850°C

Temperature (°C)	R_s (Ω)	ρ ($\Omega.cm$)	σ ($S.cm^{-1}$)
850	3.2	9.6	0.104
800	3.9	11.9	0.084
750	5.1	15.6	0.064
700	7.1	21.5	0.046
650	10.5	31.7	0.031
600	16.7	50.8	0.02
550	29.9	90.7	0.011
500	58.2	176.5	0.006
450	128.2	388.9	0.003
400	334.2	1014.1	0.001
350	1049.0	3182.8	0.0003
300	4240.0	12864.9	0.00008

Table 12 Data achieved from impedance spectra of SDC electrolyte sintered at 1500°C (SDC-5), from 300°C-850°C

Temperature (°C)	R_s (Ω)	ρ ($\Omega.cm$)	σ ($S.cm^{-1}$)
850	3.2	9.9	0.101
800	4.0	12.3	0.081
750	5.3	16.1	0.062
700	7.3	22.3	0.045
650	10.8	33.1	0.03
600	17.5	53.4	0.019
550	31.4	96.1	0.01
500	61.7	188.6	0.005
450	136.4	417.4	0.002
400	356.9	1092.0	0.0009
350	1147.0	3509.0	0.0003
300	4540.0	13889.3	0.00007

In a comparison between the conductivities of SDC samples of different sintering temperatures, it is obvious that the conductivities are almost about the same and the highest conductivities are related to SDC-4 and SDC-5. However, the sintering temperature does not have a significant effect on conductivity.

3.4. A comparison between GDC and SDC button cells

From the microstructure point of view, both SDC and GDC electrolytes, sintered at 1500°C, are highly dense, but the grain size of SDC, is slightly smaller than the one in GDC sintered at 1500°C. The experiments showed that the smaller the grain size, the

lower the ionic conductivity of the electrolyte. Figure 16 presents Arrhenius plots of GDC and SDC conductivities determined by impedance spectra.

Figure 16 Arrhenius plots of GDC and SDC conductivities determined by impedance spectra. The flashes show the applied temperature in °C

As shown in Figure 16 with increasing the temperature, the conductivity increases. As the error bars show, after taking experimental uncertainty into account, from the conductivity point of view, obviously SDC is a better choice for the electrolyte. In an overall review on GDC and SDC, the conclusion is that SDC is a better choice as the electrolyte material.

3.5. GDC and SDC electrolytes study in a full cell

The performance of SOFCs depends critically on the microstructure of each of the component layers, the composition of the materials used, and the resulting physical/chemical properties, such as permeability, electronic, and ionic conductivity, and catalytic activity. The microstructures of the materials are affected, in turn, by the

processing methods used to fabricate them. Therefore, selecting the appropriate processing technique for a given combination of materials, stack geometry, target operating temperature range, and desired composition, is essential for achieving the performance requirements of the fuel cell. A range of processing methods exists for the fabrication of SOFCs, which can be broadly classified into wet-ceramic techniques and direct deposition techniques. Both tubular and planar cells are typically fabricated by first synthesising the support layer, and then performing a series of subsequent deposition and consolidation steps, repeated as needed, to build up the functional layers. Although in testing the electrolytes, it is found that SDC is a better option than GDC, but to complete this comparison, the performance of the full cell in which GDC is used as the electrolyte is also evaluated. To make the comparison easier, the results of the two cells are presented together.

3.6. Experimental work on single cell fabrication

3.6.1. Electrolyte suspension preparation

For preparing the GDC/SDC suspension a mixture of 2 g GDC/SDC powder, 0.1 g Triethanolamine (TEA), 0.1 g benzyl butyl phthalate (BBP), 0.1 g propylene glycol (PG), 0.1 g polyvinyl butyral (PVB) and 40 g isopropanol were milled for 24 hours using the ball milling machine.

3.6.2. Fuel electrode powder synthesis and fabrication

For the preparation of the fuel electrode, nickel oxide powder (NiO) was mixed with GDC/SDC powder with a weight ratio of 65:35 for NiO and GDC/SDC powders for cells with GDC/SDC electrolyte. This mixture was ball milled in isopropanol for 24 hours. The suspension was then dried on the hot plate for ~1 hour to obtain the powder. This powder was hand-ground in an agate mortar. Using the die-pressing machine, fuel electrode powder was pressed into the fuel electrode substrate.

3.6.3. Air electrode powder and air electrode paste synthesis

The sol-gel process is one of the chemical synthesis methods adopted for synthesising a large number of glass materials and novel ceramic oxide compositions in the 1960s. Through the past few decades, it has proven to be an important wet chemical route for

laboratory synthesis and in some cases for eventual production of ceramics—generally oxide—and other powders. The most popular method of sol-gel powder preparation involves the following steps: (a) sol preparation; (b) progress of network formation culminating in gelation, often by hydrolysis–condensation reactions involving alkoxides, but also by other means like ololation (hydroxy bridge) and oxolation (oxo bridge) condensation mechanisms and kinetics—the basic factors controlling gel formation include pH control, temperature, speed of mixing, and the condensation kinetics; (c) drying of gel monoliths sometimes at controlled humidity and temperature to obtain a desired microstructure; and (d) heat treatment. It is generally very easy to obtain stoichiometric ceramic powders with high homogeneity when using the sol-gel process since the precursors are usually mixed at an atomic level in solutions. Therefore, with doped ceria derived from the sol-gel process it is possible to achieve a higher grain interior conductivity than that derived from the solid-state reaction since the distribution of the dopant in the solid solution as derived with the sol-gel process is more uniform.

The $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) powder was synthesised using a combined citrate and Ethylenediaminetetraacetic acid (EDTA) complexing method. The preparation procedure of the BSCF material is shown in Figure 17. The necessary amount of $\text{Ba}(\text{NO}_3)_2$ was first dissolved in $\text{EDTA-NH}_3\cdot\text{H}_2\text{O}$ solution under heating and stirring, then the calculated amounts of $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ were added to the solution. After stirring for a certain period of time, a proper amount of citric acid was introduced. The molar ratios of EDTA acid: citric acid: total metal ions were controlled to be around 1:1.5:1. Precipitation occurred after the addition of citric acid. $\text{NH}_3\cdot\text{H}_2\text{O}$ was then added to adjust the pH value to around 6, and the solution became transparent. EDTA- NH_3 and citrate formed a buffering solution, so the pH value of the system successfully sustained around 6 during the whole process. With the evaporation of water, a dark purple gel was obtained. The gel was then heated at 250°C for about 24 hours to make a primary powder, followed by calcination at 800°C for 2 hours to obtain the powder with final composition and particle size of $0.2\text{ }\mu\text{m}$ - $0.5\text{ }\mu\text{m}$. To prepare the air electrode paste, the dried and hand-milled BSCF powder was milled with ink, with weight ratio of 1:1, for ~20 minutes to obtain a half viscous shiny and smooth mixture. This ink used for air electrode paste preparation is a commercial product from Nextech Materials, USA.

Figure 17 Flowchart for the preparation of BSCF powder

A X-ray diffraction (XRD) study for BSCF powder was carried out to identify the phase formation using Cu k_{α} radiation at a scanning speed of 0.02° per step on a Shimadzu X-ray diffractometer, at room temperature. The XRD pattern shown in Figure 18 illustrates that all the peaks are well indexed as a cubic perovskite structure and sharp lines reflect a well-developed crystallisation, which indicate that a single crystalline phase of BSCF oxide was successfully obtained after calcination.

Figure 18 XRD pattern of the BSCF powder after calcination at 800°C for 2 h

3.6.4. Full cell fabrication

The prepared fuel electrode substrate was half-sintered at 900°C to obtain a porous substrate. The surface of the half-sintered fuel electrode was then cleaned with a tissue paper introduced with isopropanol, followed by coating of the electrolyte suspension on the surface of the fuel electrode by spin-coating machine, normally for 8-10 times with about 20 minutes in between of each step, in order to allow for drying of the previous coating. Subsequently, GDC and SDC electrolytes coated on the fuel electrode substrate were sintered at 1500°C and 1400°C, respectively, for 3 hours. The desired thickness of the electrolyte is around 10 μm -20 μm to ensure that no gas leaks through the electrolyte in case there are pores in the electrolyte structure. The surface of the sintered electrolyte was cleaned with a tissue paper introduced with isopropanol. Then the BSCF ink in an 8 mm diameter circular shape was applied at the centre of the electrolyte. So the area of the air electrode was $\sim 0.5 \text{ cm}^2$. The entire cell was then calcined at 800°C for 2 hours. As the final stage, platinum paste was applied to cover the air electrode and to cover an equal area on the fuel electrode surface in a symmetric configuration followed by drying at 900°C for 30 minutes. A schematic of the cell arrangement is shown in Figure 19. A platinum mesh was cut to cover the platinum paste and provide tabs for attaching a current lead and a voltage lead to each

electrode surface. The platinum paste was also used to attach a platinum mesh current collector to both electrodes.

Figure 19 The schematic of the solid oxide cell

3.7. Cell characterisation and electrochemical study

3.7.1. Microstructural study

For BSCF to be the air electrode material, Ni-GDC/GDC/BSCF and Ni-SDC/SDC/BSCF SOFCs were fabricated. The surface of the electrolytes and cross section of the cells were inspected using field emission scanning electron microscopy (FESEM, JEOL, JSM 7600F and JSM 6340F). Figure 20 shows the FESEM image of the cross sections of single cells with (a) GDC and (b) SDC electrolytes. It clearly presents the porous microstructure of both air electrode and fuel electrode. Both BSCF air electrode and fuel electrode have porous microstructures to assure good gas diffusion (BSCF is more porous). Both GDC and SDC electrolytes exhibit good interfacial contacts with the fuel electrode and the air electrode and are dense. The thickness of GDC film sintered at 1500°C and BSCF air electrode is $\sim 7.5\ \mu\text{m}$ and $\sim 22.5\ \mu\text{m}$, respectively. In Figure 20 (b) the thickness of SDC film sintered at 1400°C and BSCF air electrode are $\sim 7.5\ \mu\text{m}$ and $\sim 18\ \mu\text{m}$, respectively. In the case of both cells with SDC and GDC electrolyte, there is no pin hole through the structure in the cross-section views, indicating that the fabrication process is satisfactory.

Figure 20 FESEM cross-section image of the single cell with (a) BSCF air electrode (top layer), GDC electrolyte (middle layer), Ni-GDC fuel electrode (down layer) and (b) BSCF air electrode (top layer), SDC electrolyte (middle layer), Ni-SDC fuel electrode (down layer)

3.7.2. Electrochemical study

The performance of SOFCs depends critically on the microstructure of each of the component layers, the composition of the materials used, and the resulting physical/chemical properties, such as permeability, electronic, and ionic conductivity, and catalytic activity. The microstructures of the materials are affected, in turn, by the processing methods used to fabricate them.

Normally there are two ways for evaluating the performance of the cell:

1. Impedance measurement of the cell
2. Polarisation study or voltage-current density (I-V) and power-current density (I-P) curves

A three-electrode arrangement was used for all the electrochemical measurements. Figure 21 shows a schematic diagram of the test cell configuration and electrical connection arrangement used to measure the electrical performance. Major components of the testing system include delivery and control elements (pressure regulators, mass flow controllers, and gas cylinders), gas supply, steam generation and monitoring elements (humidifier and humidity sensors), solid oxide button cells, temperature measurement, high temperature furnace, and electrochemical testing equipment (galvanostat/ potentiostat and impedance response analysers). In this study, a button cell was sealed to an alumina tube by a glass-ceramic bonding/ sealing

material. The glass-ceramic seal had to be dried overnight followed by curing during a slow rate heat up in order to form a gas tight sealing without any crack formation. After the seal curing process and before flowing H_2 to the hydrogen electrode, N_2 was purged to the system in order to check the sealing to be crack free, because the temperature was high and thus any hydrogen leakage might trigger the explosion.

Figure 21 Schematic of the test cell arrangement

In the characterisation of electrolytes, it was found that SDC was a better option than GDC. However, to complete this comparison, the performance of the full cells in which GDC and SDC were used as the electrolyte was also evaluated. To make the comparison easier, the results of the two cells are presented together.

3.7.2.1. Impedance study

Impedance measurement of electrolytes was characterised by “MultiStat” machine, using “MultiStat” software. Electrochemical performance of the air electrode was characterised by an electrochemical impedance spectroscopy technique (EIS) using Autolab data analyser with the frequency range of 0.1 Hz to 0.1 MHz and amplitude of 10 mV. The impedance data were collected in open circuit potential using Frequency Response Analyser (FRA) software. No equivalent circuit was used to extract the data from the EIS work. The ohmic resistance and cell impedance data were simply read out from the EIS curve achieved from the Autolab data analyser.

For getting the voltage-current density curve data, General Purpose Electrochemical System (GPES) Manager Software was used. During the experiment, humidified hydrogen (3% water vapour) was used as fuel gas with the flow rate of 50 mLmin⁻¹. The air electrode was exposed to static air.

Regarding the reproducibility of the samples, many samples were measured and the tests were repeated. However, the errors seen in the results of the same samples were not significant to influence the results used to study a cell's electrochemical performance. For example, in the EIS curves main intercepts which are used in the measurements did not change from cell to cell of a same category. Only some noises might have been seen in the curves which do not influence the measurements. This also applies to all the measurements in the subsequent chapters.

The impedance characteristics of Ni-GDC/GDC/BSCF and Ni-SDC/SDC/BSCF single cells at 500°C, 550°C and, 600°C under open-circuit condition are shown in Figure 22 (a) and Figure 22 (b), respectively. Each impedance spectra includes two overlapping arcs, which present the electrodes polarisation resistances indicating two rate-limiting processes for the electrode reaction. The low frequency arc increases significantly with the decrease of operating temperature and is dominant. In contrast, the arc related to higher frequencies increases relatively slower than the dominant arc. R_b , R_p and R_{total} are the ohmic resistances, the electrode polarisation resistance and the total cell resistance, respectively.

Figure 22 Impedance spectra under open-circuit condition for: (a) Ni-GDC/GDC/BSCF and (b) Ni-SDC/SDC/BSCF single cell, at: 500°C, 550°C and 600°C

3.7.2.2. Study on the performance of the cells

The voltages and the corresponding power densities are expressed in Figure 23 and Figure 24 as a function of current density for Ni-GDC/GDC/BSCF and Ni-SDC/SDC/BSCF single cells, respectively, measured with hydrogen and air at temperatures from 500°C to 600°C. Open-circuit voltages (OCVs) of 0.829 V, 0.817 V, and 0.792 V were recorded at 500°C, 550°C, and 600°C, respectively, for Ni-GDC/GDC/BSCF cell. As seen in Figure 23, the power density increases with increase in the operating temperature. With humidified hydrogen as fuel and air as oxidant, this cell generates maximum power densities of 0.368 W.cm⁻², 0.619 W.cm⁻² and, 0.790 W.cm⁻² at 500°C, 550°C, and 600°C, respectively. In the next figures of this chapter, for each studied term, the symbols of the I-V and I-P graphs have the same shape and to prevent duplication only one is brought in the legend.

Figure 23 I-V and I-P curves for Ni-GDC/GDC/BSCF single cell (fuel electrode side: H₂ flow rate: 50 standard cubic centimeters per minute (sccm); air electrode chamber: open air)

SOFC is a device operating with gases. A small alteration or fluctuation in the gas pressure would cause some data points deflecting from the normal trend during the electrochemical measurement (Figure 23, power density curve at 550°C). At higher temperatures, the cell performs better due to enhanced reaction activity. A better cell performance means a higher current density at a certain cell voltage, thus a higher power density. This explains the shift of the power density curve toward large current density at higher temperatures.

For Ni-SDC/SDC/BSCF cell, OCVs at 500°C, 550°C, and 600°C are recorded as 0.848 V, 0.815 V, and 0.797 V, respectively, given in Figure 24. The power density increases with increasing the operating temperature. With humidified hydrogen as fuel and air as oxidant, the Ni-SDC/SDC/BSCF cell generates maximum power densities of 0.398 W.cm⁻², 0.810 W.cm⁻² and, 1.098 W.cm⁻² at 500°C, 550°C, and 600°C, respectively (Figure 24).

Figure 24 I-V and I-P curves for Ni-SDC/SDC/BSCF single cell (fuel electrode side: H₂ flow rate: 50sccm; air electrode chamber: open air)

For easier comparison between the performances of the two cells, a summary of the results are presented in

Table 13. By comparing the performances of the two full cells, obviously, Ni-SDC/SDC/BSCF single cell exhibits a better performance than Ni-GDC/GDC/BSCF cell, which complies with the results of the conductivity tests done on GDC and SDC electrolytes.

Table 13 OCV and MPD of cells with SDC and GDC electrolytes (with same thickness of $\sim 7.5\mu\text{m}$) at different operating temperatures

Temperature (°C)	SDC		GDC	
	OCV (V)	MPD (W.cm ⁻²)	OCV (V)	MPD (W.cm ⁻²)
500	0.848	0.398	0.829	0.368
550	0.815	0.810	0.817	0.619
600	0.797	1.1	0.792	0.790

As seen in Figure 23 and Figure 24, the cell voltage versus current density measured at 600°C exhibits a downward bending curve at higher current densities, which is obviously different from the polarisation behaviour observed at temperatures below 600°C. This is typical diffusion polarisation behaviour that arises from a limited supply of reactants. To verify if hydrogen or air had indeed been insufficiently supplied, the effects of air and hydrogen flow rates on the polarisation behaviour of the cells were examined at 600°C (Figure 25, Figure 26, Figure 27 and, Figure 28).

Figure 25 Effect of H₂ flow rate on the cell performance of Ni-GDC/GDC/BSCF single cell (measured at 600°C, air electrode side: open air)

Figure 26 Effect of air flow rate on the cell performance of Ni-GDC/GDC/BSCF single cell (measured at 600°C, fuel electrode side: H_2 flow rate, 50sccm)

Figure 27 Effect of H_2 flow rate on the cell performance of Ni-SDC/SDC/BSCF single cell (measured at 600°C, air electrode side: open air)

Figure 28 Effect of air flow rate on the cell performance of Ni-SDC/SDC/BSCF single cell (measured at 600°C, fuel electrode side: H₂ flow rate, 50sccm)

The limiting current density increases with increase in the hydrogen flow rate but does not change noticeably with increase in the air flow rate. These characteristics demonstrate that the observed diffusion polarisation is due to hydrogen diffusion limitations at the fuel electrode. The microstructure of Ni-GDC and Ni-SDC fuel electrodes, shown in Figure 20 (a) and Figure 20 (b), respectively, reveals that, though with roughly good porosity, the relatively thick fuel electrode of ~0.75 mm (for both cells), which serves as the cell support in this study, is probably the cause of diffusion limitations. The diffusion polarisation caused by limited hydrogen supply can be overcome by adopting a reduction in the fuel electrode substrate thickness and/or by applying a double-layer fuel electrode structure with thin functional fuel electrode layer on top of an fuel electrode substrate with enhanced porosity. Hence, further improvement in fuel electrode porosity is essential in enhancing the overall performance of the cell. This study will be presented in the next chapter.

CHAPTER 4. YSZ-SDC double layer electrolyte for SOFCs and SOECs

4.1. Importance of a blocking layer in the electrolyte structure and its effect on the performance of the SOC

There is a potential for a bi-layer electrolyte to render high ionic conductivity without a remarkable sacrifice of open circuit voltage and lowering the operating temperature of the SOFC (Shen et al. 2013; Wachsman and Lee 2011). In addition, a thin layer of YSZ sandwiched between the fuel electrode and an Yttria Doped Ceria (YDC) electrolyte can protect the SDC from reduction and increase the open circuit potential of SOFCs (Yahiro et al. 1988; Cho et al. 2011). When the thickness ratio of YSZ to SDC decreases, the interfacial oxygen partial pressure increases linearly, which results in a reduction in the n-type conductivity of the SDC at the YSZ/SDC interface, an increase in the OCV, and a decrease in the electronic current penetration through the bi-layer electrolyte (Chan et al. 2003; Tsai and Barnett 1998). Chour *et al.* (1997), Tsai *et al.* (1997), Mehta *et al.* (1998), and Cho *et al.* (2011) fabricated such bi-layer electrolytes and studied the effect of thin YSZ layer on the blocking of electronic current and protection of the internal electrolyte.

4.2. Experimental work on cell fabrication

As concluded in the last chapter, the sample with 33% fuel electrode porosity had the highest performance among all others, so from this point onwards, all the samples were made with the Ni-YSZ fuel electrode that has the optimum porosity. The fuel electrode preparation was the same as described in the previous chapter.

For preparing the electrolyte suspension, a mixture of 0.1 g Triethanolamine (TEA), 0.1 g benzyl butyl phthalate (BBP), 0.1 g propylene glycol (PG), 0.1 g polyvinyl butyral (PVB) and 40 g isopropanol plus 2 g of SDC and 1g of YSZ commercial powder, were milled for 24 hours using the ball milling machine, for preparation of SDC and YSZ electrolyte suspension, respectively.

After half-sintering the fuel electrode, using the spin coating method, YSZ as the blocking layer, was coated on the fuel electrode surface using the YSZ suspension, followed by SDC coating using SDC suspension. After each layer of electrolyte spin coating, the wet surface was allowed to dry for about 15 minutes in the room temperature. To study the effect of the blocking layer and find out what is the optimum thickness for the YSZ blocking layer, the thickness of the SDC electrolyte was kept constant (16 layers), while only the number of YSZ layers changes (1-5 layers). These two layers of YSZ and SDC were co-sintered at 1400°C for 2 hours to obtain a very dense YSZ-SDC bi-layer electrolyte. The samples were round and about 24 mm in diameter and 1.1 mm in thickness before sintering. After co-sintering they became about 18 mm and 0.8 mm, respectively.

To improve the performance of the cell, a composite air electrode of BSCF-SDC (20 wt.% SDC and 80 wt.% BSCF) was chosen whose ink was painted at the centre of the electrolyte layer in an 8 mm circular shape followed by calcination at 800°C for 2 hours. This ink used for air electrode paste preparation is a commercial product from Nextech Materials, USA. The composite air electrode powder was prepared in the same way as Ni-YSZ fuel electrode powder. Finally, Pt paste as the current collector was applied onto the air electrode and fuel electrode surface, at the centre in an 8mm diameter circular shape, followed by drying at 900°C for 30 minutes.

The same three-electrode arrangement used in Chapter 3 and shown in Figure 21 was used for electrochemical measurements.

The high temperature electrolysis cell testing system was assembled according to the schematic diagram shown in Figure 21. H₂ was used as an inlet carrier gas to facilitate the flow of the steam and to maintain a reducing environment in the fuel electrode. Hydrogen flow rate was controlled by a precision mass flow controller. The water vapour partial pressure of the gas mixture inside the humidifier was determined by the temperature of the water bath in the bottom and steam at the top of the vessel. Therefore, the humidifier temperature was controlled by two independent temperature controllers, one was used to control the temperature of the water at the top of the vessel and the other was used to control the temperature of the water vapour at the bottom of the vessel. The humidity sensor was located downstream of the humidifier housed by a stainless steel assembly. In order to prevent condensation of water vapour

in the inlet humidity measurement assembly, the temperature of the humidity sensor housing was maintained at the same temperature as that of the top of the humidifier.

Impedance spectrum of electrolytes and electrochemical performance of the cell was characterised by an electrochemical impedance spectroscopy technique (EIS) using MultiStat machine with the frequency range of 0.1 Hz to 0.1 MHz and amplitude of 10 mV. The impedance spectra were measured at open circuit potential (OCP) using Frequency Response Analyser (FRA) Software and are presented in the SOFC results. For the SOEC, impedance spectra under 0.1 V bias was measured for the cells tested under feedstock with different humidity levels.

To acquire the cell polarisation data, General Purpose Electrochemical System (GPES) Manager Software were used. Polarisation curves were obtained over the temperature range of 650°C-800°C for Ni-YSZ/YSZ-SDC/SDC-BSCF, using humidified hydrogen (3% water vapour) as the fuel with the carrier gas flow rate of 50 standard cubic centimetres per minute (sccm). The air electrode was exposed to the ambient air.

4.3. Microstructural observation of the YSZ blocking layer thickness

FESEM micrographs of sample with no blocking layer and samples with 1-5 blocking layers of YSZ, after a number of trials, are presented in Figure 29 for comparison. As it can be seen in all samples the YSZ layer is uniform and the thickness of the YSZ blocking layer for 1, 2, 3, 4, and 5 layers is 1.5 μm , 2.5 μm , 3.5 μm , 3.8 μm , and 4.4 μm , respectively and the SDC thickness is about the same with an average thickness of $\sim 17.4 \mu\text{m}$. From these micrographs, no pin hole through the YSZ film is detected, but in order to avoid the exposure of SDC layer to the fuel, the YSZ blocking layer should also be crack-free. On the other hand, to minimise the electrolyte resistance, the YSZ layer should be as thin as possible. So only by studying the electrochemical performance of the cell, can it be confirmed which YSZ thickness is the optimal and crack-free blocking layer. In all the samples under study, it seems that the YSZ blocking films were adhered firmly to the porous fuel electrode substrate after co-sintering. The SDC layer was also highly dense and only a few isolated pores can be seen in the cross-section images. Apart from some micro-pores at the interface,

applying the co-sintering process, a perfect bonding is formed between the two electrolyte layers. The BSCF-SDC composite air electrode and Ni-YSZ fuel electrode display a porous structure as needed for the SOFC applications. It is clear that the electrolyte films remained dense and solid after the high temperature measurements and the adhesion between the adjacent layers was excellent with no crack formation at interfaces.

Figure 29 FESEM micrographs of the (a) Ni-YSZ/SDC/BSCF-SDC with no blocking layer, and Ni-YSZ/YSZ-SDC/BSCF-SDC with; (b) 1.5 μm , (c) 2.5 μm , (d) 3.5 μm , (e) 3.8 μm , and (f) 4.4 μm of YSZ film thickness (The scale bar shown for (a), (b), (c), and (f) is 10 μm , and for (d) and (e) is 1 μm .)

4.4. Study on the effect of YSZ film thickness as the blocking layer on the SOFC and SOEC Electrochemical performance

For further examination to find out which microstructure is crack-free to provide the electrical current leakage prevention in the SDC layer and at the same time the optimum thickness, the impedance measurement under OCV for SOFC and under 0.1 V bias with different water vapour amounts in the hydrogen for SOEC and also cell polarisation study were conducted over the temperature range of 650°C-800°C for both SOFC and SOEC. For all the samples, the fuel electrode was Ni-YSZ with 33% porosity, and the air electrode was composed of 80 wt.% BSFC and 20 wt.% SDC. For the SOFC, the fuel is humidified hydrogen (3% water vapour) with 50 sccm flow rate.

4.4.1. Study on the electrochemical performance of the SOFC as a function of electrolyte blocking layer thickness

The impedance spectra of the Ni-YSZ/SDC/BSCF-SDC cell and Ni-YSZ/YSZ-SDC/BSCF-SDC cell with YSZ blocking thickness of 1.5 μm , 2.5 μm , 3.5 μm , 3.8 μm , and 4.4 μm are shown in Figure 30, Figure 31, Figure 32, Figure 33, Figure 34, and Figure 35, respectively.

Figure 30 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with no blocking layer, over the temperature range of 650°C-800°C

Figure 31 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 1.5 μm YSZ blocking layer, over the temperature range of 650°C-800°C

Figure 32 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 2.5 μm YSZ blocking layer, over the temperature range of 650°C-800°C

Figure 33 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 3.5 μm YSZ blocking layer, over the temperature range of 650°C-800°C

Figure 34 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 3.8 μm YSZ blocking layer, over the temperature range of 650°C-800°C

Figure 35 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 4.4 μm YSZ blocking layer, over the temperature range of 650°C-800°C

Figure 36 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 1.5 μm -4.4 μm and without YSZ blocking layer, tested at 700°C

The impedance spectra shown in Figure 36 are for the samples with 1.5 μm -4.4 μm YSZ blocking layer in Ni-YSZ/YSZ-SDC/SDC-BSCF and Ni-YSZ/SDC/SDC-BSCF fuel cell with no YSZ blocking layer. The test was conducted at 700°C. The summary of the impedance measurement results is presented in Table 14.

Table 14 R_{Ω} & ASR of the Ni-YSZ/YSZ-SDC/SDC-BSCF fuel cell with 1.5 μm -4.4 μm and without YSZ blocking layer, tested over the temperature range of 650°C-800°C

	Temperature (°C)	650		700		750		800	
	R_{Ω} & ASR ($\Omega\cdot\text{cm}^2$)	R_{Ω}	ASR	R_{Ω}	ASR	R_{Ω}	ASR	R_{Ω}	ASR
YSZ blocking layer thickness (μm)	No blocking layer	0.288	0.355	0.223	0.343	0.142	0.313	0.071	0.264
	1.5 μm	0.323	0.443	0.242	0.393	0.157	0.349	0.091	0.326
	2.5 μm	0.348	0.558	0.253	0.536	0.159	0.362	0.098	0.331
	3.5 μm	0.376	0.599	0.269	0.556	0.160	0.364	0.102	0.335
	3.8 μm	0.380	0.599	0.270	0.557	0.164	0.369	0.103	0.335
	4.4 μm	0.381	0.604	0.271	0.557	0.164	0.373	0.103	0.336

Looking at the data given in Table 14, one can find out the relationship between the testing temperature and R_{Ω} and ASR at different blocking layer thickness. For all the samples in this study, with increase in the testing temperature the R_{Ω} and ASR decrease. Also an interesting trend in R_{Ω} and ASR values is observed at each testing temperature. With increase in the YSZ blocking layer thickness, R_{Ω} and ASR increase, because in an oxidising environment, any increase in bi-layer thickness will cause an increase in ohmic loss. Also the sample with no blocking layer or unsuccessful blocking layer has high internal electronic conductivity of the SDC film which leads to a lower R_{Ω} and ASR and it is also noticeable that the increase in the R_{Ω} and ASR value is so small after the effect of successful blocking layer kicks in at 3.5 μm YSZ thickness. So, only by studying the performance of the cell, it can be understood which thickness is optimum for the YSZ blocking layer.

The voltage-current density and power-current density curves of the Ni-YSZ/SDC/BSCF-SDC cell with no blocking layer and Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 1.5 μm , 2.5 μm , 3.5 μm , 3.8 μm , and 4.4 μm YSZ blocking layer, evaluated over the temperature range of 650°C-800°C are shown in Figure 37, Figure 38, Figure 39, Figure 40, Figure 41, and Figure 42, respectively. The hydrogen flow rate was set at 50 sccm for all the performance tests. The summary of the performance results is presented in Table 15.

Figure 37 I-V and I-P curves of the Ni-YSZ/SDC/BSCF-SDC fuel cell with no blocking layer, tested over the temperature range of 650°C-800°C

Figure 38 I-V and I-P curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 1.5 μm YSZ blocking layer tested over the temperature range of 650°C-800°C

Figure 39 I-V and I-P curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 2.5 μm YSZ blocking layer tested over the temperature range of 650°C-800°C

Figure 40 I-V and I-P curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 3.5 μm YSZ blocking layer tested over the temperature range of 650°C-800°C

Figure 41 I-V and I-P curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 3.8 μm YSZ blocking layer tested over the temperature range of 650°C-800°C

Figure 42 I-V and I-P curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 4.4 μm YSZ blocking layer tested over the temperature range of 650°C-800°C

Figure 43 I-V and I-P curves of Ni-YSZ/YSZ-SDC/SDC-BSCF fuel cell with 1.5 μm-4.4 μm and without YSZ blocking layer, tested at 700°C

Table 15 Current density at 0.5 V and MPD of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 1.5 μm -4.4 μm and without YSZ blocking layer, tested over the temperature range of 650°C-800°C

	Temperature (°C)	650		700		750		800	
	CD ($\text{A}\cdot\text{cm}^{-2}$) & MPD ($\text{W}\cdot\text{cm}^{-2}$)	CD at 0.5 V	MPD	CD at 0.5 V	MPD	CD at 0.5 V	MPD	CD at 0.5 V	MPD
YSZ blocking layer thickness (μm)	No blocking layer	1.002	0.55	1.240	0.709	1.648	1.08	2.091	1.37
	1.5 μm	0.880	0.44	1.179	0.593	1.63	0.82	2.055	1.28
	2.5 μm	0.716	0.36	1.000	0.53	1.456	0.81	2.049	1.16
	3.5 μm	1.454	0.726	1.711	0.856	2.417	1.22	2.798	1.48
	3.8 μm	1.377	0.69	1.634	0.835	2.201	1.206	2.697	1.46
	4.4 μm	1.228	0.61	1.535	0.77	2.182	1.09	2.641	1.39

As shown in the polarisation (I-V) curves of Figure 43, under low current densities, the curve is linear but at higher current densities an obvious concave-down curvature can be seen. This is due to the insufficient gas supply for the reaction which prevents the current to go any higher. This phenomenon is called limiting current behaviour and has been explained earlier.

From Table 15, at all testing temperatures, the sample with no blocking layer shows a higher performance than the samples with 1.5 μm and 2.5 μm YSZ blocking layer. This is because the additional blocking layer does not effectively block the electrons, instead it introduces additional ohmic loss to the cell, thus causing poorer performance compared with that without any blocking layer. The blocking of electrons take significant effect when the blocking layer is increased to 3.5 μm , giving the highest current density at 0.5 V as well as the maximum power density for all temperatures. Further increase in the thickness of YSZ layer will not have any effect on blocking of electron penetration but the additional ohmic resistance would induce poorer performance as reflected in the results presented in Table 15. Essentially, the sample with a blocking layer of 3.5 μm and tested at 700°C, where the full blocking effect has

kicked in, the MPD and OCV have shown obvious improvement from 0.709 W.cm^{-2} and 1.044 V for the sample without blocking layer to 0.856 W.cm^{-2} and 1.094 V for the sample with $3.5 \text{ }\mu\text{m}$ YSZ blocking layer, respectively (Figure 43). The decrease in the maximum power density from 0.856 W.cm^{-2} for the sample with $3.5 \text{ }\mu\text{m}$ YSZ blocking layer to 0.835 W.cm^{-2} and 0.77 W.cm^{-2} for the samples with $3.8 \text{ }\mu\text{m}$ and $4.4 \text{ }\mu\text{m}$ YSZ, respectively, is due to the increase in the thickness of the electrolyte, which increases the ohmic resistance of the cell. The same trend is observed in the current density at 0.5 V from 1.711 A.cm^{-2} for the sample with $3.5 \text{ }\mu\text{m}$ YSZ blocking layer to 1.634 A.cm^{-2} and 1.535 A.cm^{-2} for the samples with $3.8 \text{ }\mu\text{m}$ and $4.4 \text{ }\mu\text{m}$ YSZ, respectively (Figure 43). Also at any thickness of the YSZ blocking layer, a clear increase trend in the MPD and current at 0.5 V positional and decrease in OCV can be seen when the testing temperature increases from 650°C to 800°C .

From the polarisation measurement results, the following remarks can be concluded. First, the one and two layers of YSZ deposition by the spin coating of the YSZ suspension onto the main SDC electrolyte are not effective in blocking the internal electronic conduction, thus they serve no purpose to the SDC electrolyte. Second, the blocking layer thickness plays an important role in the OCVs and MPDs in all cells. Third, the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with $3.5 \text{ }\mu\text{m}$ YSZ blocking layer shows the highest performance among all the investigated cells and at all testing temperatures and is regarded as the optimum YSZ blocking layer thickness without any crack or pin-hole through the structure. The reason is that if the thickness of the YSZ thin film is enough it can suppress ceria reduction on the fuel electrode side, thus increases the generated power output more than the SDC single layer cell. This also indicates that the two YSZ and SDC electrolyte films and the Ni-YSZ fuel electrode substrate thermo-mechanically match well, although some references have reported a non-negligible difference in thermal expansion coefficient (TEC) between doped-ceria material and YSZ (Inoue et al. 1989; Kharton et al. 2004; Zhou et al. 2004). During the high-temperature co-sintering, the interfacial diffusion that happens between the SDC and YSZ films causes the formation of solid solutions at the interface of these two layers. This leads to observing a good match between the fuel electrode and electrolyte layers. In terms of thermal expansion behaviour, formation of solid solutions will create a functionally graded layer between the SDC and YSZ layers,

which would help to decrease the thermo-mechanical breakdown of the fuel cell with YSZ-SDC bi-layer electrolyte.

4.4.2. Study on the electrochemical performance of the SOEC as a function of electrolyte blocking layer thickness

The same investigations of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell were done in the electrolyser mode under the same 50 sccm hydrogen flow rate (as a carrier gas and to offer reducing atmosphere) and over the temperature range of 650°C-800°C. In addition, the effect of different amount of water vapour in the hydrogen presented in humidity level, on the performance of the SOEC was studied in detail.

The impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC cells without any blocking layer and with 1.5 μm , 2.5 μm , 3.5 μm , 3.8 μm , and 4.4 μm YSZ blocking layer thickness, as shown in Figure 44, Figure 45, Figure 46, Figure 47, Figure 48, and Figure 49 ,respectively, were measured under 0.1 V bias at different water vapour concentrations tested at 800°C. Figure 50 compares the impedance spectra of all samples at 50% of water vapour concentration in the hydrogen. The summary of the results at 800°C is presented in Table 16.

Figure 44 Impedance spectra of Ni-YSZ/SDC/BSCF-SDC electrolyser cell as a function of water vapour concentration, with no blocking layer, tested at 800°C

Figure 45 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell as a function of water vapour concentration, with 1.5 μm YSZ blocking layer, tested at 800°C

Figure 46 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell as a function of water vapour concentration, with 2.5 μm YSZ blocking layer, tested at 800°C

Figure 47 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell as a function of water vapour concentration, with 3.5 μm YSZ blocking layer, tested at 800°C

Figure 48 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell as a function of water vapour concentration, with 3.8 μm YSZ blocking layer, tested at 800°C

Figure 49 Impedance spectra of Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell as a function of water vapour concentration, with 4.4 μm YSZ blocking layer, tested at 800°C

Figure 50 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell as a function of YSZ blocking layer thickness, tested under 50% $\text{H}_2\text{O}/\text{H}_2$ fuel at 800°C

Table 16 R_{Ω} and ASR of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell for different YSZ blocking layer thickness and different water vapour concentration, tested at 800°C

	Water vapour concentration (%)	10		30		50		70	
	R_{Ω} & ASR ($\Omega \cdot \text{cm}^2$)	R_{Ω}	ASR	R_{Ω}	ASR	R_{Ω}	ASR	R_{Ω}	ASR
YSZ blocking layer thickness (μm)	No blocking layer	0.075	0.185	0.076	0.134	0.079	0.096	0.081	0.08
	1.5 μm	0.096	0.231	0.098	0.166	0.102	0.102	0.102	0.083
	2.5 μm	0.098	0.248	0.101	0.172	0.104	0.123	0.105	0.092
	3.5 μm	0.103	0.181	0.104	0.133	0.104	0.1	0.105	0.09
	3.8 μm	0.103	0.182	0.104	0.134	0.104	0.101	0.105	0.091
	4.4 μm	0.103	0.182	0.104	0.134	0.105	0.1	0.105	0.091

As shown in Figure 50, for the sample with no blocking layer and 1.5 μm and 2.5 μm , the impedance spectra are typically characterised by a large semicircle at low frequencies and a small semicircle at high frequencies, indicating that there are at least two electrode processes during the high temperature steam electrolysis. The sample with no blocking layer shows a significantly smaller R_{Ω} and ASR as compared with the samples with blocking layer because of additional ohmic resistance brought by the YSZ layers.

Data presented in Table 16 reveal that with increase in the water vapour concentration in the hydrogen, the ASR value decreases, hence more hydrogen is produced through the electrolysis. Meanwhile, no big change in R_{Ω} is observed when the water vapour amount of the hydrogen increases because the operating temperature was kept constant (800°C). Therefore, in general when the water vapour concentration increases, for all the samples it is observed that the R_{Ω} increases while ASR decreases.

At each humidity level with increase in the YSZ blocking layer thickness, R_{Ω} increases, but no specific trend is observed in ASR values. The sample with no

blocking layer exhibits the lowest ASR at all humidity percentages in compare with rest of the samples. The reason is that the sample with no blocking layer or unsuccessful blocking layer has a high internal electronic conduction of the SDC film which leads to a lower R_{Ω} and ASR. It can also be seen that at lower water vapour concentration percentages (10% and 30%) the samples with successful blocking layer (according to SOFC results, 3.5 μm , 3.8 μm , and 4.4 μm) show lower ASR value than the samples with unsuccessful blocking layer (1.5 μm and 2.5 μm) and at higher water vapour concentration percentages (50% and 70%) the difference in ASR values of all samples is so small. Although in any of these two sets of successful and unsuccessful samples, the increase trend of ASR with increasing the electrolyte layer thickness can be seen, but the change in both R_{Ω} and ASR is not significant after the blocking effect kicks in for the sample with 3.5 μm YSZ layer and the impedance spectra for the samples with 3.8 μm , and 4.4 μm YSZ layer are almost overlapped (Figure 50). Therefore, once the blocking layer performs, the change in ASR will not be distinctive.

To confirm that the 3.5 μm is the optimum thickness for the YSZ as the blocking layer in SOFC also true for SOEC, the electrochemical study is continued with evaluating the performance of the BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell with the corresponding electrolytes over the temperature range of 650°C-800°C, with and without blocking layer and also under different humidity levels at 800°C.

The voltage-current density and power-current density curves of the Ni-YSZ/SDC/BSCF-SDC cell with no blocking layer and Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 1.5 μm , 2.5 μm , 3.5 μm , 3.8 μm , and 4.4 μm YSZ blocking layer, tested over the temperature range of 650°C-800°C and under 3% $\text{H}_2\text{O}/\text{H}_2$ composition, are shown in Figure 51, Figure 52, Figure 53, Figure 54, Figure 55, and, Figure 56 respectively. The summary of the performance results is presented in Table 17.

Figure 51 I-V curves of the Ni-YSZ/SDC/BSCF-SDC cell with no blocking layer tested over the temperature range of 650°C-800°C

Figure 52 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 1.5 μm YSZ blocking layer tested over the temperature range of 650°C-800°C

Figure 53 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 2.5 μm YSZ blocking layer tested over the temperature range of 650°C-800°C

Figure 54 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 3.5 μm YSZ blocking layer tested over the temperature range of 650°C-800°C

Figure 55 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 3.8 μm YSZ blocking layer tested over the temperature range of 650°C-800°C

Figure 56 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 4.4 μm YSZ blocking layer tested over the temperature range of 650°C-800°C

Negative current densities demonstrate electrons consumption per unit time per unit geometric area and cell potential values at zero current density correspond to OCV. As presented in Table 17, with increase in the thickness of the YSZ blocking layer, the current density at 1.3 V decreases, i.e., for the sample tested at 700°C, the current density at 1.3 V drops from 0.326 A.cm⁻² for the sample without any blocking layer to 0.185 A.cm⁻² for the sample with 4.4 µm YSZ blocking layer. The higher current density of the samples with no or unsuccessful blocking layer is due to internal electronic conductivity of SDC, while lower current density of the samples with successful blocking layer is due to blocking effect of the YSZ layer which blocks the internal electronic conduction of the SDC film and hence, shows a decrease in the current density value. At lower operating temperature (650°C) the OCV for the samples with successful blocking layer is higher than the OCV of the samples with no or unsuccessful blocking layer. With increasing the operating temperature to 700°C and 750°C it can be seen that the OCV of the sample with no blocking layer is slightly higher than the OCV of the sample with 4.4 µm YSZ blocking layer which with further increase in the operating temperature (800°C) it becomes slightly higher than the OCV of the sample with 3.8 µm YSZ blocking layer. However in both sets of the samples with no or unsuccessful blocking layer and samples with successful blocking layer the OCV decreases with increasing the electrolyte thickness. For example, for the sample tested at 700°C, the OCV decreases from 1.044 V to 1.010 V and from 1.094 V to 1.042 V for the samples with no or unsuccessful blocking layer and the samples with 3.5 µm-4.4 µm YSZ blocking layer, respectively. It is also noticeable that the increase in the testing temperature does not show a big difference in the performance, because the amount of water vapour in the pure hydrogen fuel is only 3% which is not enough for the electrolysis reaction at high current density, but in general with increase in the testing temperature from 650°C to 800°C, the current density at 1.3 V increases while the OCV decreases. This trend is observed for all the investigated samples in this study.

Table 17 OCV and Current density at 1.3 V for the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with different YSZ blocking layer thickness, with 50% of water vapour in the hydrogen and tested over the temperature range of 650°C-800°C

	Temperature (°C)	650		700		750		800	
	CD (A.cm ⁻²) & OCV (V)	CD at 1.3 V	OCV	CD at 1.3 V	OCV	CD at 1.3 V	OCV	CD at 1.3 V	OCV
YSZ blocking layer thickness (µm)	No blocking layer	0.260	1.051	0.326	1.044	0.399	1.034	0.461	1.03
	1.5 µm	0.210	1.045	0.261	1.032	0.342	1.016	0.398	0.998
	2.5 µm	0.192	1.021	0.246	1.010	0.323	0.996	0.387	0.975
	3.5 µm	0.179	1.116	0.230	1.094	0.312	1.076	0.377	1.057
	3.8 µm	0.160	1.079	0.206	1.070	0.290	1.060	0.350	1.027
	4.4 µm	0.149	1.057	0.185	1.042	0.270	1.026	0.320	1.010

To complete the study of the effect of humidity level on the performance of the Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell with the corresponding electrolytes (no blocking and the 5 different blocking layers), 10%, 30%, 50%, and 70% humidity was applied to the hydrogen fed into the Ni-YSZ side, which their I-V curves shown in Figure 57, Figure 58, Figure 59, Figure 60, Figure 61, and Figure 62, tested at 800°C. The summary of the results is presented in Table 18.

It can be seen that at low humidity levels (10% and 30%), the I-V curve shows an obvious concave-up curvature at high current density ends. This happens due to the gas flow supply problem, which with increase in the fuel humidity level and enough hydrogen supply, the curvature changes to a linear curve.

Figure 57 I-V curves of the Ni-YSZ/SDC/BSCF-SDC cell as a function of water vapour concentration, with no blocking layer, tested at 800°C

Figure 58 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 1.5 µm YSZ blocking layer, tested at 800°C

Figure 59 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 2.5 μm YSZ blocking layer, tested at 800°C

Figure 60 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 3.5 μm YSZ blocking layer, tested at 800°C

Figure 61 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 3.8 μm YSZ blocking layer, tested at 800°C

Figure 62 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 4.4 μm YSZ blocking layer, tested at 800°C

Table 18 Current density at 1.3 V for the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with different YSZ blocking layer thickness, as a function of water vapour concentration, tested at 800°C

	Water vapour concentration (%)	10	30	50	70
		Current density (A.cm⁻²) at 1.3 V			
YSZ blocking layer thickness (μm)	No blocking layer	0.517	0.599	0.689	0.763
	1.5 μm	0.498	0.574	0.646	0.706
	2.5 μm	0.472	0.555	0.618	0.684
	3.5 μm	0.418	0.492	0.582	0.653
	3.8 μm	0.447	0.488	0.581	0.651
	4.4 μm	0.416	0.517	0.651	0.789

With increase in the humidity level the current density at 1.3 V increases and the OCV decreases. For each humidity percentage, with increase in the blocking layer thickness, obvious trend is observed, i.e., when effective blocking kicks in, the current density would increase which means that more hydrogen is produced through the electrolysis. Hence, the requirements in electrons blocking in SOEC and SOFC mode of operation are quite different. When “forced” current is applied in the SOEC mode, more stringent requirement in electrons blocking is needed. It is also observed that at low humidity level, less blocking layer is needed as compared with those with high humidity levels. To fully understand the effect of electrons blocking relative to bare SDC electrolyte, Faradic efficiency has to be determined, which can be accomplished by combined polarisation measurement and gas composition (GC) measurement using the GC. However, the latter is not within the scope of this PhD study.

Detailed investigations confirmed that the YSZ thin film has served as an effective blocking layer to prevent electrical current leakage in the SDC layer and also provides chemical, mechanical, and structural integrity in the cell, which leads to the overall enhanced performance. Based on the above microstructural, electrochemical, and

power measurement results, it is obvious that an appropriate bi-layer electrolyte is essential for the optimisation of the power density characteristic and electrolyte stability, i.e., the bi-layer electrolyte structure with an appropriate YSZ thickness can provide the chemical, mechanical, and structural stability of the YSZ-SDC electrolyte in single cells.

CHAPTER 5. Optimum amount of porosity in Ni-YSZ as the fuel electrode in SOFCs and SOECs

5.1. Importance of porosity amount in fuel electrode structure

Among all the components of SOC, the fuel electrode plays an important role in the oxidation of fuel to produce electrons (SOFC mode) and reduction of H_2O and CO_2 to produce H_2 and CO (SOEC mode) (Kim et al. 2008). It acts as the main site for the reaction products removal through the whole fuel electrode to avoid concentration polarisation as well as provide essential electrical conductivity to decrease ohmic polarisation (Cho and Choi 2008). The SOFC and SOEC fuel electrode needs long triple phase boundaries (TPBs) and adequate gas diffusion for the quick transport of both fuel and product gases. Very much attention is paid to the pore former's effect on the TPB area which produces additional porosity. However, the area where gas diffusion passes is especially needed and would be different from the anodic and cathodic area appropriate for electrochemical reaction. Then, the porous structures of fuel electrodes have been proposed to fulfil the anodic and cathodic functions of SOFC and SOEC, respectively, for further improvement of the performance of the cells (Jono et al. 2007). Indeed, not only the porosity but also sintering shrinkage caused by difference in thermal expansion coefficients (TEC) of fuel electrode and electrolyte are important and effective to the overall performance of an fuel electrode-supported SOFC. If the sintering shrinkage and difference between the TECs of the fuel electrode and electrolyte film are close to each other, the stress between them will decrease. This intensive stress may produce cracks in the electrolyte and distort the fuel cell which leads to a decrease in the performance of the cell (Bao et al. 2005a). When additional pores are present in the structure of the composite, the metal can expand into the pores, and lower the TEC of the composite (Clemmer and Corbin 2004).

As the fuel electrode material in the fuel cell and in the electrolyser cell is the same, to avoid duplication and make the descriptions easier, we will mention the fuel electrode in SOFC only, but the results of both SOFC and SOEC will be presented separately.

The most commonly used fuel electrode material for SOFCs is nickel–yttria stabilised zirconia (Ni/YSZ) cermet (Kim 1999; Haslam et al. 2005; Sanson et al. 2008; Talebi et al. 2010; Bao et al. 2005b). In the Ni-YSZ composite, Ni plays the catalyst role for the hydrogen oxidation, while YSZ provides an extended reaction zone with the porous ceramic network created. Even if the ratios of NiO and YSZ are kept constant in the fuel electrode samples, the TEC is still varied with the amount of pore formers. It shows that not only the size of the pore, but also the interfaces between NiO and YSZ particles are influenced by the pore former (Hu et al. 2008).

The gas permeability, the electrical conductivity and therefore cell performance are highly dependent on the microstructure of the supporting fuel electrode. The network of the porous fuel electrode plays two roles: providing 1) the mechanical strength of the entire cell, 2) a facile gas flow to and from the electrolyte (Sumi et al. 2013). On the other hand, the Ni particles to enhance the fuel electrode catalytic activity must form a well-distributed and homogenous matrix.

The porosity, distribution of phases and particle size affect the cell performance significantly (Andersen et al. 2011; He et al. 2009; Yoon et al. 2007). Therefore, optimisation of the microstructure of the cell components is essential in order to achieve the optimum fuel cell performance. Although the porosity of the Ni-YSZ fuel electrode increases by in-situ reduction of NiO available in the primary fuel electrode material, the final value of the fuel electrode porosity of the cell with Ni-YSZ structure is not high enough to provide an easy flow of the gases during the cell operation (Qiang et al. 2009; Fu et al. 2012). Hence, adding a pore former enhances the gas accessibility to the fuel electrode active three-phase boundary (Fu et al. 2012; Liang et al. 2012; Liu et al. 2010a).

In this chapter, the effect of the amount of graphite used as the pore former in the microstructure of the fuel electrode on the cell performance of the SOFC and SOEC is investigated. Electrochemical and spectroscopic tests are carried out to establish the correlation between microstructure and performance.

5.2. Experimental work

5.2.1. Fuel electrode preparation

For the preparation of the fuel electrode, nickel oxide powder (NiO) was mixed with YSZ powder with a weight ratio of 60:40 for NiO and YSZ powders. This mixture was ball milled in isopropanol for 24 hours. The suspension was then dried on the hot plate for ~1 hour to obtain the NiO-YSZ fuel electrode powder. This powder was then hand-ground in an agate mortar for at least 20 minutes. To study the effect of different amounts of graphite as the pore former and to determine which one is the optimum amount of pore former, samples with 5 wt%, 7 wt%, 10 wt% and sample with no additional pore former were fabricated. The graphite powder had the purity of 99% and the particle size of <20 μm . Small amounts of isopropanol were added to achieve a better mixture of graphite powder with the fuel electrode powder. The mixture must be ground until the two powders are fully mixed. After drying, using the die-pressing machine, this powder was pressed into a desired shape to form the fuel electrode substrate. The samples were round and ~24 mm in diameter and ~1.1 mm in thickness before sintering, which after co-sintering with the electrolyte, they became ~18 mm and ~0.8 mm, respectively.

5.2.2. Full cell preparation

For further improvement of the cell performance, a double-layer, YSZ-SDC, electrolyte and a composite air electrode, BSCF-SDC, are used in preparation of the cell. As described in the previous chapter, a thin layer of YSZ was added to the main electrolyte, SDC, to perform as a blocking layer. The composite air electrode contained 20 wt.% SDC and 80 wt.% BSCF material and was prepared with the same way as NiO-YSZ fuel electrode powder. The composite air electrode ink (commercial product from Nextech Materials, USA) was painted at the centre of the electrolyte layer in an 8 mm circular shape, so the area of the air electrode is ~0.5 cm^2 , followed by calcination at 800°C for 2 hours. As the final stage, Pt paste as the current collector was applied on the air electrode and fuel electrode surface, at the centre in an 8 mm diameter circular shape, followed by drying at 900°C for 30 minutes.

5.2.3. Porosity measurement, characterisation and impedance study

5.2.3.1. *Fuel electrode porosity measurement*

Fuel electrode porosity was analysed using Image-Pro 6.3 software, which is automatic image analysis software. This software automatically calculates the percentage of the porosity of the material, using the optical microscope image connected to the system with a specific resolution. The image analysis software marks the pores (dark spots) on the image and calculates the overall area of the pores, then the fuel electrode porosity is determined by the pore area divided by the image area. The porosity values obtained with this approach represent a 2D porosity. However, if the pores are distributed uniformly in the fuel electrode substrate or if the sample is very thin, a 2D porosity can be used to represent a 3D one. Figure 63 compares the microstructure of the fuel electrodes with different amounts of graphite as the pore former. The results are presented in Table 19. By adding 0 wt.%, 5 wt.%, 7 wt.%, and 10 wt.% of graphite to the fuel electrode material, 18%, 23%, 33%, and 40% porosity were achieved in the Ni-YSZ fuel electrode structure, respectively. The increase in porosity of the fuel electrode material is a result of the added pore former to the fuel electrode during fabrication.

In order to perform the microstructural and electrochemical studies of the cells based on different fuel electrode porosity percentages reasonable, the double-layer electrolyte thicknesses and air electrode compositions were kept the same for all the samples.

Figure 63 The microstructure of the fuel electrodes with different amounts (a) 0%, (b) 5%, (c) 7%, and (d) 10% of graphite as the pore former in the Ni-YSZ/YSZ-SDC/BSCF-SDC cell

Table 19 The porosity of fuel electrode samples with different pore former concentrations after NiO reduction

Pore former concentration (wt. %)	0	5	7	10
Porosity (%)	18	23	33	40

5.2.3.2. Study of the microstructure

The cross section of the cells were inspected using field emission scanning electron microscopy (FESEM, JEOL, JSM 7600F). Figure 64 (a), 64 (b), 64(c), and 64(d) show the FESEM cross-section images of the single cells with 18%, 23%, 33% and, 40% fuel electrode porosity in Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell, respectively.

Figure 64 FESEM cross-section images of the single cells with (a) 18%, (b) 23%, (c) 33% and, (d) 40%, fuel electrode porosity in the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell

By inspection, with increasing the pore former amount, the porosity percentage increases, but the interesting part is in Figure 64 (d), which is the sample with 40% fuel electrode porosity. As it can be seen, due to high porosity, the pores in the fuel electrode substrate are highly connected with each other, forming open pores and inducing cracks in the fuel electrode structure, which leads to a lower mechanical strength of the fuel electrode and hence the entire cell. So, from the microstructure point of view, adding 10 wt.% of graphite to the fuel electrode material is over the optimum amount, however this needs to be confirmed with the electrochemical study of the cells and also to find out what is the optimum amount of pore former for the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell.

5.2.3.3. *Study on the effect of fuel electrode porosity on the electrochemical performance of the SOFC and SOEC*

Microstructure of the fuel electrode has a major effect on the performance of fuel electrode supported SOFCs and SOECs. Low polarisation, high electrical conductivity

and gas permeability are the indispensable features of fuel electrodes to achieve high power densities (Sarıkaya et al. 2012). The desired properties of the fuel electrodes were obtained by modifying their microstructural development using pyrolyzable pore former particles such as graphite, without introducing any functional layers and compositional modifications.

The same three-electrode arrangement cell testing system and procedure as described in Chapter 4 were used.

5.2.3.3.1. Study on the electrochemical performance of the SOFC as a function of fuel electrode porosity

Figure 65, Figure 66, Figure 67, and Figure 68 show the impedance spectra of samples with 18%, 23%, 33%, and 40% porosity in the fuel electrode structure, respectively. The summary of the results are presented in Table 20. Due to the increase in porosity, the reduction rate of the fuel electrode should be increased. Larger amounts of added porosity should reasonably lead to more hydrogen gas diffusion into the microstructure and for diffusion of the water vapour reaction product from the fuel electrode. In the fuel cell operation, greater diffusion supplies for easier access to and from the active TPB areas where the reactions occur and therefore should reduce polarisation because of gas diffusion resistance.

Figure 65 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 18% fuel electrode porosity (No addition of the pore former), tested over the temperature range of 650°C-800°C

Figure 66 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 23% fuel electrode porosity (5 wt.% of the pore former), tested over the temperature range of 650°C-800°C

Figure 67 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 33% fuel electrode porosity (7 wt.% of pore former), tested over the temperature range of 650°C-800°C

Figure 68 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 40% fuel electrode porosity (10 wt.% of pore former) tested over the temperature range of 650°C-800°C

Table 20 R_{Ω} and ASR of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with different fuel electrode porosities tested over the temperature range of 650°C-800°C

	Temperature (°C)	650		700		750		800	
	R_{Ω} & ASR ($\Omega \cdot \text{cm}^2$)	R_{Ω}	ASR	R_{Ω}	ASR	R_{Ω}	ASR	R_{Ω}	ASR
Fuel electrode porosity percentage (%)	18	0.920	2.881	0.761	1.506	0.488	1.491	0.24	1.093
	23	0.895	1.166	0.500	0.993	0.321	0.782	0.196	0.692
	33	0.383	0.605	0.269	0.559	0.160	0.362	0.103	0.36
	40	0.660	1.095	0.415	0.639	0.232	0.417	0.131	0.349

From Table 20 one can find that in all samples, with increase in the testing temperature, R_{Ω} and ASR decrease, which is a reasonable trend. To see the effect of fuel electrode porosity, looking at any of the testing temperatures, it is obvious that with increase in the fuel electrode porosity, R_{Ω} and ASR decrease, but for the sample with 33% porosity the R_{Ω} and ASR are the lowest (Figure 69), which are in good agreement with the observations in FESEM images seen in Figure 64. So, in the sample with 40% porosity, increase in ohmic resistance is likely due to the cracks that occur in the microstructure of the sample. Also, the drop in the resistance at low frequencies with the increase in the temperature is attributed to the smaller impedance contributions at lower frequency which are thermally activated. Consequently, the number of the TPB sites is greatly increased for the sample with 33% fuel electrode porosity, resulting in a decrease in the cell ASR. For example for the sample tested at 700°C, the low to high ASR values are 0.559 $\Omega \cdot \text{cm}^2$, 0.639 $\Omega \cdot \text{cm}^2$, 0.993 $\Omega \cdot \text{cm}^2$, and 1.506 $\Omega \cdot \text{cm}^2$ for the samples with 33%, 40%, 23%, and 18% fuel electrode porosity, respectively (Figure 69). By testing the performances of these cells in both fuel cell and electrolyser mode, it would be easier to find out which sample has the optimum amount of fuel electrode porosity.

Figure 69 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell as a function of fuel electrode porosity, tested at 700°C

The voltage-current density and power-current density curves of the cells fabricated with the corresponding fuel electrodes and tested over the temperature range of 650°C-800°C are presented in Figure 70, Figure 71, Figure 72, and, Figure 73. To prevent duplication, only the I-V and I-P curves of the test done at 700°C are presented (Figure 74). The summary of results including the current density of each sample at 0.5 V and MPD of each cell are shown in Table 21.

Figure 70 I-V and I-P curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 18% fuel electrode porosity tested over the temperature range of 650°C-800°C

Figure 71 I-V and I-P curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 23% fuel electrode porosity tested over the temperature range of 650°C-800°C

Figure 72 I-V and I-P curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 33% fuel electrode porosity tested over the temperature range of 650°C-800°C

Figure 73 I-V and I-P curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with 40% fuel electrode porosity tested over the temperature range of 650°C-800°C

Figure 74 I-V and I-P curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell as a function of fuel electrode porosity, tested at 700°C

Table 21 Current density at 0.5 V and MPD of the Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cell with different fuel electrode porosities, tested over the temperature range of 650°C-800°C

	Temperature (°C)	650		700		750		800	
	CD (A.cm ⁻²) & MPD (W.cm ⁻²)	CD at 0.5 V	MPD	CD at 0.5 V	MPD	CD at 0.5 V	MPD	CD at 0.5 V	MPD
Fuel electrode porosity percentage (%)	18	0.99	0.49	1.35	0.69	1.88	1.03	2.10	1.20
	23	1.25	0.62	1.54	0.77	2.29	1.10	2.65	1.33
	33	1.46	0.73	1.78	0.89	2.34	1.22	2.81	1.48
	40	1.40	0.70	1.71	0.86	2.35	1.18	2.80	1.41

As the fuel electrode is relatively thick and hydrogen gas is diffusing into the electrode at the same time that the reaction product (water vapour) is diffusing out of the electrode, gas diffusion can be an issue. This is referred to as counter diffusion of hydrogen gas and water vapour. As shown in I-V curves, under low current densities, the curve is linear but at higher current densities an obvious concave-down curvature can be seen. This is due to the insufficient gas supply for the reaction which prevents the current to go any higher. This behaviour is called limiting current behaviour, which is due to the concentration polarisation and is more critical in the case of cells with very low porosity which leads to higher gas diffusion resistance. For the samples with 18%, and 23% porosity this obvious concave-down curvature at high current density ends is observed while, in the case of the cells with 33% and 40% porosity fuel electrode, it is almost linear. In fact, the performance of the cell with low pore former concentration is limited by gas transport at high current densities. The cell with 33% fuel electrode porosity presents the highest maximum power density among all the investigated cells at all the testing temperatures.

As shown in Figure 74 and presented in Table 21, with increase in the fuel electrode porosity, current density (CD) at 0.5 V and MPD increase. This is due to higher fuel diffusion through the pores, but increasing the fuel electrode porosity beyond 33%

shows a drop in the performance of the cell. For example at 700°C the cell with 33% fuel electrode porosity achieves the MPD of 0.891 W.cm⁻² which is higher than 0.86 W.cm⁻², 0.77 W.cm⁻², and 0.69 W.cm⁻² for the samples with 40%, 23% and 18% fuel electrode porosity, respectively. With creating excessive porosity, i.e., more than 33%, by adding more pore former, excessive pores would form thus inducing ohmic loss instead. So, the overall conclusion is 33% fuel electrode porosity is the optimum amount of fuel electrode porosity and shows a desired performance among all the Ni-YSZ/YSZ-SDC/BSCF-SDC solid oxide fuel cells. The results are in a good agreement with both microstructural and impedance study of the cells.

5.2.3.3.2. Study on the electrochemical performance of the SOEC as a function of fuel electrode porosity

To study the effect of humidity difference in the fuel gas, impedance measurement was done for the Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell, under 0.1 V bias. The relative humidity applied to the hydrogen fuel was 10%, 30%, 50%, and 70% (volume percent) and the testing temperature was 800°C and the corresponding impedance spectra are shown in Figure 75, Figure 76, Figure 77, and Figure 78, respectively. Humidified hydrogen (3% water vapour) was used as the fuel applied with 50 sccm flow rate. The summary of the results is presented in Table 22.

Figure 75 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 18% fuel electrode porosity, tested at 800°C

Figure 76 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 23% fuel electrode porosity, tested at 800°C

Figure 77 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 33% fuel electrode porosity, tested at 800°C

Figure 78 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 40% fuel electrode porosity, tested at 800°C

Table 22 R_{Ω} and ASR of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with different fuel electrode porosities and different water vapour concentrations, tested at 800°C

	Water vapour concentration (%)	10		30		50		70	
	R_{Ω} & ASR ($\Omega \cdot \text{cm}^2$)	R_{Ω}	ASR	R_{Ω}	ASR	R_{Ω}	ASR	R_{Ω}	ASR
Fuel electrode porosity percentage (%)	18	0.241	0.777	0.250	0.549	0.254	0.399	0.260	0.234
	23	0.197	0.589	0.197	0.536	0.197	0.224	0.197	0.155
	33	0.103	0.208	0.104	0.136	0.104	0.109	0.105	0.096
	40	0.131	0.286	0.131	0.197	0.132	0.159	0.132	0.133

Looking at any of the water vapour concentrations, for the Ni-YSZ/YSZ-SDC/BSCF-SDC SOEC with increase in the fuel electrode porosity, a similar decreasing trend in R_{Ω} and ASR values seen in SOFC is observed. Also for the sample with 33% fuel electrode porosity, the R_{Ω} and ASR are the lowest among all the investigated samples. To prevent duplication in analysis only the impedance spectra of the test done under 50% $\text{H}_2\text{O}/\text{H}_2$ fuel are presented (Figure 79). The results are in good agreement with the observation in FESEM images shown in Figure 64. It is obvious that for certain fuel electrode porosity, with increase in the humidity, R_{Ω} is almost the same for all the samples while ASR decreases.

Figure 79 Impedance spectra of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of fuel electrode porosity, tested under 50% $\text{H}_2\text{O}/\text{H}_2$ fuel at 800°C

The voltage-current density and power-current density curves of the cells fabricated with the corresponding fuel electrodes and tested over the temperature range of 650°C - 800°C are presented in Figure 80, Figure 81, Figure 82, and Figure 83. Humidified hydrogen with 3% water vapour was used as fuel with flow rate of 50 sccm. For the samples with 18%, and 23% porosity, an obvious concave-up curvature at high current density ends is observed for all testing temperatures, while in the case of the cell with 33% and 40% fuel electrode porosity, they are very close to linear at low testing temperatures and have a slight concave-up curvature at high testing temperatures. This behaviour is due to the concentration polarisation, which is more critical in the case of cells with very low porosity. In fact, the performance of the cell with low porosity is limited by gas transport at high current densities. To prevent duplication, only the I-V curves of the test done at 700°C are presented (Figure 84). The summary of results including the current density of each sample at 1.3 V is shown in Table 21.

Figure 80 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 18% fuel electrode porosity tested over the temperature range of 650°C-800°C

Figure 81 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 23% fuel electrode porosity tested over the temperature range of 650°C-800°C

Figure 82 I-V curves of Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 33% fuel electrode porosity tested over the temperature range of 650°C-800°C

Figure 83 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 40% fuel electrode porosity tested over the temperature range of 650°C-800°C

Negative current densities demonstrate power consumption and cell potential values at zero current density correspond to OCV. As shown in Figure 84 and presented in

Table 23, with increase in the fuel electrode porosity, the current density at 1.3 V increases. This is due to higher hydrogen diffusion through the pores. Even though higher porosity would suggest greater gas diffusion within the fuel electrode, with further increase in the fuel electrode porosity, a drop in the performance of the cell is observed. This occurred in the case of the fuel electrode with 10 wt% of graphite used as a pore former. In this case, not only the triple phase boundaries density and so the performance decreases, but also the mechanical strength of the cell suffers. So, the overall conclusion is that the sample with 33% fuel electrode porosity which shows the highest performance among all the investigated cells has the optimum fuel electrode porosity for the Ni-YSZ/YSZ-SDC/BSCF-SDC solid oxide electrolyser cell. These results are in a good agreement with both microstructural and impedance study of the cells. It is also noted that the increase in the testing temperature does not show significant effect on the performance, because there is only 3% water vapour in the fuel which is not enough for the electrolysis reaction.

Figure 84 I-V curves of Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of fuel electrode porosity, tested at 700°C

Table 23 Current density at 1.3 V for the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with different fuel electrode porosities tested over the temperature range of 650°C-800°C

	Temperature (°C)	650	700	750	800
	Current density (A.cm ⁻²) at 1.3 V				
Fuel electrode porosity percentage (%)	18	0.088	0.094	0.112	0.136
	23	0.119	0.128	0.142	0.169
	33	0.180	0.230	0.310	0.377
	40	0.170	0.218	0.300	0.354

To complete the study of the effect of water vapour on the performance of the Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell with the corresponding fuel electrodes, 10%, 30%, 50%, and 70% humidity was applied to the hydrogen fed into the Ni-YSZ side, and their corresponding I-V curves at 800°C are shown in Figure 85, Figure 86, Figure 87, and Figure 88, respectively. The summary of the results is presented in Table 24. It can be seen that at low porosity percentages (18% and 23%), the I-V curve shows an obvious concave-up curvature at high current density ends and is even observed at high water vapour concentration. This happens due to the feedstock supply problem. However, with increase in the fuel electrode porosity and enough feedstock supply, the curvature changes to a linear curve.

With increase in the water vapour concentration the current density increases. At certain water vapour concentration, although a decreasing trend of the current density (at 1.3 V) with increase in the fuel electrode porosity is observed, the sample with 33% fuel electrode porosity shows a higher current density at 1.3 V than the sample with 40% fuel electrode porosity. This shows that the sample with 33% fuel electrode porosity performs better among all the investigated SOECs. For example, for the test done with 50% water vapour concentration, the current density at 1.3 V increases from 0.278 A.cm⁻² to 0.346 A.cm⁻² and 0.694 A.cm⁻² for the sample with 18%, 23%, and 40% fuel electrode porosity, respectively, while the sample with 33% fuel electrode porosity shows 0.827 A.cm⁻² at 1.3 V.

Figure 85 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 18% fuel electrode porosity, tested at 800°C

Figure 86 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 23% fuel electrode porosity, tested at 800°C

Figure 87 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 33% fuel electrode porosity, tested at 800°C

Figure 88 I-V curves of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell as a function of water vapour concentration, with 40% fuel electrode porosity, tested at 800°C

Table 24 Current density at 1.3 V for the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with different fuel electrode porosities, as a function of water vapour concentration, tested over the temperature range of 650°C-800°C

	Water vapour concentration (%)	10	30	50	70
		Current density (A.cm⁻²) at 1.3 V			
Fuel electrode porosity percentage (%)	18	0.172	0.226	0.278	0.326
	23	0.213	0.259	0.346	0.546
	33	0.479	0.614	0.827	0.900
	40	0.411	0.529	0.694	0.767

All the trends observed in the SOEC are similar to SOFC's. However, the polarisation performance of the Ni-YSZ/YSZ-SDC/BSCF-SDC SOEC is not as high as the SOFC's and this is due to the YSZ blocking layer effect in the electrolyte which was discussed in the previous chapter. Detailed investigations illustrate that the pore structure has a significant impact on the gas permeability, electrical conductivity and polarisation of the fuel electrode in SOFCs and SOECs. In a summary, it can be confirmed that 33% porosity is the optimal porosity for the fuel electrode of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell which can be achieved by addition of 7 wt.% of graphite to the fuel electrode material.

To further improve the entire cell performance, the last stage in this PhD study is to modify the BSCF based air electrode for SOFC and SOEC and the details are presented in the next chapter.

CHAPTER 6. BSCF-SDC composite air electrode for SOFCs and SOECs

6.1. Improving SOC cell performance by modification of the air electrode

As it is known that in the intermediate operating temperature range, the performance of the air electrode of the cell tends to limit the cell's performance, it is therefore necessary to optimise the air electrode material and performance (Li et al. 2008b; Endo et al. 2000; Ioroi et al. 1997; Lee et al. 2003; Maguire et al. 2000; Minh 1993). Conventional SOCs are composed of YSZ electrolyte, Ni-YSZ cermet fuel electrode and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) air electrode, and they operate at around 1000°C (Hibino et al. 1999; Kamata et al. 1998). The high operating temperature is beneficial for decreasing the electrolyte's ohmic resistance and increasing the electrode's reaction kinetics, however, it also brings about severe drawbacks, such as increasing electrode sintering rate, difficulties in cell sealing and interconnection, and promoting the interfacial reactions between cell components (Steele and Heinzel 2001). High operating/materials costs and inadequate operational stability are the two major factors hindering the widespread application of high-temperature SOCs. It is generally agreeable that the reduction of SOCs operating temperature to the intermediate temperature range of 500°C-800°C can greatly speed up the commercialisation of the technology (Gong et al. 2006; Xia et al. 2002), as this can effectively lower the operational and materials costs and extend the operating lifetime. However, based on conventional cell materials and configurations with decrease in operating temperature, new issues turn up for SOCs, such as a significant increase in both the cathodic polarisation resistance and electrolyte ohmic resistance (Steele 2000a; Baumann et al. 2006; Doshi et al. 1999; Brant and Dessemond 2000; Kenjo et al. 2003).

Cobalt-based mixed-conducting oxides specifically in combination with doped-ceria electrolyte phase have been found to be the excellent materials for air electrode in ITSOFCs (Adler 1998; Agudero et al. 2007; Chang et al. 2006; Kumar et al. 2004; Liu et al. 2006a; Shao and Halle 2004).

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) is a mixed conductor with super high ionic conductivity, which is proven to be a high-performance air electrode for SOC based on oxygen-ion conducting electrolyte (An et al. 2010; Guo et al. 2009; Hirabayashi et al. 2005; Tomita et al. 2006; Zhang et al. 2006c; Zhu et al. 2006b). The cell performance is closely relevant to the phase reaction between the air electrode and the electrolyte layers (Lin et al. 2008b).

One of the main problems of cobalt-based perovskite air electrodes is their high TEC, typically higher than $19.7 \times 10^{-6} \text{ K}^{-1}$ in air between room temperature and 900°C (Jacobson 2010; Wang et al. 2003). SDC is reported to have a TEC $\sim 12.2 \times 10^{-6} \text{ K}^{-1}$ (Yahiro et al. 1988). Due to the big difference between the TECs of SDC and BSCF, there is a high possibility of delamination of electrode at the interface with the electrolyte. To make BSCF more thermo-mechanically compatible with the SDC electrolyte, the formation of a composite electrode by introducing SDC as the compositional material is proposed in order to diminish the mismatch of the TECs of electrode and electrolyte, hence improve the cell durability and perhaps performance. However, despite SDC has a high ionic conductivity, it suffers from low electronic conductivity and hence, the formation of a composite electrode with SDC may reduce the electrical conductivity of the air electrode if it is not properly designed. Inadequate electronic conductivity can produce a large contact and charge-transfer resistance. As an appropriate air electrode should have sufficient ionic and electronic conductivity, by making a composite air electrode, the performance of the cell will improve.

6.2. Experimental work on cell preparation

To find out what is the optimum amount of SDC should be in the composite air electrode, different amounts of SDC were mixed with BSCF powder. All the cell preparation stages and testing techniques were the same as those mentioned in Chapter 4 and thus to prevent duplication they are not repeated here. For the BSCF-SDC/YSZ-SDC/Ni-YSZ cell, Ni-YSZ was made to have the optimum 33% porosity and the SDC electrolyte had a $3.5 \mu\text{m}$ YSZ blocking layer. To prepare the composite air electrode 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.%, and 50 wt.% of commercial SDC powder was mixed with 90 wt.%, 80 wt.%, 70 wt.%, 60 wt.%, and 50 wt.% of BSCF powder prepared by sol-gel method, respectively. The two powders were hand-ground in a

mortar for at least 20 minutes and after adding the ink (commercial product from Nextech Materials, USA), they were hand-ground for another 15 minutes to achieve a shiny and smooth mixture and the cell was prepared with the same method mentioned in previous chapters. All samples with BSCF-SDC composite air electrodes and a sample with BSCF air electrode were studied and compared to determine the optimum amount of SDC in the air electrode, knowing that mechanical mixing of SDC with BSCF results in the adhesion of fine SDC particles to the BSCF grains surface. O₂-TPD, XRD, and SEM-EDX results have shown that the phase reaction between SDC and BSCF is negligible, concentrated only at the BSCF and SDC interface, and throughout the entire air electrode with the formation of new (Ba,Sr,Sm,Ce)(Co,Fe)O_{3-δ} perovskite phase at a firing temperature of 900°C, 1000°C, and ≥ 1050°C, respectively (Wang et al. 2008b). The FESEM micrographs of BSCF-SDC/YSZ-SDC/Ni-YSZ single cell show the great connection and quality of the electrolyte interface with the electrodes, as well as the highly dense bi-layer electrolyte and porous electrodes structures (Figure 89).

Figure 89 FESEM micrographs of BSCF-SDC/YSZ-SDC/Ni-YSZ single cell

6.3. Studying the effect of air electrode composition on the SOFC and SOEC electrochemical performance

After successfully synthesising the BSCF-SDC/YSZ-SDC/Ni-YSZ single cell, the electrochemical performance of the cell as a function of air electrode composition was evaluated in both fuel cell and electrolyser cell mode. The focus of the investigations

was on the electrochemical performance of the cell with pure BSCF air electrode and BSCF + SDC composite air electrode with 10 wt.%-50 wt.% SDC mixed with BSCF, over the temperature range of 650°C-800°C. The impedance measurements for SOFC were under OCV condition, while in SOEC mode measurements were conducted under 0.1 V bias. The effect of humidity level for 10%, 30%, 50% and 70% of water vapour in the hydrogen was carried out in the electrolyser mode. The investigation was completed by measuring the polarisation of cells in order to find the optimal and most appropriate ratio between SDC and BSCF in the air electrode composition. The composite air electrode can mitigate the issue of thermal expansion mismatch between BSCF and SDC, enhance the triple-phase boundaries and improve the adhesion of the electrode to the electrolytes.

6.3.1. Studying the electrochemical performance of the SOFC as a function of air electrode composition

A three-electrode arrangement was used for electrochemical measurements. Similar to the previous chapters, the impedance spectrum of electrolytes and electrochemical performance of the cell were characterised by an electrochemical impedance spectroscopy technique (EIS) using “MultiStat” machine with the frequency range of 0.1 Hz to 0.1 MHz and amplitude of 10 mV. The impedance spectra are measured at open circuit potential (OCP) using Frequency Response Analyser (FRA) software and are presented in the SOFC results. Figure 90, Figure 91, Figure 92, Figure 93, Figure 94, and Figure 95 show the impedance spectra of samples with pure BSCF air electrode, and samples with 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.%, and 50 wt.% of SDC mixed with 90 wt.%, 80 wt.%, 70 wt.%, 60 wt.%, and 50 wt.% of BSCF, respectively. The summary of the results is presented in Table 25.

Figure 90 Impedance spectra of BSCF/YSZ-SDC/Ni-YSZ fuel cell, over the temperature range of 650°C-800°C

Figure 91 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell with 10%SDC-90%BSCF composite air electrode, over the temperature range of 650°C-800°C

Figure 92 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell with 20%SDC-80%BSCF composite air electrode, over the temperature range of 650°C-800°C

Figure 93 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell with 30%SDC-70%BSCF composite air electrode, over the temperature range of 650°C-800°C

Figure 94 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell with 40%SDC-60%BSCF composite air electrode, over the temperature range of 650°C-800°C

Figure 95 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell with 50%SDC-50%BSCF composite air electrode, over the temperature range of 650°C-800°C

Figure 96 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell as a function of air electrode composition, tested at 700°C

Table 25 R_{Ω} & ASR of the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell with different air electrode compositions, tested over the temperature range of 650°C-800°C

	Temperature (°C)	650		700		750		800	
		R_{Ω} & ASR ($\Omega.cm^2$)		R_{Ω} & ASR ($\Omega.cm^2$)		R_{Ω} & ASR ($\Omega.cm^2$)		R_{Ω} & ASR ($\Omega.cm^2$)	
Air electrode composition SDC-BSCF (wt.%)	0-100	0.497	1.114	0.347	0.736	0.227	0.484	0.148	0.443
	10-90	0.420	0.883	0.300	0.541	0.191	0.458	0.125	0.402
	20-80	0.376	0.601	0.269	0.533	0.160	0.359	0.102	0.339
	30-70	0.541	1.298	0.417	0.766	0.218	0.578	0.161	0.504
	40-60	0.705	1.644	0.501	0.868	0.319	0.695	0.169	0.555
	50-50	0.715	1.682	0.577	1.147	0.365	1.01	0.211	0.627

The electrochemical impedance spectra of the samples contain two parts. The high frequency (left) arc is due to the contribution of ohmic polarisation, including the effective resistance between working electrode and counter electrode, while the low frequency (right) arc is due to electrode polarisation resistance, including the charge transfer resistance at electrode-electrolyte interface where the electrochemical reactions take place, and the equivalent resistance for the oxygen adsorption, decomposition and mass transfer. As it can be seen in Table 25, with increase in the operating temperature of the fuel cell from 650°C to 800°C, R_{Ω} and ASR decrease which is an expected trend. To find out the effect of the amount of SDC in BSCF based air electrode, looking at any of the testing temperatures, it can be observed that the sample with 20% SDC-80% BSCF air electrode, has the lowest R_{Ω} and ASR and for the rest of the samples, the sequence of the samples having lowest R_{Ω} and ASR to highest is as follows: 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF and 50% SDC-50% BSCF, respectively. For example for the sample tested at 700°C, the pair of ohmic resistance and ASR for the sample with 20% SDC-80% BSCF air electrode is 0.269 $\Omega \cdot \text{cm}^2$ and 0.533 $\Omega \cdot \text{cm}^2$, respectively, which increases to 0.3 $\Omega \cdot \text{cm}^2$ and 0.541 $\Omega \cdot \text{cm}^2$, 0.347 $\Omega \cdot \text{cm}^2$ and 0.736 $\Omega \cdot \text{cm}^2$, 0.417 $\Omega \cdot \text{cm}^2$ and 0.766 $\Omega \cdot \text{cm}^2$, 0.501 $\Omega \cdot \text{cm}^2$ and 0.868 $\Omega \cdot \text{cm}^2$, and 0.577 $\Omega \cdot \text{cm}^2$ and 1.147 $\Omega \cdot \text{cm}^2$ for the samples with 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF, and 50% SDC-50% BSCF, respectively (Figure 96). So, the samples with 10 wt.% and 20 wt.% SDC in composite air electrode show lower R_{Ω} and ASR than the sample with pure BSCF air electrode and hence they are the appropriate candidates for the composite air electrode of the SOFC while the samples with more than 20 wt.% SDC composed with BSCF, show an increase in R_{Ω} and ASR, however the overall change in R_{Ω} values is not so big.

To further understand the sample behaviour, the performance of the cells was evaluated. To acquire the cell polarisation data, General Purpose Electrochemical System (GPES) Manager Software was used. Polarisation curves were obtained over the temperature range of 650°C-800°C for BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell, using humidified hydrogen (3% water vapour) as the fuel with the carrier gas flow rate of 50 sccm. The air electrode was exposed to the ambient air.

The voltage-current density and power-current density curves of the cells fabricated with the corresponding air electrodes and tested over the temperature range of 650°C-800°C are presented in Figure 97, Figure 98, Figure 99, Figure 100, Figure 101, and Figure 102 and the results are summarised in Table 26.

Figure 97 I-V and I-P curves of the BSCF/YSZ-SDC/Ni-YSZ fuel cell, tested over the temperature range of 650°C-800°C

Figure 98 I-V and I-P curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell, with 10%SDC-90%BSCF composite air electrode, tested over the temperature range of 650°C-800°C

Figure 99 I-V and I-P curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell, with 20%SDC-80%BSCF composite air electrode, tested over the temperature range of 650°C-800°C

Figure 100 I-V and I-P curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell, with 30%SDC-70%BSCF composite air electrode, tested over the temperature range of 650°C-800°C

Figure 101 I-V and I-P curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell, with 40%SDC-60%BSCF composite air electrode, tested over the temperature range of 650°C-800°C

Figure 102 I-V and I-P curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell, with 50%SDC-50%BSCF composite air electrode, tested over the temperature range of 650°C-800°C

Figure 103 I-V and I-P curves of BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell as a function of air electrode composition, tested at 700°C

Table 26 Current density at 0.5 V and MPD of the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell with different air electrode compositions, tested over the temperature range of 650°C-800°C

	Temperature (°C)	650		700		750		800	
		CD (A.cm ⁻²)		CD (A.cm ⁻²)		CD (A.cm ⁻²)		CD (A.cm ⁻²)	
		&		&		&		&	
		MPD (W.cm ⁻²)		MPD (W.cm ⁻²)		MPD (W.cm ⁻²)		MPD (W.cm ⁻²)	
Air electrode composition SDC-BSCF (wt.%)	0-100	1.276	0.64	1.535	0.77	1.954	0.99	2.773	1.39
	10-90	1.357	0.68	1.622	0.81	2.276	1.14	2.787	1.42
	20-80	1.454	0.73	1.711	0.85	2.415	1.22	2.798	1.48
	30-70	1.10	0.55	1.483	0.74	1.876	0.94	2.634	1.32
	40-60	0.939	0.47	1.417	0.71	1.715	0.86	2.541	1.27
	50-50	0.838	0.42	1.374	0.69	1.661	0.83	2.425	1.22

A good electrode needs to have high ionic and electronic conductivity. Pure BSCF is well known for having reasonable ionic and good electronic conductivity. But as mentioned earlier, in order to overcome the problem of mismatch in TECs of electrolyte and electrode and also to enhance the ionic conductivity, SDC was composed with BSCF as SDC has high ionic conductivity. However, SDC has a low electronic conductivity. Hence, although the addition of SDC will increase the ionic conductivity of the air electrode, it decreases the electronic conductivity of the electrode. So, it is very important to find out the optimum amount of SDC in the composite air electrode in order to improve the overall performance of the fuel cell. To achieve this desired goal, the samples with corresponding air electrodes are compared with the sample having pure BSCF as the air electrode.

Doping of Ce^{3+} and Sm^{3+} into the A-site of BSCF perovskite causes an improvement in the electrical conductivity of the oxide. Such enhancement can be illustrated in part by the fact that the doping of Sm^{3+} and Ce^{3+} into A-site of the BSCF results in the shrinking of the lattice. Due to smaller ionic size of $\text{Ce}^{3+}/\text{Sm}^{3+}$ in compare with $\text{Ba}^{2+}/\text{Sr}^{2+}$, their doping in the A-site of the BSCF promotes the B-site metal ions to take a higher valence state. Consequently, there would be a decrease in the distance between the B-site metals and thus the electron exchange between the B-site ions is easier. Besides, $\text{Ce}^{3+}/\text{Sm}^{3+}$ have a higher valence state than $\text{Ba}^{2+}/\text{Sr}^{2+}$, and thus the doping of $\text{Ce}^{3+}/\text{Sm}^{3+}$ into the A-site of the BSCF reduces the oxygen vacancy concentration, which is also helpful for increasing the p-type conductivity.

As it can be seen in Table 26, with increase in the operating temperature from 650°C to 800°C, for any of the samples an increasing trend in MPD and the current density at 1.3 V and a decreasing trend in OCV are observed. At any operating temperature, increasing 10 wt.% and 20 wt.% of SDC to BSCF air electrode causes increase in MPD and the current density at 1.3 V. This is due to the increase in ionic conductivity of the air electrode caused by SDC material. However, adding more than 20 wt.% (30 wt.%, 40 wt.% and 50 wt.%) shows a drop in the performance of the cell in compare with the sample with pure BSCF air electrode, which drops more with increasing the SDC contribution in the air electrode microstructure. Such a decrease in the air electrode performance in compare with pure BSCF can be related to the reduced oxygen vacancy concentration due to the incorporation of $\text{Ce}^{3+}/\text{Sm}^{3+}$ in the A-site of

BSCF. It can also be due to a decrease in the electronic conductivity. This unveils the fact that when more than 20 wt.% of SDC is added to BSCF air electrode, the increase in ionic conductivity is lower than the decrease in electronic conductivity caused by adding SDC and hence leads to a lower performance. As the sample with 20% SDC-80% BSCF air electrode shows the highest performance among all the investigated cells, it can be concluded that the 20 wt.% of the SDC is the optimum amount to be added to BSCF as the air electrode of the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell, which has the desired ionic and electronic conductivity. For example, as it can be seen in Figure 103, at operating temperature of 700°C, the highest to lowest MPD achieved are 0.85 W.cm⁻², 0.81 W.cm⁻², 0.77 W.cm⁻², 0.74 W.cm⁻², 0.71 W.cm⁻², and 0.69 W.cm⁻² for the samples with 20% SDC-80% BSCF, 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF, and 50% SDC-50% BSCF air electrode, respectively. These results are in a good agreement with the impedance study of the cells.

6.3.2. Studying the electrochemical performance of the SOEC as a function of fuel humidity level

The same investigation on the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell under the same 50 sccm hydrogen flow rate and all other conditions were conducted in the electrolyser mode over the temperature range of 650°C-800°C. In addition, the effect of different humidity level on the performance of the SOEC was studied in detail.

Figure 104, Figure 105, Figure 106, Figure 107, Figure 108, and Figure 109 show the Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell as a function of different humidity levels, tested at 800°C. The results are summarised in Table 27.

Figure 104 Impedance spectra of BSCF/YSZ-SDC/Ni-YSZ electrolyser cell as a function of fuel humidity percentage, tested at 800°C

Figure 105 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell as a function of fuel humidity percentage, with 10%SDC-90%BSCF composite air electrode, tested at 800°C

Figure 106 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell as a function of fuel humidity percentage, with 20%SDC-80%BSCF composite air electrode, tested at 800°C

Figure 107 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell as a function of fuel humidity percentage, with 30%SDC-70%BSCF composite air electrode, tested at 800°C

Figure 108 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell as a function of fuel humidity percentage, with 40%SDC-60%BSCF composite air electrode, tested at 800°C

Figure 109 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell as a function of fuel humidity percentage, with 50%SDC-50%BSCF composite air electrode, tested at 800°C

Figure 110 Impedance spectra of BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell as a function of air electrode composition, tested under 50% H₂O/H₂ fuel at 800°C

Table 27 R_{Ω} and ASR of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell with different air electrode compositions and different fuel humidity percentages, tested at 800°C

		Water vapour concentration (%)		10		30		50		70	
		R_{Ω} & ASR ($\Omega \cdot \text{cm}^2$)		R_{Ω}	ASR	R_{Ω}	ASR	R_{Ω}	ASR	R_{Ω}	ASR
Air electrode composition	0-100	0.151		0.281	0.159	0.174	0.164	0.130	0.167	0.116	
	10-90	0.125		0.216	0.126	0.167	0.127	0.115	0.128	0.099	
	20-80	0.103		0.208	0.104	0.135	0.105	0.110	0.106	0.098	
	30-70	0.170		0.287	0.175	0.187	0.182	0.142	0.187	0.118	
	40-60	0.181		0.328	0.187	0.203	0.202	0.153	0.198	0.119	
	50-50	0.220		0.412	0.228	0.258	0.236	0.199	0.244	0.169	
SDC-BSCF (wt.%)											

Impedance spectra are typically characterised by a large semicircle at low frequencies and a small semicircle at high frequencies, indicating that there are at least two electrode processes during the high temperature steam electrolysis. For SOECs, the ASR can directly indicate the electrochemical properties of the air electrode, determining their hydrogen production ability (Yang et al. 2010).

As presented in Table 27, with increase in the water vapour level, the ASR decreases, hence more hydrogen is produced as a result of electrolysis. Basically, because the operating temperature was kept constant (800°C), there is no big change in the ohmic resistance values when the water vapour amount increases. But when the humidity level increases, for all the samples it is observed that the ASR decreases. At each humidity level the trends are the same as those in SOFC. It is observed that the sample with 20% SDC-80% BSCF air electrode, has the lowest R_{Ω} and ASR and R_{Ω} is negligibly affected by the humidity level. For the rest of the samples, the sequence of the samples having the lowest R_{Ω} and ASR to the highest is as follows: 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF and 50% SDC-50% BSCF. For example for the sample tested under 50% H_2O/H_2 fuel at 800°C, the ohmic resistance and ASR of the sample with 20% SDC-80% BSCF air electrode are 0.105 $\Omega.cm^2$ and 0.111 $\Omega.cm^2$, respectively, which increases to 0.127 $\Omega.cm^2$ and 0.115 $\Omega.cm^2$, 0.164 $\Omega.cm^2$ and 0.130 $\Omega.cm^2$, 0.182 $\Omega.cm^2$ and 0.142 $\Omega.cm^2$, 0.202 $\Omega.cm^2$ and 0.153 $\Omega.cm^2$, and 0.236 $\Omega.cm^2$ and 0.199 $\Omega.cm^2$ for the samples with 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF, and 50% SDC-50% BSCF, respectively (Figure 110). So, the samples with 10 wt.% and 20 wt.% SDC composed with BSCF show lower R_{Ω} and ASR than the sample with pure BSCF air electrode and hence they are the appropriate candidates for the composite air electrode of the SOEC. The much lower cell ASR demonstrates that the porous network prepared in the sample with 20% SDC-80% BSCF is a promising air electrode for high temperature electrolysis cells.

To further understand the samples behaviour, the performance of the cells was under evaluation. To acquire the cell polarisation data, General Purpose Electrochemical System (GPES) Manager Software was used. Polarisation curves were obtained over the temperature range of 650°C-800°C for BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser

cell, using humidified hydrogen (3% water vapour) as the fuel with the carrier gas flow rate of 50 sccm. The air electrode was exposed to the ambient air.

The voltage-current density and power-current density curves of the cells fabricated with the corresponding air electrodes and tested over the temperature range of 650°C-800°C are presented in Figure 111, Figure 112, Figure 113, Figure 114, Figure 115, and Figure 116 and summarised in Table 28. Negative current densities demonstrate power consumption and cell potential values at zero current density correspond to OCV.

Figure 111 I-V curves of the BSCF/YSZ-SDC/Ni-YSZ cell tested over the temperature range of 650°C-800°C

Figure 112 I-V curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell with 10%SDC-90%BSCF composite air electrode, tested over the temperature range of 650°C-800°C

Figure 113 I-V curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell with 20%SDC-80%BSCF composite air electrode, tested over the temperature range of 650°C-800°C

Figure 114 I-V curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell with 30%SDC-70%BSCF composite air electrode, tested over the temperature range of 650°C-800°C

Figure 115 I-V curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell with 40%SDC-60%BSCF composite air electrode, tested over the temperature range of 650°C-800°C

Figure 116 I-V curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell with 50%SDC-50%BSCF composite air electrode, tested over the temperature range of 650°C-800°C

Table 28 OCV and Current density at 1.3 V for the BSCF-SDC/YSZ-SDC/Ni-YSZ cell with different air electrode composition, tested over the temperature range of 650°C-800°C

	Temperature (°C)	650		700		750		800	
		CD (A.cm ⁻²) & OCV (V)	CD at 1.3 V	OCV	CD at 1.3 V	OCV	CD at 1.3 V	OCV	CD at 1.3 V
Air electrode composition SDC-BSCF (wt.%)	0-100	0.148	1.082	0.217	1.046	0.288	1.017	0.345	0.985
	10-90	0.168	1.095	0.227	1.087	0.297	1.051	0.355	1.036
	20-80	0.182	1.112	0.236	1.094	0.316	1.073	0.377	1.057
	30-70	0.129	1.052	0.196	1.029	0.263	0.991	0.323	0.971
	40-60	0.111	1.031	0.177	1.016	0.245	0.996	0.311	0.966
	50-50	0.096	1.02	0.152	0.999	0.227	0.979	0.303	0.956

As presented in Table 28, the same trends observed in SOFC are seen for SOEC. With increase in the operating temperature from 650°C to 800°C, for any of the samples a decreasing trend in OCV and an increasing trend in the current density at 1.3 V are observed. At any of the testing temperatures, increasing 10 wt.% and 20 wt.% of SDC to BSCF air electrode causes increase in the current density at 1.3 V. This is due to the increase in ionic conductivity of the air electrode caused by SDC material. However, when adding more than 20 wt.% SDC (30 wt.%, 40 wt.% and 50 wt.%) a drop in the performance of the cell in compare with the sample with pure BSCF air electrode is observed and the drop is more severe with increasing the SDC contribution in the air electrode microstructure. Such a decrease in the air electrode performance in compare with pure BSCF can be related to the reduced oxygen vacancy concentration due to the incorporation of $\text{Ce}^{3+}/\text{Sm}^{3+}$ in the A-site of BSCF. This proves that when more than 20 wt.% of SDC is added to BSCF air electrode, the increase in ionic conductivity is lower than the decrease in electronic conductivity caused by adding SDC and hence leads to a lower performance. As the sample with 20% SDC-80% BSCF shows the highest performance among the investigated cells, it can be concluded that the 20 wt.% of the SDC is the optimum amount to be added to BSCF as the air electrode of the BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell, which has the desired ionic and electronic conductivity. For example, at operating temperature of 700°C, the highest to lowest current density at 1.3 V are 0.236 A.cm⁻², 0.227 A.cm⁻², 0.217 A.cm⁻², 0.196 A.cm⁻², 0.177 A.cm⁻², and 0.152 A.cm⁻² for the samples with 20% SDC-80% BSCF, 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF, and 50% SDC-50% BSCF air electrode, respectively. This trend is observed for all the investigated samples. All these results are in a good agreement with the impedance study of the cells.

To complete the study of the effect of water vapour concentration on the performance of the BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell with the corresponding air electrodes, 10%, 30%, 50%, and 70% humidity levels were applied to the hydrogen fed into the Ni-YSZ side, and their corresponding I-V curves are shown in Figure 117, Figure 118, Figure 119, Figure 120, Figure 121, and Figure 122, tested at 800°C. The summary of the results is presented in Table 29.

Figure 117 I-V curves of the BSCF/YSZ-SDC/Ni-YSZ cell as a function of fuel humidity percentage, tested at 800°C

Figure 118 I-V curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell as a function of fuel humidity percentage, with 10%SDC-90%BSCF composite air electrode, tested at 800°C

Figure 119 I-V curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell as a function of fuel humidity percentage, with 20%SDC-80%BSCF composite air electrode, tested at 800°C

Figure 120 I-V curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell as a function of fuel humidity percentage, with 30%SDC-70%BSCF composite air electrode, tested at 800°C

Figure 121 I-V curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell as a function of fuel humidity percentage, with 40%SDC-60%BSCF composite air electrode, tested at 800°C

Figure 122 I-V curves of the BSCF-SDC/YSZ-SDC/Ni-YSZ cell as a function of fuel humidity percentage, with 50%SDC-50%BSCF composite air electrode, tested at 800°C

Table 29 Current density at 1.3 V for the BSCF-SDC/YSZ-SDC/Ni-YSZ cell with different air electrode compositions, as a function of water vapour concentration, tested at 800°C

	Water vapour concentration (%)	10		30		50		70	
	CD (A.cm ⁻²) & OCV (V)	CD at 1.3 V	OCV	CD at 1.3 V	OCV	CD at 1.3 V	OCV	CD at 1.3 V	OCV
Air electrode composition SDC-BSCF (wt.%)	0-100	0.421	0.966	0.517	0.944	0.588	0.913	0.635	0.893
	10-90	0.422	1.01	0.537	0.985	0.607	0.953	0.659	0.905
	20-80	0.436	1.035	0.542	1.008	0.622	0.984	0.708	0.975
	30-70	0.403	0.957	0.510	0.941	0.582	0.910	0.629	0.878
	40-60	0.398	0.946	0.487	0.925	0.577	0.895	0.624	0.875
	50-50	0.361	0.941	0.476	0.924	0.570	0.891	0.621	0.872

It can be seen that at low water vapour concentration (10% and 30%), I-V curve shows an obvious concave-up curvature at high current density ends. This happens due to the feedstock supply issues, i.e., with increase in the electrode porosity and enough water vapour supply, the curvature would change to a linear line.

For all the samples, with increase in the humidity level, the current density at 1.3 V increases and the OCV decreases. For each humidity percentage, the same trend with 3% humidity is observed. With increasing 10 wt.% and 20 wt.% of SDC to BSCF air electrode the current density at 1.3 V increases. This is due to the increase in ionic conductivity of the air electrode caused by SDC material. On the other hand, adding more than 20 wt.% SDC (30 wt.%, 40 wt.% and 50 wt.%) shows a drop in the performance of the cell in compare with the sample with pure BSCF air electrode which drops more with increasing the SDC contribution in the air electrode microstructure, however this drop is very small as the operating temperature was kept constant. Such a decrease in the air electrode performance in compare with pure BSCF can be related to the reduced oxygen vacancy concentration due to the incorporation of Ce³⁺/Sm³⁺ in the A-site of BSCF. This again confirms that when more than 20 wt.% of

SDC is added to BSCF air electrode, the increase in ionic conductivity is lower than the decrease in electronic conductivity caused by adding SDC and hence leads to a lower performance. As the sample with 20% SDC-80% BSCF shows the highest performance among the investigated cells, it can be concluded that the 20 wt.% of the SDC is the optimum amount to be added to BSCF as the air electrode of the BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell, which has the desired ionic and electronic conductivity. For example, at water vapour concentration of 50%, the highest to lowest current density at 1.3 V are 0.622 A.cm^{-2} , 0.607 A.cm^{-2} , 0.588 A.cm^{-2} , 0.582 A.cm^{-2} , 0.577 A.cm^{-2} , and 0.570 A.cm^{-2} for the samples with 20% SDC-80% BSCF, 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF, and 50% SDC-50% BSCF air electrode, respectively.

Detailed investigations demonstrate that optimising the air electrode's composition leads to an overall enhanced performance. Based on the above electrochemical and performance evaluation results, it is obvious that a 20% SDC-80% BSCF is an optimised air electrode composition for the BSCF-SDC/YSZ-SDC/Ni-YSZ cell which presents a desired electrochemical performance.

CHAPTER 7. Conclusion

This chapter gives a summary on the results presented in the previous chapters. To achieve all these results electrochemical performance and impedance spectrum of electrolytes of the cell were characterised using humidified hydrogen (3% water vapour) as the fuel over the temperature range of 650°C-800°C for YSZ/YSZ-SDC/SDC-BSCF SOFC and SOEC. The air electrode was exposed to the ambient air. From all the results, the following main conclusion can be drawn:

7.1. Conclusion of studying ceria based electrolytes for SOFCs

- GDC and SDC are successfully synthesised and characterised. Samples sintered at 1400°C-1500°C present relative densities as high as 97.7% suggesting that this temperature range leads to improved densification of electrolyte as reflected by the high open circuit voltages. The Arrhenius plots of GDC and SDC conductivities exhibit that SDC electrolyte presents higher conductivity compared to GDC, especially those sintered at 1400°C and 1500°C.
- Based on polarisation results, maximum power densities of 0.368 W.cm⁻², 0.619 W.cm⁻² and, 0.790 W.cm⁻² were achieved at 500°C, 550°C, and 600°C, respectively, for the Ni-GDC/GDC/BSCF fuel cell. The Ni-SDC/SDC/BSCF cell generates maximum power densities of 0.398 W.cm⁻², 0.810 W.cm⁻² and, 1.1 W.cm⁻², respectively. With respect to the same thickness of electrolytes, it can be concluded that the fuel cell with SDC electrolyte presents a higher performance in compare with the fuel cell with GDC electrolyte.
- Furthermore, it is realised that the limiting current density increases with increase in the hydrogen flow rate but does not change noticeably with increase in the air flow rate. These characteristics demonstrate that the observed diffusion polarisation is due to hydrogen diffusion limitations at the fuel electrode.

7.2. Conclusion of studying the effect of YSZ blocking layer and its optimisation on the performance of the SOFC and SOEC

Ni-YSZ/YSZ-SDC/BSCF-SDC cell with pore 7 wt.% of graphite as the pore former in the Ni-YSZ structure, dense SDC as the electrolyte and porous 20 wt.%SDC-80 wt.% BSCF as the air electrode are the three distinguishable layers well adhered to each other. In order to prevent the OCV loss and enhance the chemical stability of doped ceria electrolyte in reducing atmospheres, using the spin coating technique SDC was coated with a very thin layer of YSZ film to form a bi-layer electrolyte, co-sintered at 1400°C for 2 hours to obtain a very dense YSZ-SDC bi-layer electrolyte. From the comparison of these samples with the sample with no blocking layer, the following conclusion is drawn.

- From the FESEM micrographs of sample with no blocking layer and samples with 1-5 blocking layers of YSZ it can be seen that in all samples the YSZ layer is uniform and the thickness of the YSZ blocking layer for 1, 2, 3, 4, and 5 layers is 1.5 μm , 2.5 μm , 3.5 μm , 3.8 μm , and 4.4 μm , respectively and the SDC thickness is about the same with an average thickness of $\sim 17.4\mu\text{m}$. It is clear that the electrolyte films remain dense and solid after the high temperature measurements and the adhesion between the adjacent layers is excellent with no obvious crack formation at interfaces.
- In the impedance spectra of the Ni-YSZ/SDC/SDC-BSCF cell and Ni-YSZ/YSZ-SDC/SDC-BSCF cell with the corresponding YSZ blocking thickness an interesting trend in R_{Ω} and ASR values is observed at each testing temperature. With increase in the YSZ blocking layer thickness, the R_{Ω} and ASR increase, because in oxidising environment, any increase in bi-layer thickness will cause an increase in ohmic loss. It is also noticeable that the increase in the R_{Ω} and ASR value is so small after the effect of successful blocking layer kicks in at 3.5 μm YSZ thickness.
- At all testing temperatures, the sample with no blocking layer shows a higher performance than the samples with 1.5 μm and 2.5 μm YSZ blocking layer. This is because the additional blocking layer does not effectively block the

electrons, instead it introduces additional ohmic loss to the cell. The blocking of electrons take significant effect when the blocking layer is increased to 3.5 μm , giving the highest current density at 0.5 V as well as the maximum power density for all temperatures. Further increase in the thickness of YSZ layer will not have any effect on blocking of electron penetration but the additional ohmic resistance would induce poorer performance as reflected in the results presented in Table 15. Essentially, the sample with a blocking layer of 3.5 μm and tested at 700°C, where the full blocking effect has kicked in, the MPD and OCV have shown obvious improvement from 0.709 W.cm^{-2} and 1.044 V for the sample without blocking layer to 0.856 W.cm^{-2} and 1.094 V for the sample with 3.5 μm YSZ blocking layer, respectively. The maximum power density decreases from 0.856 W.cm^{-2} for the sample with 3.5 μm YSZ blocking layer to 0.835 W.cm^{-2} and 0.77 W.cm^{-2} for the samples with 3.8 μm and 4.4 μm YSZ, respectively. The same trend is observed in the current densities at 0.5 V from 1.711 A.cm^{-2} for the sample with 3.5 μm YSZ blocking layer to 1.634 A.cm^{-2} and 1.535 A.cm^{-2} for the samples with 3.8 μm and 4.4 μm YSZ, respectively.

- From the polarisation measurement results, the following remarks can be concluded. First, the one and two layers of YSZ deposition onto the main SDC electrolyte are not effective in blocking the internal electronic conduction, thus they serve no purpose to the SDC electrolyte. Second, the blocking layer thickness plays an important role in the OCVs and MPDs in all cells. Third, the Ni-YSZ/YSZ-SDC/BSCF-SDC cell with 3.5 μm YSZ blocking layer shows the highest performance among all the investigated cells and at all testing temperatures and is regarded as the optimum YSZ blocking layer thickness without any crack or pin-hole through the structure.
- In the electrolyser mode, from the impedance measurements it can be understood that the sample with no blocking layer shows a significantly smaller R_{Ω} in compare with the samples with blocking layer because of additional ohmic resistance brought by the YSZ layers.
- With increase in the water vapour concentration of the hydrogen, the ASR value decreases, hence more hydrogen is produced through the electrolysis.

Meanwhile, no big change in R_{Ω} is observed when the water vapour amount of the hydrogen increases because the operating temperature was kept constant (800°C). Therefore, in general when the hydrogen humidity increases, for all the samples it is observed that the R_{Ω} and ASR decrease.

- At each humidity level with increase in the YSZ blocking layer thickness, R_{Ω} increases, but no specific trend is observed in ASR values. The sample with no blocking layer exhibits the lowest ASR at all humidity percentages in compare with rest of the samples. It can also be seen that at lower water vapour concentration percentages (10% and 30%) the samples with successful blocking layer (according to SOFC results, 3.5 μm , 3.8 μm , and 4.4 μm) show lower ASR value than the samples with unsuccessful blocking layer (1.5 μm and 2.5 μm) and at higher water vapour concentration percentages (50% and 70%) the difference in ASR values of all samples is so small. Although in any of these two sets of successful and unsuccessful samples, the increase trend of ASR with increasing the electrolyte layer thickness can be seen, but the change in both R_{Ω} and ASR is not significant after the blocking effect kicks in for the sample with 3.5 μm YSZ layer and the impedance spectra for the samples with 3.8 μm , and 4.4 μm YSZ layer are almost overlapped. Therefore, once the blocking layer performs, the change in ASR will not be distinctive.
- The polarisation curves of the Ni-YSZ/SDC/BSCF-SDC cell with no blocking layer and Ni-YSZ/YSZ-SDC/BSCF-SDC cell with the corresponding YSZ blocking layers demonstrate that with increase in the thickness of the YSZ layer, current density at 1.3 V decreases.
- In both sets of the samples with no or unsuccessful blocking layer and samples with successful blocking layer the OCV decreases with increasing the electrolyte thickness. For example, for the sample tested at 700°C, the OCV decreases from 1.044 V to 1.010 V and from 1.094 V to 1.042 V for the samples with no or unsuccessful blocking layer and the samples with 3.5 μm -4.4 μm YSZ blocking layer, respectively.
- For the Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell with the corresponding electrolytes (no blocking and the five different blocking layers), for each humidity percentage, with increase in the blocking layer thickness, obvious

trend is observed, i.e., when effective blocking kicks in, the current density would increase which means that more hydrogen is produced through the electrolysis. Hence, the requirements in electrons blocking in SOEC and SOFC mode of operation are quite different.

- Detailed investigations on the microstructural, electrochemical, and power measurement results confirmed that the bi-layer electrolyte structure with 3.5 μm YSZ thickness can provide the chemical, mechanical, and structural stability of the YSZ-SDC electrolyte in Ni-YSZ/YSZ-SDC/BSCF-SDC single cell.

7.3. Conclusion of studying Optimum amount of porosity in Ni-YSZ as the fuel electrode in SOFCs and SOECs

- After choosing the SDC as the electrolyte, in order to enhance the fuel electrode performance graphite was added to NiO-YSZ fuel electrode as a pore former. The SDC electrolyte had a thin ($\sim 3.5 \mu\text{m}$) YSZ blocking layer and the BSCF air electrode was composited with 20 wt.% of SDC. So, Ni-YSZ/YSZ-SDC/BSCF-SDC fuel cells with 5 wt.%, 7 wt.%, and 10 wt.% of graphite added into the Ni-YSZ structure were fabricated Successfully. By adding 0 wt.%, 5 wt.%, 7 wt.%, and 10 wt.% of graphite to the fuel electrode material 18%, 23%, 33%, and 40% porosity was achieved in the Ni-YSZ fuel electrode structure, respectively.
- From the cross section of the cells inspected using FESEM, it was observed that due to high porosity, the pores of the sample with 40% fuel electrode porosity are connected inducing a crack in the fuel electrode structure, which leads to a lower mechanical strength of the fuel electrode and hence the entire cell.
- Looking at any of the testing temperatures, it is obvious that with increase in the fuel electrode porosity, R_{Ω} and ASR decrease. For the sample with 33% porosity the R_{Ω} and ASR are the lowest which are in good agreement with the observations in FESEM images. Consequently, the number of the TPB sites is greatly increased for the sample with 33% fuel electrode porosity, resulting in a

decrease in the cell ASR. For example for the sample tested at 700°C, the low to high ASR values are 0.559 $\Omega\cdot\text{cm}^2$, 0.639 $\Omega\cdot\text{cm}^2$, 0.993 $\Omega\cdot\text{cm}^2$, and 1.506 $\Omega\cdot\text{cm}^2$ and ohmic resistance values are 0.269 $\Omega\cdot\text{cm}^2$, 0.415 $\Omega\cdot\text{cm}^2$, 0.5 $\Omega\cdot\text{cm}^2$, 0.761 $\Omega\cdot\text{cm}^2$ for the samples with 33%, 40%, 23%, and 18% fuel electrode porosity, respectively. So, in the sample with 40% porosity, increase in the ohmic resistance is likely due to the crack formation in the sample and the TPBs may have been disrupted with additional porosity.

- The voltage-current density and power-current density curves of the cells fabricated with the corresponding fuel electrodes and tested over the temperature range of 650°C-800°C illustrate that the cell with 33% fuel electrode porosity presents the highest maximum power density among all the investigated cells at all the testing temperatures. For example at 700°C the cell with 33% fuel electrode porosity achieves the MPD of 0.891 $\text{W}\cdot\text{cm}^{-2}$ which is higher than 0.86 $\text{W}\cdot\text{cm}^{-2}$, 0.77 $\text{W}\cdot\text{cm}^{-2}$, and 0.69 $\text{W}\cdot\text{cm}^{-2}$ for the samples with 33%, 40%, 23% and 18% fuel electrode porosity, respectively.
- The impedance measurements of the Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell, under 0.1 V bias at 800°C indicate that for certain fuel electrode porosity, with increase in humidity level, R_Ω is almost the same for all the samples while ASR decreases. Looking at any of the water vapour concentrations, with increase in the fuel electrode porosity, a similar decrease trend in R_Ω and ASR values seen in SOFC is observed. Also for the sample with 33% fuel electrode porosity the R_Ω and ASR are lowest among all the investigated samples.
- The sample with 33% fuel electrode porosity which shows the highest performance among all the investigated cells has the optimum amount of fuel electrode porosity for the Ni-YSZ/YSZ-SDC/BSCF-SDC solid oxide electrolyser cell. These results are in a good agreement with both microstructural and impedance study of the cells.
- Studying the effect of different humidity levels on the performance of the Ni-YSZ/YSZ-SDC/BSCF-SDC electrolyser cell with the corresponding fuel electrodes operated at 800°C, it is concluded that at certain water vapour

concentration, although a decreasing trend of the current density (at 1.3 V) with increase in the fuel electrode porosity is observed, the sample with 33% performs better among the investigated SOECs.

- All the trends observed in the SOEC are similar to SOFC's. However, the polarisation performance of the Ni-YSZ/YSZ-SDC/BSCF-SDC solid oxide electrolyser cell is not as high as the SOFC's and this is due to the YSZ blocking layer effect in the electrolyte. In a summary, it can be understood that 33% porosity is the optimum amount of porosity for the fuel electrode of the Ni-YSZ/YSZ-SDC/BSCF-SDC cell which can be achieved by addition of 7 wt.% of graphite to the fuel electrode material.

7.4. Conclusion of studying the optimisation of BSCF-SDC composite air electrode and its effect on the performance of SOFC and SOEC

To make BSCF more thermo-mechanically compatible with the SDC electrolyte, the formation of a composite electrode by introducing SDC as the compositing material which has high ionic conductivity, is proposed in order to decrease the mismatch of the TECs of electrode and electrolyte, hence improve the cell performance. In this study after successfully synthesising the BSCF-SDC/YSZ-SDC/Ni-YSZ single cell with 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.%, and 50 wt.% of commercial SDC powder mixed with BSCF powder to make the composite air electrode, the electrochemical study is done on the cells. The combination of YSZ-SDC bi-layer electrolyte with SDC-BSCF composite electrode in both SOFC and SOEC systems is bringing the original contributions of this research to the field of SOFC and SOEC. The following conclusion is drawn from the results of this chapter.

- To find out the effect of the amount of SDC in BSCF based air electrode, looking at any of the testing temperatures, it can be observed that the sample with 20% SDC-80% BSCF air electrode, has the lowest R_{Ω} and ASR and for the rest of the samples, the sequence of the samples having lowest R_{Ω} and ASR to highest is as follows: 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF and 50% SDC-50% BSCF, respectively. For

example for the sample tested at 700°C, the pair of ohmic resistance and ASR for the sample with 20% SDC-80% BSCF air electrode is 0.269 $\Omega\cdot\text{cm}^2$ and 0.533 $\Omega\cdot\text{cm}^2$, respectively, which increases to 0.3 $\Omega\cdot\text{cm}^2$ and 0.541 $\Omega\cdot\text{cm}^2$, 0.347 $\Omega\cdot\text{cm}^2$ and 0.736 $\Omega\cdot\text{cm}^2$, 0.417 $\Omega\cdot\text{cm}^2$ and 0.766 $\Omega\cdot\text{cm}^2$, 0.501 $\Omega\cdot\text{cm}^2$ and 0.868 $\Omega\cdot\text{cm}^2$, and 0.577 $\Omega\cdot\text{cm}^2$ and 1.147 $\Omega\cdot\text{cm}^2$ for the samples with 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF, and 50% SDC-50% BSCF, respectively.

- The polarisation curves of the cells fabricated with the corresponding air electrodes and tested over the temperature range of 650°C-800°C show that at any operating temperature, increasing 10 wt.% and 20 wt.% of SDC to BSCF air electrode causes increase in MPD and the current density at 1.3 V. This is due to the increase in ionic conductivity of the air electrode caused by SDC material. However, adding more than 20 wt.% (30 wt.%, 40 wt.% and 50 wt.%) shows a drop in the performance of the cell in compare with the sample with pure BSCF air electrode which unveils the fact that when more than 20 wt.% of SDC is added to BSCF air electrode, the increase in ionic conductivity is lower than the decrease in electronic conductivity caused by adding SDC and hence leads to a lower performance. So, it can be concluded that the 20 wt.% of the SDC is the optimum amount to be added to BSCF as the air electrode of the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell, which has the desired both ionic and electronic conductivity. For example, at operating temperature of 700°C, the highest to lowest MPD value achieved are 0.85 $\text{W}\cdot\text{cm}^{-2}$, 0.81 $\text{W}\cdot\text{cm}^{-2}$, 0.77 $\text{W}\cdot\text{cm}^{-2}$, 0.74 $\text{W}\cdot\text{cm}^{-2}$, 0.71 $\text{W}\cdot\text{cm}^{-2}$, and 0.69 $\text{W}\cdot\text{cm}^{-2}$ for the samples with 20% SDC-80% BSCF, 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF, and 50% SDC-50% BSCF air electrode, respectively. These results are in a good agreement with the impedance study of the cells.
- The same investigations on the BSCF-SDC/YSZ-SDC/Ni-YSZ fuel cell under the same conditions were conducted in the electrolyser mode over the temperature range of 650°C-800°C. At each humidity level the trends are the same as those in SOFC. For example for the sample tested under 50% $\text{H}_2\text{O}/\text{H}_2$ fuel at 800°C, the ohmic resistance and ASR of the sample with 20% SDC-80% BSCF air electrode are 0.105 $\Omega\cdot\text{cm}^2$ and 0.111 $\Omega\cdot\text{cm}^2$, respectively, which

increases to $0.127 \Omega\cdot\text{cm}^2$ and $0.115 \Omega\cdot\text{cm}^2$, $0.164 \Omega\cdot\text{cm}^2$ and $0.130 \Omega\cdot\text{cm}^2$, $0.182 \Omega\cdot\text{cm}^2$ and $0.142 \Omega\cdot\text{cm}^2$, $0.202 \Omega\cdot\text{cm}^2$ and $0.153 \Omega\cdot\text{cm}^2$, and $0.236 \Omega\cdot\text{cm}^2$ and $0.199 \Omega\cdot\text{cm}^2$ for the samples with 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF, and 50% SDC-50% BSCF, respectively. The much lower cell ASR demonstrates that the porous network prepared in the sample with 20% SDC-80% BSCF is a promising air electrode for high temperature electrolysis cells.

- The polarisation curves of the cells fabricated with the corresponding air electrodes and tested over the temperature range of 650°C - 800°C show the same trends observed in SOFC.
- To study the effect of water vapour concentration on the performance of the BSCF-SDC/YSZ-SDC/Ni-YSZ electrolyser cell with the corresponding air electrodes, different humidity levels were applied to the hydrogen fed into the Ni-YSZ side. It is observed that with increase in the water vapour concentration the current density at 1.3 V increases and the OCV decreases.
- For each humidity percentage, the same trend with 3% humidity is observed. For example, at humidity level of 50%, the highest to lowest current density at 1.3 V are $0.622 \text{ A}\cdot\text{cm}^{-2}$, $0.607 \text{ A}\cdot\text{cm}^{-2}$, $0.588 \text{ A}\cdot\text{cm}^{-2}$, $0.582 \text{ A}\cdot\text{cm}^{-2}$, $0.577 \text{ A}\cdot\text{cm}^{-2}$, and $0.57 \text{ A}\cdot\text{cm}^{-2}$ for the samples with 20% SDC-80% BSCF, 10% SDC-90% BSCF, pure BSCF, 30% SDC-70% BSCF, 40% SDC-60% BSCF, and 50% SDC-50% BSCF air electrode, respectively.
- Detailed investigations demonstrate that optimising the air electrode's composition leads to an overall enhanced performance. Based on the electrochemical and performance evaluation results, it is concluded that a 20% SDC-80% BSCF is an optimised air electrode composition for the BSCF-SDC/YSZ-SDC/Ni-YSZ cell which presents a desired electrochemical performance.

7.5. Recommendations for future work

- In open air condition which the partial pressure of oxygen is 0.21 atmospheres, the BSCF air electrode is stable, but under high current loading, the partial

pressure of oxygen decreases in air electrode side and BSFC will be reduced. So, although the high current density and so high power density is desired for a fuel cell, but when the air electrode is BSCF, because the decomposition is taking place for the BSCF, it is necessary to know how stable is this air electrode under high current loading to ensure that BSCF air electrode can be used of relatively long term performance in practical applications.

- As BSCF is not a good electronic conductor, it is interesting to study the effect of addition of a second electronic conductor, such as Ag and Pd, on the electrochemical performance of BSCF air electrode at low temperatures. In order to enhance the catalytic activity of the air electrode for oxygen reduction and thus to increase the electrochemical performance of planar fuel electrode-supported SOFCs, Pd and Ag can be added to the air electrode. The routes to be used to add these noble metals will be: infiltration of the air electrode with a Pd solution, mixing of air electrode powders with different metal precursors (Pd on activated carbon, Ag powder, Ag_2O , Ag acetate, Ag citrate, Ag_2CO_3 , colloidal Ag, AgNO_3), and synthesis of BSCF powder with the addition of AgNO_3 . Thermal decomposition of these precursors will result in the formation of large pores in the air electrode (Haanappel et al. 2004).
- When “forced” current is applied in the SOEC mode, more stringent requirement in electrons blocking is needed. It is also observed that at low humidity level, less blocking layer is needed as compared with those with high humidity levels. To fully understand the effect of electrons blocking relative to bare SDC electrolyte, Faradic efficiency has to be determined, which can be accomplished by combined polarisation measurement and gas composition measurement.

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