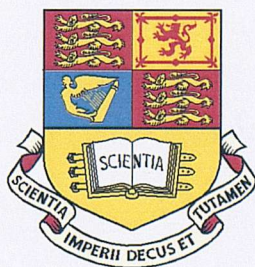


DEVELOPMENT OF ANODE MATERIALS FOR ELECTROCATALYTIC SYNTHESIS OF HCN

*A thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy of the University of London and the
Diploma of Imperial College London*

by

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Declaration

This thesis is a record of the work carried out by me in the Department of Materials, Imperial College London between October 2002 and February 2006. The thesis comprises my original work, except where clearly stated to the contrary. No part of this dissertation has been, or is currently being submitted for any other degree, diploma or other qualification at any other University.

Abstract

Hydrogen cyanide though highly toxic, is widely used as an industrial chemical in the production of synthetic fibers, plastics and is produced in large quantities worldwide. The common synthesis routes are the Andrussow ammoxidation process (reaction of methane, ammonia and oxygen) and the Degussa ammonolysis process (reaction of methane and ammonia). For exothermic processes it is potentially attractive to carry out a chemical synthesis in combination with a fuel cell in order to cogenerate electricity from some of the excess free energy of the reaction. The cogeneration of HCN and electricity from methane and ammonia in a high temperature SOFC ($\sim 1100^\circ\text{C}$) has been investigated previously. However, use of methanol instead of methane is more attractive since the reaction temperatures are significantly lower ($400 - 500^\circ\text{C}$). The objective of the work described in the thesis was to investigate the cogeneration of electricity and HCN from methanol and ammonia in a SOFC at $500 - 600^\circ\text{C}$. This required developing a SOFC anode that would be effective for electrochemical oxidation and also catalyse the synthesis of HCN.

Iron antimony oxide (FSO) is known to be an active and selective catalyst for methanol ammoxidation to hydrogen cyanide and therefore was chosen as the catalytic component in the SOFC anode studied here. The other components of the anode were the common cermet ones of Ni and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO-10). Since the SOFC operating temperature was aimed at approximately 500°C , CGO-10 was chosen for the electrolyte. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ / CGO-10 (LSCF/CGO-10) composite was chosen as the cathode because it is known to have good activity at these relatively low temperatures. The catalytic activity of the anode, and its constituent materials, for ammoxidation and ammonolysis reactions was studied in micro reactor experiments using gas chromatography to analyse the reaction products. On the basis of these results the most suitable composition for the SOFC anode was determined.

HCN synthesis from methanol-ammonia-steam mixtures was achieved with a yield of 40% with cogeneration of electrical energy in the SOFC. In addition to HCN, the anode off-gas products contained CO_2 , H_2O , N_2 , H_2 and CH_4 . Since the oxygen flow through the SOFC was much lower than the input gas flows of reactants, there was no evidence for electrochemical ammoxidation taking place in the SOFC. Rather, HCN was produced by ammonolysis of methanol and the H_2 produced by side reactions was oxidised electrochemically in the SOFC.

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Abbreviations and Symbols

ASR	Area-Specific Resistance
$\text{Ce}_{1-x}\text{Cu}_x\text{O}_{2-x}$	Copper doped ceria
CeO_2	Ceria
CFCR	Ceramic fuel cell reactor
CGO-10	$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$
CH_3OH	Methanol
CH_4	Methane
CO	Carbon monoxide
$\text{CO}+\text{H}_2$	Syngas
CO_2	Carbon dioxide
conc.	concentration
Cr_2O_3	Chromium (III) oxide
CTE	Chemical thermal expansion
d_{50}	Median diameter
E_a	Apparent activation energy
EDS	Energy Dispersive Spectrometry
EDX	Energy Dispersive X-ray analysis
EMF	Electromotive force
eqn	Equation
eV	electron volt
F	Faraday's constant (95484.56 C/mol)
Fe_2O_3	Iron (III) oxide
Fe_3O_4	Iron (II, III) oxide
FeSbO_4	Iron antimonate
FSO	Iron antimony oxide
h	hour
HCHO	Formaldehyde
HCN	Hydrogen cyanide
I	current density
IT-SOFC	Intermediate solid oxide fuel cell
K	Kelvin
k_b	Boltzmann constant (1.38×10^{-23} J/K.)
keV	kiloelectron volt
kJ	Kilojoules
kV	kilovolt
kW	kilowatt
LSCF	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$
mA	milliamperes
mmHg	millimetres of mercury
MW	Megawatt
N	Avogadro's constant
Ni-CGO	$\text{Ni}-\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$
NiO	Nickel (II) Oxide
NO_x	Oxides of nitrogen
OCV	Open-circuit voltage
PEG	Polyethylene glycol
ppm	parts per million
PVB	polyvinyl butyral
S/cm	Siemens/centimetre

Sb_2O_3	Stannous oxide
Sb_2O_4	Stannic oxide
SEM	Scanning Electron Microscopy
SOFC	Solid oxide fuel cell
SO_x	Oxides of sulphur
STP	Standard Temperature and Pressure
V	Voltage
W	Watt
wt %	weight percent
XRD	X-ray diffraction
Y:BaCeO_3	Yttrium doped barium cerate
Y_2O_3	Yttrium oxide
YSZ	Yttria Stabilised Zirconia
$\text{\AA}$	Angstrom
ΔG	Gibb's free energy change
ΔG°	Standard Gibb's free energy change
θ	Angle of incidence
λ	X-ray wavelength
σ	Apparent conductivity
Ω	Ohm
ρ	Apparent resistivity
μmol	micromole
μm	micrometre

Chapter 1

Introduction

1.1 Aim and scope of the project

The aim of the PhD project is to develop anode materials for the simultaneous production of electricity and hydrogen cyanide (HCN) by methanol ammoxidation in an intermediate temperature solid oxide fuel cell (IT-SOFC). Hydrogen cyanide is normally synthesised at a high temperature (greater than 1000°C) by ammoxidation of methane (Andrussow process) or by ammonolysis of methane (Degussa process) whereas ammoxidation of methanol has been proposed as an advantageous process due to the relatively low reaction temperature of 400-500°C.

This overall aim is pursued through the following objectives:

1. To design and construct an experimental setup for the HCN synthesis in micro reactor and a fuel cell test rig that enables accurate, steady state measurements.
2. To identify and evaluate a suitable SOFC anode for HCN synthesis.
3. To determine the feasibility of simultaneous production of HCN and electricity.

1.2 Thesis content

Chapter 2 first presents a summary of hydrogen cyanide synthesis by catalytic ammoxidation and ammonolysis followed by a similar discussion of compatible SOFC technology. Finally, experiments on cogeneration of chemicals and electricity in a fuel cell are surveyed.

Chapter 3 describes the main experimental setup for HCN synthesis, preparation methods of the electrocatalyst and various experimental techniques for characterisation. Important parameters of the experimental design are investigated. The gas chromatography instrumentation specifically configured for this type of measurement is explained and the gas chromatograph analytical methods are documented.

The electrocatalyst characterisation results and the GC calibrations are presented in Chapter 4.

The first part of Chapter 5 contains the results of the micro reactor synthesis of HCN from methanol and ammonia under different conditions using potential SOFC anode electrocatalysts. The selectivity to HCN and its yield are compared within all experiments. The second part constitutes the characterisation of the catalysts after synthesis.

Chapter 6 contains the fuel cell experiments, the main part of the project, to check the feasibility of chemical electro cogeneration.

Chapter 7 concludes this study and gives recommendations for future work.

Chapter 2

Background Literature

2.1 Hydrogen cyanide

Hydrogen cyanide (also called formonitrile; hydrocyanic acid; prussic acid), though highly toxic, is a useful chemical building block for the production of various important chemicals such as adiponitrile to produce nylon, methyl methacrylate to produce acrylic plastics, sodium cyanide for gold recovery, triazines for agricultural herbicides, methionine for animal food supplement, chelating agents for water treatment and many other fine and specialty chemicals [1]. Specific industrial processes involving cyanide include metal cleaning, reclaiming, and/or hardening, electroplating or photo processing. Hydrogen cyanide was first prepared in dilute solution by Scheele in 1782 and further as a pure compound by Gay-Lussac in 1815. In early years, hydrogen cyanide was sold in small crates of glass bottles for fumigation of old furniture for sale as antiques in England. Hydrogen cyanide is found in nature in some vegetable substances, e.g., bitter almond, peach stones, cherry and cherry laurel leaves.

Hydrogen cyanide is a weak acid; it has a linear structure, triply bonded ($\text{HC}\equiv\text{N}$). It is a colourless, volatile and extremely poisonous chemical compound whose vapour has a bitter almond odour. It melts at -14°C ; and boils at 26°C . It is miscible with water or ethanol in all proportions and is soluble in ether.

2.1.1 Manufacturing and processing

In early times hydrogen cyanide was manufactured from beet sugar residues and recovered from coke oven gas. These methods were replaced by the Castner process in which coke and ammonia were mixed with liquid sodium to form sodium cyanide and was contacted with sulphuric acid, to liberate hydrogen cyanide gas, which was condensed for use. This process has since been implemented in large-scale plants, using ammonia and hydrocarbons. There are three main commercial routes for hydrogen cyanide production. The main dominant commercial process is the Andrussow process (eqn 2.1), which involves the reaction of ammonia, methane and air over a platinum catalyst at high temperature. The second process is called the Blausaure – Methan-Ammoniak (BMA) process which involves the reaction of ammonia and methane in the

absence of air. This process was developed by Degussa in Germany and is therefore called the Degussa process (eqn 2.2). Hydrogen cyanide can also be obtained as a by-product in the manufacture of acrylonitrile by the ammoxidation of propylene which is called the Sohio process (eqn 2.3).

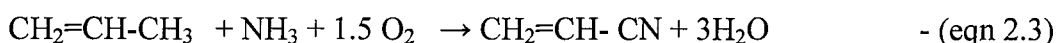
Andrussow process (ammoxidation of methane, aerobic) [2, 3]



Degussa process (ammonolysis of methane, anaerobic) [4, 5]



Sohio process (ammoxidation of propylene) [6]



These commercial processes use precious metal catalysts (90% Pt/10% Rh in gauze form) and the catalyst temperature is about 1100°C [7]. During the Andrussow process, prevention of ammonia and hydrogen cyanide decomposition is one of the critical aspects of successful operation. An advantage of the Degussa process is the useful hydrogen waste gas, but the disadvantage is the high investment and maintenance for the converter.

On the other hand, the Nitto process uses methanol instead of methane for the production of hydrogen cyanide (eqn 2.4). This process is considered to be superior in operability due to the relatively low reaction temperature of 400-500°C, whereas the other processes, are carried out at a high temperature around 1000°C using expensive platinum based catalysts [8].

Nitto process (ammoxidation of methanol, aerobic)



Further, methanol is more convenient than methane because of its ease in storage and transport; fewer restrictions on plant locations. Moreover, methanol ammoxidation to hydrogen cyanide uses an inexpensive stable iron antimony oxide based catalyst which has high selectivity and is discussed later in this chapter.

2.1.2 Ammoxidation catalysis

Ammoxidation catalysis is an industrially important process that is used to produce the two most commercially important nitrile chemicals, acrylonitrile, (C_3H_3N) and HCN. Ammoxidation (or alternatively, oxidative ammonolysis) is a relatively new catalytic process which produce nitriles in a single step directly from hydrocarbon, air and ammonia. Ammoxidation catalysis was first technically observed by Wohl (1922) on naphthalene over V_2O_5 . Systematic investigation of the catalytic ammoxidation of alkenes, alcohols, alicyclics and alkyl aromatics started in the 1950s and developed mainly during the 1960s. Nitrile formation from hydrocarbons is influenced by the structure of the reactant hydrocarbon, nature and composition of the catalyst used. From experiments and patent literature on ammoxidation it is understood that oxidation and/or oxidative dehydrogenation processes play an important part in the reaction. Generally, any organic molecule undergoing selective catalytic oxidation to an aldehyde has a tendency to undergo selective ammoxidation producing the corresponding nitrile molecule. In other words, when the ammoxidation reaction produces a nitrile, oxidation leads to the corresponding aldehyde or acid. Table 2.1 lists both selective oxidation and ammoxidation reactions of the same compound.

The selectivity and yield of the nitrile product are higher with alcohol ammoxidation than with other hydrocarbons, like alkenes and alkanes, because an alcohol substrate is partially oxidised and activated more effectively than corresponding alkene and alkane. The low pK_a values of alcohol (~ 16 for methanol) [10] and the acid-base character of metal oxide catalysts, allows this step to be easily facilitated by a number of (amm) oxidation catalysts and allow the selective ammoxidation of alcohols to be carried out under milder reaction conditions, generally at temperatures around $400^\circ C$.

Table 2.1 - Selective oxidation and ammoxidation reaction of some corresponding compounds [9]

Selective oxidation	Selective ammoxidation
Propylene oxidation to acrolein $\text{CH}_2=\text{CHCH}_3 + \text{O}_2 \rightarrow \text{CH}_2=\text{CHCHO} + \text{H}_2\text{O}$	Propylene ammoxidation to acrylonitrile $\text{CH}_2=\text{CHCH}_3 + \frac{3}{2} \text{O}_2 + \text{NH}_3 \rightarrow \text{CH}_2=\text{CHCN} + 3 \text{H}_2\text{O}$
Toluene oxidation to benzaldehyde $\text{C}_6\text{H}_5\text{CH}_3 + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{CHO} + \text{H}_2\text{O}$	Toluene ammoxidation to benzonitrile $\text{C}_6\text{H}_5\text{CH}_3 + \frac{3}{2} \text{O}_2 + \text{NH}_3 \rightarrow \text{C}_6\text{H}_5\text{CN} + 3 \text{H}_2\text{O}$

Ammoxidation reactions are generally irreversible and highly exothermic. Table 2.2 gives thermodynamic information for some selected ammoxidation reactions.

Table 2.2 - Thermodynamic information of some selective catalytic ammoxidation reactions and non-selective oxidation reactions [9]

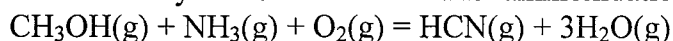
Ammoxidation reaction	$\Delta H_{\text{reaction}}^{\circ}$	$\Delta G_{\text{reaction}}^{\circ}$
	kJ (700K)	kJ (700K)
$2\text{HCHO} + \text{O}_2 + 2\text{NH}_3 \rightarrow 2\text{HCN} + 4\text{H}_2\text{O}$	-364	-412
$\text{CH}_3\text{OH} + \text{NH}_3 + \text{O}_2 \rightarrow \text{HCN} + 3\text{H}_2\text{O}$	-342	-444
$\text{CH}_4 + 1.5\text{O}_2 + \text{NH}_3 \rightarrow \text{HCN} + 3\text{H}_2\text{O}$	-465	-530
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-800	-800
$2\text{NH}_3 + 1.5\text{O}_2 \rightarrow \text{N}_2 + 3 \text{H}_2\text{O}$	-632	-680

Table 2.2 shows that non-selective reactions are found to be thermodynamically favourable leading to complete oxidation products like CO_2 , N_2 and H_2O than the selective reactions.

To enhance the rate of the selective ammoxidation reactions to high nitrile yields, a suitable catalyst must be used and normally selective ammoxidation is practiced commercially using heterogeneous solid catalysts [11].

The thermodynamic data for the formation of hydrogen cyanide from methanol and ammonia by ammoxidation and ammonolysis and the formation of water from the product hydrogen in the reaction are given in Table 2.3, 2.4 and 2.5.

Table 2.3 - Calculated thermodynamic data of methanol ammoxidation to HCN :



T (°C)	ΔH° (kJ)	ΔS° (J/K)	ΔG° (kJ)	K	Log(K)
0	-343.934	128.118	-378.929	2.94E+72	72.469
100	-341.325	136.306	-392.187	8.02E+54	54.904
200	-339.419	140.865	-406.069	6.80E+44	44.833
300	-338.171	143.275	-420.289	2.03E+38	38.307
400	-337.489	144.384	-434.681	5.41E+33	33.733
500	-337.307	144.644	-449.138	2.22E+30	30.347
600	-337.515	144.395	-463.593	5.44E+27	27.736
700	-338	143.871	-478.008	4.57E+25	25.66
800	-338.686	143.202	-492.363	9.28E+23	23.967
900	-339.544	142.438	-506.645	3.63E+22	22.56
1000	-340.518	141.641	-520.849	2.35E+21	21.371

Table 2.4 - Calculated thermodynamic data of methanol ammonolysis to HCN :



T (°C)	ΔH° (kJ)	ΔS° (J/K)	ΔG° (kJ)	K	Log(K)
0	139.229	215.239	80.437	4.14E-16	-15.383
100	143.819	229.603	58.143	7.25E-09	-8.14
200	147.692	238.834	34.688	1.48E-04	-3.83
300	150.833	244.879	10.481	1.11E-01	-0.955
400	153.302	248.862	-14.22	1.27E+01	1.104
500	155.162	251.448	-39.245	4.48E+02	2.652
600	156.498	253.079	-64.478	7.20E+03	3.858
700	157.416	254.078	-89.84	6.65E+04	4.823
800	157.991	254.643	-115.279	4.09E+05	5.612
900	158.256	254.881	-140.758	1.85E+06	6.268
1000	158.273	254.896	-166.248	6.63E+06	6.821

Table 2.5 - Calculated thermodynamic data of water formation from the reaction of hydrogen and oxygen : $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) = 2\text{H}_2\text{O}(\text{g})$

T (°C)	ΔH° (kJ)	ΔS° (J/K)	ΔG° (kJ)	K	Log(K)
0	-483.163	-87.121	-459.366	7.12E+87	87.852
100	-485.144	-93.298	-450.33	1.11E+63	63.044
200	-487.111	-97.97	-440.757	4.60E+48	48.663
300	-489.004	-101.603	-430.77	1.83E+39	39.262
400	-490.791	-104.478	-420.461	4.26E+32	32.629
500	-492.469	-106.804	-409.893	4.96E+27	27.695
600	-494.013	-108.685	-399.115	7.56E+23	23.878
700	-495.416	-110.207	-388.168	6.87E+20	20.837
800	-496.677	-111.441	-377.083	2.27E+18	18.356
900	-497.799	-112.442	-365.888	1.96E+16	16.293
1000	-498.791	-113.255	-354.601	3.55E+14	14.55

2.1.3 Ammoxidation catalysts

Catalytic ammoxidation of alcohols was a direct outgrowth of propylene ammoxidation technology developed for acrylonitrile manufacture. Sn-Sb-O based catalysts were found to be effective for the propylene ammoxidation reactions [12, 13] and using the same catalyst, high yields of up to 88% of HCN were obtained from methanol ammoxidation. This led to patents for Bi-Mo-O [14, 15] and Fe-Sb-O [16, 17] ammoxidation catalysts.

Various catalysts have been proposed for methanol ammoxidation to hydrogen cyanide.

Some of them are

- platinum-rhodium netting [18,19],
- molybdenum oxides [20],
- tin antimony oxides [21],
- iron antimony oxides and
- metal phosphates [22-24]

Among them, it was found that Fe-Sb-O based catalysts play a very important role in methanol ammoxidation to hydrogen cyanide. In 1975 Sedriks commented that the most common commercial process for direct production of hydrogen cyanide (HCN) was based on the Andrussov process and though other commercial routes existed, they were less common [25]. Patents assigned to Nitto Chemical Industries and Sumitomo

Chemical Company on vapour phase ammoxidation of methanol over supported catalysts is concerned more about the non commercial route [14].

2.1.4 Iron antimony oxide (FSO)

Very limited literature is available on the ammoxidation of methanol to hydrogen cyanide using iron antimony oxides. Iron antimony oxide has industrial importance due to its catalytic performance in selective oxidation of hydrocarbons. Initially, iron antimony oxide was developed as a fluid-bed catalyst mainly for acrylonitrile production by ammoxidation of propylene (Sohio process) in 1960, followed by development of a series of improved FSO catalysts for the Sohio process. Later it was found that it could catalyse ammoxidation of other organic compounds like alcohols and aromatic hydrocarbons. In 1974, Nitto found Fe-Sb-O catalysts also catalyse the synthesis of hydrogen cyanide through ammoxidation of methanol and the first commercial plant was constructed by Nitto. FSO contributes to low NO_x emission and almost complete ammonia utilisation. Also it leads to simple, energy-saving and environmentally friendly processes. The catalyst is inexpensive and stable and the resulting process is economical and superior in operability.

Apart from ammoxidation of methanol and propylene, iron antimony oxide catalysts are active and selective in several reactions, including:

- oxidative dehydrogenation of butane
- oxidative dehydrogenation of ethyl benzene
- oxidation of methanol and alkyl aromatics
- propane ammoxidation and
- propene oxidation

The active component of the iron antimony oxide is FeSbO₄ and can be prepared from Fe₂O₃ and Sb₂O₃ [26-28]. It can also be obtained by precipitation or mixing of hydrated antimony pentoxide with iron compounds. Amador stated that FeSbO₄ prepared by heating Fe₂O₃ with Sb₂O₃ at 1373K in air, is a rutile-type compound [29]. FSO also occurs as the mixed tripuhyite in nature. Li *et al.* reported that FeSbO₄ with excess Fe₂O₃ produces more mobile oxygen species and more active sites on the surface

resulting in better catalytic performance than the corresponding single oxide catalysts [30]. In addition, antimony oxide in the catalyst is responsible for selective partial oxidation as Sb (III) ions appear to act as sites for trapping gaseous oxygen and for generating mobile oxide ions [31].

2.1.5 Activity and physical properties of promoted FSO catalysts

Iron antimony oxide has good activity, stability and outstanding catalytic performance on adding selected promoters. Depending on the specific conditions of reaction, FSO can become deactivated gradually when used over a long period of time [32]. The catalytic activity of FSO can be improved by the addition of specific promoter additive elements such as Ni, Co, Cr, Te, Bi and Mo. The promoted FSO catalysts give high yields for the ammoxidation of various organic compounds such as olefins, alcohols, alkyl-substituted (hetero) aromatic compounds, etc [33]. From diffraction studies, FSO catalysts have a statistical rutile-like framework with Fe and Sb cations distributed in the octahedral sites between oxygen ions and the additive elements exist as solid solutions in the iron antimonate or form independent rutile or trirutile structures [34].

The ratio of iron and antimony in the catalyst is an important parameter for high yield and selectivity. In general, a Sb/Fe ratio of 1 or greater gives better selectivity in the desired product [35-37]. However, Teller *et al.* reported that if antimony content is increased more in the FSO catalyst, it leads to the formation of numerous fine Sb₂O₄ crystallites on the catalyst surface especially during the calcination process, which is undesirable for a commercial catalyst [37]. Carbuicchio proposed that excess antimony completely covers the iron antimonate catalyst surface in the form of Sb₂O₄ [35]. This could be avoided by addition of elements like Ni, Co, Cu, Zn and Mg. These components form antimonates with either rutile or trirutile structures to suppress the appearance of these Sb₂O₄ crystallites. Addition of Al, Cr or Ce to FSO, improves thermal stability and also prevents the formation of Sb₂O₄ crystallites. Methanol is very reactive and easily reduces iron antimony oxides which deteriorating quickly during ammoxidation of methanol. Under such conditions, unpromoted FSO catalysts are readily reduced to form antimony and ferrous oxide losing catalytic activity even under mild reaction conditions. Addition of V, Mo or W increases the redox stability of the catalyst. Among these additives, vanadium seems to be the most effective, but it has an adverse effect on the selectivity. On account of selectivity, molybdenum is found to be

preferable [38] but its rapid vaporisation causes some concern. The selectivity to the product can be increased by the addition of P, B, Te, Bi, K, and Cs. These elements function to adjust the acid-base properties, the adsorption-desorption properties, etc. Allen *et al.* studied the Te addition to FSO to increase the selectivity for acrylonitrile [39]. FSO containing phosphorus as the promoter component is also suitable for the ammoxidation of methanol to hydrogen cyanide. In spite of the decrease in the reaction rate, phosphorus contributes to the selectivity to hydrogen cyanide [40]. Further, Sb_2O_4 crystallites transform to SbOPO_4 , in the presence of phosphorus. As the phosphorus component increases, the SbOPO_4 phase changes into a different phase which is not yet identified, and then turns amorphous and the crystallites disappear completely.

After thorough studies by Sasaki *et al.* on promoters, vanadium and phosphorus were found to improve the performance of the catalyst synergistically [33]. Phosphorus increases the selectivity to hydrogen cyanide whereas vanadium increases the redox stability. Thus most of the commercial catalysts contain vanadium and phosphorus as the main additive elements to the FSO. Sasaki studied ammoxidation of methanol to hydrogen cyanide in the lower temperature range of 350 - 500 °C, and higher yield of HCN was obtained using Fe-Sb-P / Fe-Sb-P-V catalyst systems [7]. Due to the above mentioned properties, iron antimony oxide was used in this research project as part of the SOFC anode electrocatalyst.

2.2 Introduction to fuel cells

Fuel cells were originally envisioned in the nineteenth century when Sir William Robert Grove developed the simple concept of a fuel cell generating electricity by reversing water electrolysis from hydrogen and oxygen. The principle he discovered in 1839 remains the same even today as 'A fuel cell is an electrochemical device that continuously converts chemical energy into electrical energy (and some heat) for as long as fuel and oxidant are supplied'. The process involves the occurrence of electrochemical reactions with power generation when continuous non-mixing streams of fuel and air (oxidant) are supplied to the fuel cell. Initially the fuel cell was called gaseous voltaic battery by Grove, and later fuel cell by Ludwig Mond and Charles Langer (1889). The first fuel cell plant was built by Francis T Bacon (1959) to produce significant electric power. He constructed a hydrogen-oxygen cell using alkaline

electrolyte and nickel electrodes. Fuel cells are in general used as generators of electrical energy. Some of the main applications are currently seen as stationary electric power plants, auxiliary power units in transportation vehicles and on-board power for aircraft or space vehicles.

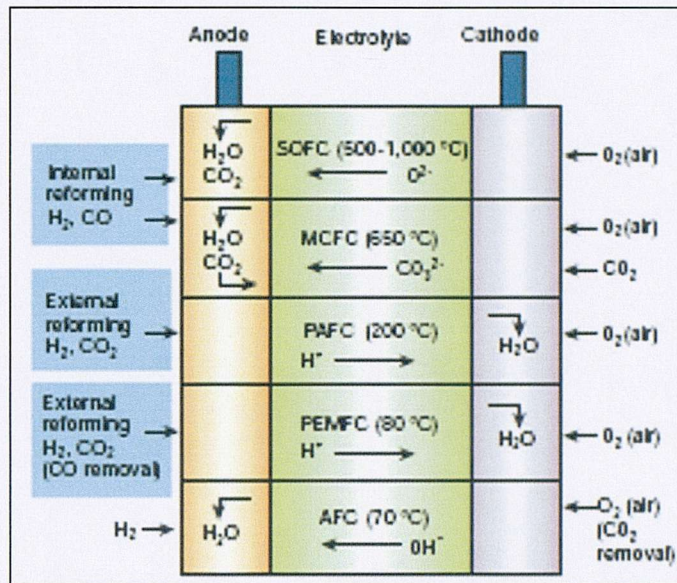


Figure 2.1 - Electrochemical reactions of fuel cell types [43]

Fuel cell technology is environmentally acceptable as the fuel cells have higher efficiency with reduced emissions of CO_2 , SO_x and NO_x for a given power output when compared with an internal combustion engine.

Five types of fuel cells are being developed around the world. The type of electrolyte used not only dictates the performance characteristics of the fuel cell but also gives the fuel cell its name. The chief difference between each are the materials used for the electrolyte membrane, anode and cathode. The characteristics of the different types of fuel cell are summarized in Figure 2.1 and Table 2.6. Of the fuel cell technologies, AFC and PAFC are the first generation fuel cells. These are the oldest and mature technologies used today, but have proved not viable for commercial exploitation in civilian mobile or stationary applications. MCFC, PEM and SOFC are second generation fuel cells which are currently under development. SOFC and MCFC are high temperature fuel cells and as SOFC is the main focus of this research work, it is discussed in more detail.

Table 2.6 - Different types of fuel cells and their features

Features		Fuel cell type			
Name	Alkaline (AFC)	Polymer electrolyte (PEM)	Phosphoric acid (PAFC)	Molten carbonate (MCFC)	Solid oxide (SOFC)
Electrolyte	Potassium hydroxide	Ion exchange membrane	Phosphoric acid	Alkali carbonates mixture	Yttria stabilised zirconia
Operating temperature (°C)	90-100	50-100	150-220	600-700	600-1000
Charge carrier	OH^-	H^+	H^+	CO_3^{2-}	O^{2-}
Electrolyte state	Immobilized liquid	Solid	Immobilized liquid	Immobilized liquid	Solid
Cell hardware	Metal based	Carbon- or metal based	Graphite-based	Stainless steel	Ceramic
Feed for fuel Processor	Pure H_2	Pure H_2	Natural gas, methanol, gasoline, diesel, jet fuel	Gas from coal or biomass, natural gas, gasoline, diesel, jet fuel	Gas from coal or biomass, natural gas, gasoline, diesel, jet fuel
Oxidant for cell	O_2 / air	O_2 / air	O_2 / air	O_2 / air/ CO_2	O_2 / air
Cell efficiency (%LHV)	-	40-50	40-50	50-60	50-60
System output	10kW – 100kW	<1kW – 250kW	50kW – 1MW	<1kW – 1MW	5kW – 3MW

2.3 Oxide ion conducting Solid Oxide Fuel Cell (SOFC)

SOFCs are very efficient devices to produce electrical power from direct conversion of chemical fuels. Though Nernst and his colleagues proposed the basic ideas and materials during the end of the 19th century, considerable advances both in theory and experiment are still being made over 100 years later. A major challenge in SOFC development involves long-term durability of electrode materials for operation with the various fuels of interest including H₂, CO and CH₄. The anode and cathode components of the SOFC require different materials based upon their need to resist chemical attack in the reducing and oxidising environments respectively. Furthermore, both electrode components must be chemically and thermo mechanically compatible with the electrolyte. Because of the temperature cycling that a practical fuel cell would undergo (due to start up and shut down) the materials must have similar coefficients of thermal expansion (CTE's) [44].

2.3.1 Components of the SOFC

The high operating temperatures of SOFC are mainly dictated by the slow oxygen transfer rate through the electrolyte at lower temperatures. This combined with the multi-component nature of the fuel cell and the required life expectancy of several years restricts the choice of materials for cell and manifold components.

2.3.1.1 Electrolyte

The SOFC electrolyte is an oxide ion conducting ceramic material and its main function is to conduct ions between the anode and the cathode. As the electrolyte separates the fuel from the oxidant in the fuel cell, it must be stable in both the reducing and oxidising environments, impermeable to the reacting gases, and have sufficiently high ionic conductivity and low electronic conducting at the operating temperature. Figure 2.2 shows a plot of the ionic conductivities of some candidate solid electrolytes. Until recently SOFCs have been based on the most common electrolyte of zirconia stabilised with addition of a percentage of yttria (Y₂O₃) for the high temperature SOFC to achieve acceptable power densities. YSZ is favoured over many other oxide materials due to its good chemical stability in reducing and oxidising environments, compatibility with other fuel cell components, non-toxicity and relatively low cost. Above 700 °C, YSZ becomes a good conductor of oxide ions (O²⁻) and therefore is used for high temperature SOFC (800-1100 °C). Some of the

alternative metal oxides used to stabilise zirconia are CaO, MgO and some rare-earth oxides [45, 46]. These oxides are highly soluble in zirconia forming cubic fluorite solid solutions giving a high stability at high temperature but their conductivities are inferior to YSZ.

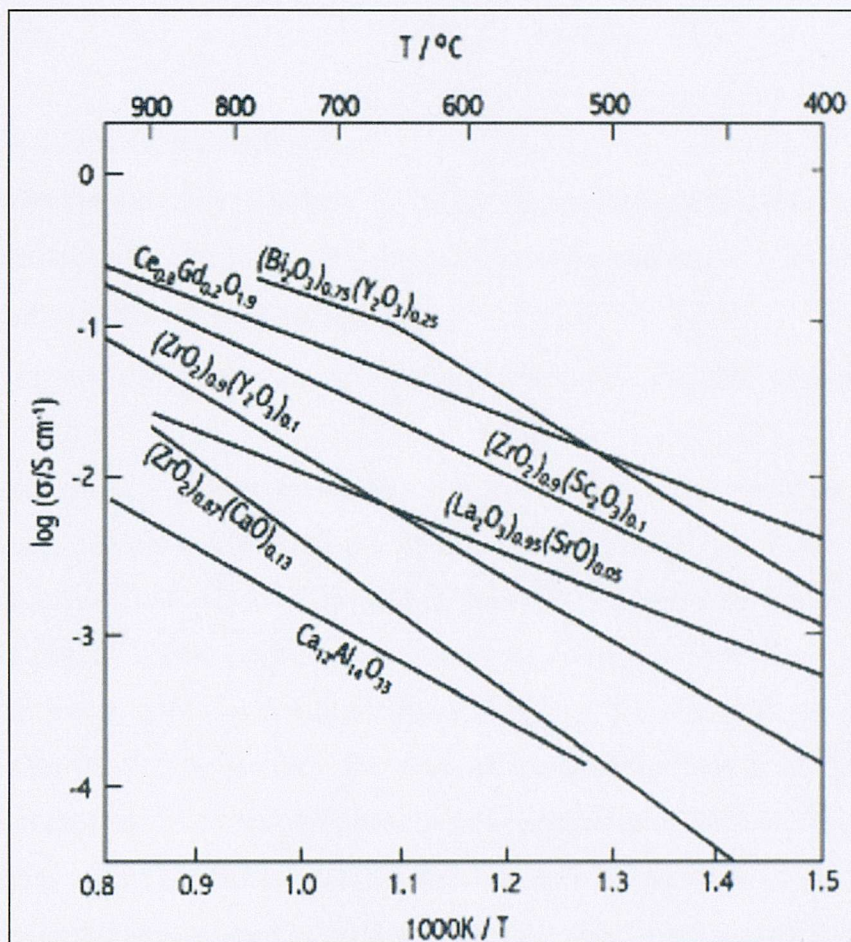


Figure 2.2- Specific ionic conductivities of certain solid oxide electrolytes [47]

Doped ceria electrolytes replace zirconia for reduced temperature operation below 700°C. CeO₂ doped with divalent or trivalent oxide develops high oxygen-ion conductivity at elevated temperatures. However, the ionic conductivity regime is narrow at above 700°C. In reducing environments, ceria based systems lose oxygen and develop electronic conductivity [46]. In addition to stabilised zirconia and doped ceria, other potentially attractive SOFC electrolytes include perovskites like lanthanum gallate and calcium titanate. Doped bismuth oxide has high conductivity at 600-800°C but due to its easy reduction, high reactivity, and very low strength and toughness; it is not practical for SOFC [48, 49].

2.3.1.2 SOFC anodes

The main functions of the anode are to facilitate the adsorption and oxidation of hydrogen (or other oxidisable gases) from the fuel feed, thus permitting the oxygen ions from electrolyte to react and release electrons to the external circuit. The anode must therefore be both an electronic and ionic conductor. A good anode must meet the following criteria:

- Stability in a reducing environment
- Electronic conductivity of at least $50 \Omega^{-1} \text{cm}^{-1}$ at operating temperatures [50]
- Electrocatalyst for oxidation of a range of fuel compositions
- CTE that matches other cell components ($\sim 13 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$) [51]
- Have chemical and mechanical stability with electrolyte and interconnect

These criteria are usually satisfied by using a composite mixture of a metal and ionic conductor (cermet). These factors limit the choice to nickel, cobalt and noble metals for the metallic component of SOFC anodes at elevated temperatures. Nickel is the most common anode electrocatalyst and shows high activity for H_2 , CO and hydrocarbon oxidation, good reforming activity and relatively low cost in comparison to precious metals [52-56]. It has been the main anode material used in SOFC since 1964, largely because of its known performance and economics. Unlike the electrolyte, the anode must be porous in nature as well as stable at high temperature. In most cases the anode is fabricated as a mixture of nickel oxide with electrolyte and then the NiO is reduced to metallic nickel on exposure to the anode feed in the SOFC thus increasing the anode porosity. The porosity increase is caused by the volume change as a result of oxygen loss due to the conversion of the oxide to its metallic form. As the characteristics and the stability of the anode microstructure are considered to significantly affect electrode performance, the control of the electrode microstructure is one of the most important factors in the preparation of nickel/YSZ anodes. A minimum of 30 vol% nickel in the cermet is required to meet the CTE and electronic conductivity requirements [43, 57 and 58]. If the nickel content of the anode cermet is too high, the thermal mismatch with the electrolyte will be high which will lead to electrolyte cracking or anode delamination. In addition to excellent electrochemical performance, the fabrication of Ni cermets is quite simple in principle.

Relatively few new materials have been proposed to replace the Ni-YSZ cermet and none has proven to match its performance except by doped ceria replacing YSZ. Recent works have shown that a composite Ni/CGO anode has excellent IT-SOFC properties at 700°C and below [59-63]. Doped ceria provides a high ionic conductivity allowing oxide ion diffusion farther into the anode and a structural support for the anode preventing sintering of nickel particles. Ceria being a mixed ionic and electronic conductor (MIEC), it increases the number of reaction sites by facilitating electron and oxygen ion transport in the anode cermet, whereas in Ni-YSZ, nickel is responsible for electronic and YSZ for ionic conductivity. A number of researches have been carried out on nickel/ceria cermet anodes showing sufficiently good performance with both ceria and zirconia based SOFC electrolytes [59-66].

Other than improving the electrical performance, ceria in Ni-CGO anode cermets enhances the resistance to carbon deposition especially on hydrocarbon oxidation [67]. Methane can be oxidised on a CGO electrode at 1000°C with an oxidation rate higher than that for Ni-YSZ [68]. The amount of dopant added to the Ni-CGO anode is another important aspect to be considered. Since $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO-10) has good stability, it is considered to be a good choice to be added in the anode cermet with nickel. 85:15 mol% Ni-CGO anode showed a higher power density with methane (90 mW cm^{-2}) at 600°C than did a 75:25 mol % mixture, indicating that a high nickel content gives better results [69]. On balance, 50-60 mol% Ni in an anode optimises electrocatalytic reaction, porosity, electronic conductivity and reforming activity, and maintains low thermal expansion stresses between the anode and the electrolyte [70].

Other than nickel catalysts, Brett *et al.* investigated the performance of Cu-ceria based catalysts in the steam reforming of methanol in an IT-SOFC [71]. However, Cu is a poor oxidation catalyst for the activation of hydrocarbons and the anode is difficult to fabricate due to the low melting temperature of CuO. Ni/Cu based cermet anodes have been found to combine good methanol reforming and electrocatalytic activity for hydrogen oxidation leading to low area specific resistance (ASR) [71, 72].

2.3.1.3 SOFC Cathodes

SOFC cathodes also present significant issues in designing and operating SOFCs. As it functions in a highly oxidising environment, base metals cannot be used in the cathode and further noble metals like platinum, palladium and gold, though good cathodes are too expensive.

A cathode that displays good performance must meet the following criteria:

- Stable in an oxidizing environment and at temperatures up to 1000 °C
- Electronic conductivity of at least $50 \Omega^{-1}\text{cm}^{-1}$ [73]
- Porosity of >30 % [73]
- Exhibit good catalytic activity for oxygen reduction
- Good chemical compatibility with other cell components
- CTE that matches other cell components

Silver has relatively good electrode performance on YSZ electrolyte but it is potentially unstable because of its low melting temperature and volatility. The development of cathodes has mainly focused on the doped lanthanum manganite as this material exhibits the properties mentioned above. At present the most common cathode material used in SOFC systems is Sr-doped lanthanum manganite (LSM). LSM has a high electrical conductivity in oxidising atmospheres, compatibility with YSZ electrolyte and acceptable thermal expansion match with other cell components. CGO electrolyte enables the SOFCs to operate at relatively low temperatures of around 500- 600°C. A number of other materials such as strontium doped lanthanum cobaltite (LSC) have much higher electronic conductivity and catalytic activity than LSM [73]. However, LSC presents the disadvantages of a high thermal expansion coefficient and low stability. For use with ceria-based electrolyte, (La, Sr) (Co, Fe) O₃ based cathodes have been developed. A typical composition is La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃ (LSCF) and is stable throughout a wide range of temperature. Tai *et al.* carried out substantial studies of LSCF and suggested that it is a potential cathode for SOFCs operating at 600-800°C [74]. Ralph *et al.* [75] reported that the area specific resistance of LSCF on CGO electrolyte was 0.3 ohmcm² at 700°C. Dusastre and Kilner [76] investigated the electrochemical properties of the interface between composite 30-70

wt% CGO-LSCF composite which resulted in a significant reduction in the ASR to typically less than 1 ohm cm^2 at 590°C .

2.3.2 SOFC Fuels – Ammonia and methanol

Indirect hydrogen sources are appreciable for fuel cell systems, and it is advantageous to use them without dilution or pre-reaction if possible. The heat required for the endothermic reforming or decomposition reactions leading to hydrogen production can be supplied from the waste heat from the fuel cell which also helps to cool the cell extending its life-time. Methanol and ammonia are two major products of the chemical industry and both are easy to handle and transport. Methanol and ammonia are almost equal indirect hydrogen carriers based on cost and overall efficiencies. So far methanol has drawn sufficient attention that a methanol economy has been proposed. Ammonia has an advantage with respect to methanol in that no carbon is generated during cracking whereas severe carbon poisoning often occurs with methanol and low temperature electrocatalysts. Also ammonia has a higher specific energy than methanol and a system using ammonia as feedstock is simpler in principle.

2.3.2.1 Methanol

The use of liquid fuel is often preferred for commercial use due to its ease of carriage, less safety concern and existing supply infrastructures. For IT-SOFCs operating at temperatures as low as 500°C , methanol is considered to be a suitable fuel [77-80]. Coutelieris *et al.* [81] considered the feasibility of different fuels, (e.g. methane, methanol, ethanol and gasoline) for SOFCs and concluded that methanol and ethanol are very promising alternatives to hydrogen in terms of emf output and efficiency.

2.3.2.2 Methanol reforming

Hydrogen is commonly used in fuel cells and is regarded as one of the most important energy sources for future production of electricity, heat and power. However, if hydrogen for an SOFC, is produced from fossil fuels by external reforming, there is a significant compromise in overall efficiency. The operating temperature of an SOFC is sufficient to provide heat for the endothermic reforming reaction of hydrocarbons.

Methanol can be externally reformed outside the SOFC to provide hydrogen rich gas feed to the fuel cell. However internal reforming of methanol is a more desirable

option. Noble metals like platinum and palladium are known good catalysts for methanol reforming. Although methanol reforming has been investigated extensively, there is limited literature on the use of methanol in SOFCs. Ni-based cermets are the most commonly used anodes with methanol fuel in SOFC at temperature less than 700°C. Sahibzada *et al.* have studied cell performance of a cell consisting of CGO electrolyte, a NiO-YSZ cermet anode and LSCF cathode and different fuel types such as direct methanol, moist hydrogen, internal and external reformed methanol. The addition of palladium to the NiO-YSZ anode was found to promote the internal reforming of methanol [82].

Steam reforming of hydrocarbons is the most popular way of converting light hydrocarbons to hydrogen. Several researchers have worked on the catalytic reforming of methanol with steam [80- 85].

Jiang *et al.* [87] investigated the methanol-steam reforming reaction using a copper based catalyst which resulted negligible carbon deposition. $\text{Ce}_{1-x}\text{Cu}_x\text{O}_{2-x}$ type mixed oxide catalysts were investigated by Liu *et al.* [86] and they showed high selectivities for methanol steam reforming. Gomez-Sainero *et al.* found that $\text{Pd/CeO}_2\text{-Sm}_2\text{O}_3$ is another effective catalyst for methanol steam reforming producing hydrogen in IT-SOFC [79].

2.3.2.3 Carbon formation

Carbon deposition on the catalyst is one of the major concerns with hydrocarbon fuels resulting in its deactivation and poor durability and performance of the system. The possible carbon formation reactions on the catalyst surface are:



The degree of carbon formation depends on the type of catalyst used in the fuel cell system and therefore it is an important aspect in catalyst selection. Carbon deposition can be reduced by using CeO_2 as a major component in the anode [88]. The high

resistance of CeO_2 toward carbon deposition is due to its highly mobile oxygen vacancies which can bring oxygen rapidly to its surface. Various researchers have reported on the oxidation of gaseous hydrocarbons at high temperature at the CeO_2 surface (methane [89- 91]; ethane and propane [92] and carbon monoxide [93]).

2.3.2.4 Addition of steam

Addition of steam to the hydrocarbon can reduce, or even prevent carbon deposition but it reduces electrical performance and increases complexity. The effectiveness of the steam addition depends on the steam to carbon ratio (S/C ratio).

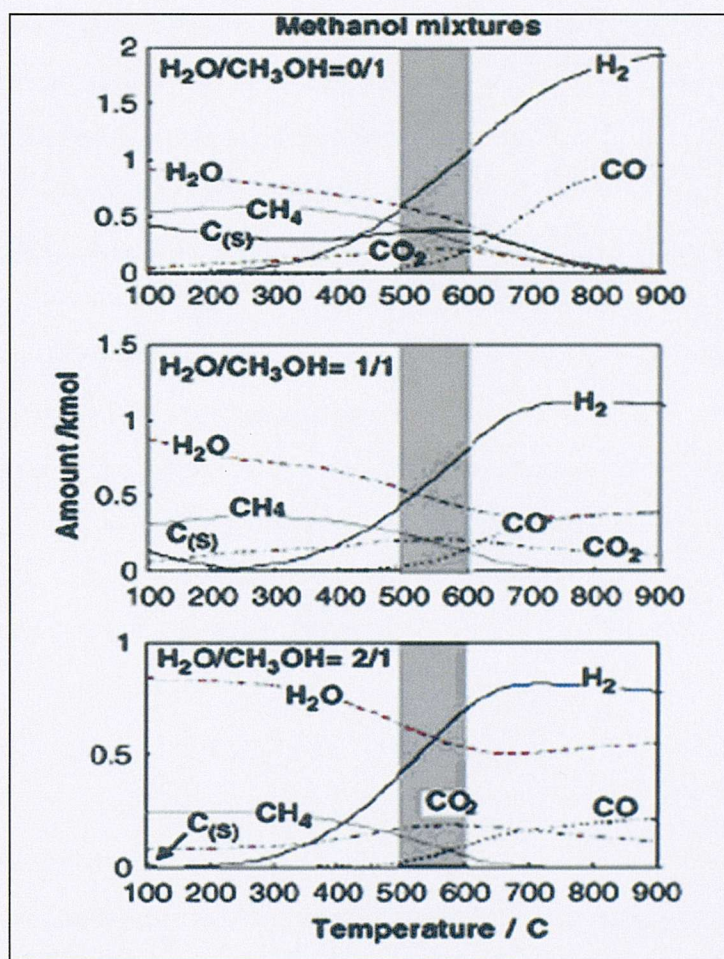


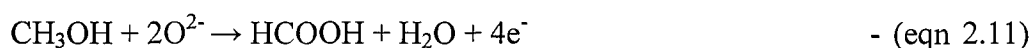
Figure 2.3 - Thermodynamically calculated equilibrium compositions of steam/methanol mixtures with temperature. The shaded band is a possible range of operating temperatures [71].

If the S/C ratio is low, carbon formation (eqn 2.5), and also carbon monoxide and carbon dioxide methanation reactions may occur as:



Figure 2.3 shows the S/C ratio thermodynamically required to avoid carbon formation with methanol. Alcohols like methanol and ethanol can mix easily with water, so that they can be premixed with water of the required amount without any need for additional fuel processing. The thermochemical calculations were performed to reveal equilibrium gas compositions and the amount of water to be added to prevent carbon formation [94-96]. Sasaki *et al.* [94] concluded that no carbon deposition is thermodynamically expected above 230°C for S/C = 1.0 and above 140°C for S/C = 2. Further, on comparing with the methane-steam system, it was found that less water is sufficient with methanol to avoid carbon deposition especially at higher temperatures. Saunderson *et al.* [97] studied using methanol and ethanol with Ni-based anodes without steam and found good cell performance without any obvious carbon deposition.

Krishnan *et al.* [98] and Lu *et al.* [99] studied the cell performance on direct electrochemical oxidation of hydrocarbons using Cu/CeO₂/YSZ anodes and reported negligible carbon deposition in the absence of steam. They suggested that the electrochemical oxidation of methanol occurs via intermediate steps:



2.3.2.5 Ammonia

Ammonia is an inorganic hydrogen carrier and is the highest volume chemical produced worldwide. Ammonia is readily available, has high energy content, exhibits a narrow explosion limit, easy storage and transportation, low level detection and decomposes relatively easily with no need for added steam or oxygen. However, it has received relatively little consideration for use as a direct fuel for fuel cells although there is current interest in using ammonia as a fuel in intermediate temperature fuel cells [100-104].

Catalytic cracking of ammonia (ammonia decomposition) is represented as:



Numerous supported metals (including Fe, Ni and Ru) and metallic platinum have been used for ammonia decomposition [105- 109]. Wojcik *et al* reported that ammonia gave a similar power performance to that of hydrogen in a SOFC with a silver anode coupled with an iron catalyst [100].

2.4 Proton conducting fuel cell

In the previous section, oxide ion- conducting solid oxide fuels cells were discussed. In a similar way, proton conducting SOFCs (PCFC) may be used in a ceramic fuel cell reactor. In principle, a chemical gradient is established across the ceramic electrolyte and protons are transported from the anode and react with oxygen at the cathode. In the 1980s, ceramic materials based on strontium and barium cerates were discovered as having high protonic conductivities [110,111]. Figure 2.4 illustrates the comparative proton conductivities of the many oxides that have been investigated in the literature.

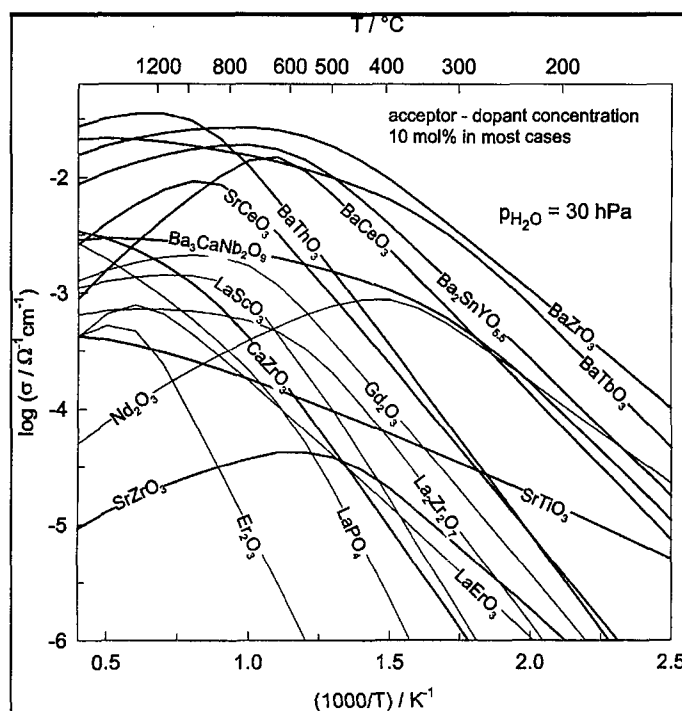


Figure 2.4- Proton conductivities of various oxides [112]

The majority of high temperature proton conductors being investigated for their high ionic conductivity are perovskite-type oxides represented by the general chemical formula, ABO_3 . The perovskites based on SrCeO_3 and BaCeO_3 as well as analogous oxides, where Ce^{4+} is substituted by Zr^{4+} , are good solid state proton conductors. In hydrogen containing atmospheres and at elevated temperatures, these oxides exhibit protonic conduction when doped with trivalent cations. Ma *et al.* [113] have shown that at high partial pressures of oxygen, doped BaCeO_3 , systems also exhibit a mixed oxide ionic and p -type (hole) electronic conduction, while low oxygen partial pressures their conduction is almost pure protonic.

2.4.1 Suitable reactions for the proton conducting fuel cells

The use of a proton conductor as the solid electrolyte for SOFCs requires hydrogen as the fuel. This may be provided as pure hydrogen or as in situ thermally available hydrogen from hydrocarbons or other hydrogen sources such as alcohols or ammonia through reforming or dehydrogenation routes. In the latter case, using a high temperature proton conducting electrolyte may allow for some cogeneration of useful chemicals beside electricity. Power output characteristics have been investigated for SOFCs using various high temperature proton conducting electrolytes. A fuel cell using Y:BaCeO_3 as the electrolyte with metal electrodes and TiH_2 as hydrogen source was found to operate stably for at least 10 hours at 600°C [114].

Iwahara *et al.* [115] performed fuel cell tests using ethane fuel, 5 % Yb: SrCeO_3 as the solid electrolyte and platinum as electrode material. They drew a stable and steady current and demonstrated an e.m.f value of 0.96V at 900°C . Various fuels have also been used in PCFCs with BaCeO_3 -based electrolytes which have a higher conductivity than SrCeO_3 -based oxides. Recent investigations of methane PCFCs using Y:BaCeO_3 as the electrolyte material have led to some interesting results demonstrating the possibility of self-regulated methane reforming [116,117]. Suggestions have been made in the literature for other possible uses of proton conducting ceramics in novel PCFCs for methane-coupling [118]; H_2S fuelled PCFCs for desulphurisation [119,120], and zero-emission methane cracking [119]. Panagos *et al.* [121] have shown that industrially important catalytic hydrogenation reactions that are equilibrium-limited, such as ammonia synthesis or methanol production, can be carried out beneficially in a proton- conducting CFCR. Their results showed that

using CFCR similar conversions could be achieved at atmospheric pressure, whereas a conventional catalytic reactor would require an operating pressure of over 100 bars. Maffei *et al.* [122] reported a direct ammonia fuel cell using a doped BaCeO₃ proton-conducting electrolyte at 700°C. Other commonly used proton-conducting electrolytes perovskite like SrZrO₃ and BaZrO₃ have been used in ammonia fuel cells at temperatures lower than those having oxide ion conducting electrolytes, such as lanthanum gallate.

In general, there is potential for using PCFCs for cogeneration of chemicals and electrical power. For HCN synthesis the main advantage of using a PCFC is that the product water does not dilute the fuel/ product stream as much. The main issues still requiring improvements include reducing the ohmic drop contribution to the polarisation of the cell mainly through advancement of thin membrane fabrication technology as well as improving the choice of electrode materials to make them more suited to the fuel-oxidant environment of PCFCs.

2.5 Cogeneration of chemical energy and electricity

The fuel cell is an electrochemical device, which converts the chemical energy of a fuel and an oxidant into electric power. A fuel cell reactor for chemicals and energy cogeneration is a new potential application for fuel cell systems. The processes involved in cogenerating energy and chemical substances are very similar to those involved in conventional heterogeneous catalysis [123, 124]. It appears that the catalysts used in heterogeneous chemical processes can also be suitable electrocatalysts for cogeneration processes. This process requires an overall reaction having a negative free energy change (ΔG) for the total process; however the chemical production is now the main motivation and the electrical power is the by-product. This concept was first proposed by Langer *et al.* [125] who investigated the electrochemical hydrogenation of organic compounds. The recent advances in fuel cell technology provide new impetus for investigating the electro-synthesis of chemicals with simultaneous cogeneration of electrical energy. The chemical cogeneration process involves a conventional fuel cell reactor, in which the reactant fuels and the oxidant are introduced into the respective anode and cathode compartments. An external load to extract the electrical energy and an arrangement is required for recovering the main chemical products formed in the reaction. In a

conventional fuel cell, the electrochemical oxidation of hydrogen at the anode and oxygen reduction at the cathode produces electric energy and pure water as chemical by-product or carbon dioxide with a hydrocarbon- based fuel. Some of the main advantages of cogeneration process are as follows:

- Cogeneration of chemical products and electricity can be more efficient overall.
- The size of the reactor could be reduced and the reactants more easily separated from the products.
- The process selectivity can be controlled by changing the external load or the electrode catalyst.

The chemicals produced in the cogeneration processes in the fuel cell must have commercial value. The limited number of publications on the electro cogeneration process indicates that research in this field is still in the primary stage. The main focus so far has been to investigate only the feasibility of the processes but the situation is slowly improving from the commercial point of view as fuel cell technology advances.

Some different cogeneration processes that have been considered are summarised in Table 2.7. Since this research work is concerned with SOFC, the main industrial application of electro cogeneration in SOFCs and other fuel cell applications are simply outlined in Table 2.7. Langer *et al.* [125] demonstrated the first FC producing hydroxylamine in acid media. Formation of hydroxylamine is industrially important as it is the intermediate of Nylon-6 polymer production. Hydrochloric acid and electricity were obtained from a $\text{H}_2\text{-Cl}_2$ acidic fuel cell operating at 50°C [126, 127]. HCl has wide application in the production of chlorides, as a chemical intermediate in the hydrochlorination of rubber and for etching semi-conductor crystals.

Alcaide *et al.* [128] have investigated the cogeneration of hydrogen peroxide in an AFC. Important chemicals such as hydrogen peroxide, aniline, cyclohexamine and propyl alcohol have been synthesised successfully in proton exchange membrane (PEM) fuel cells with the cogeneration electrical power. Farr and Vayenas [129] first reported cogeneration of nitric acid and electricity from ammonia in a high temperature SOFC using YSZ electrolyte.

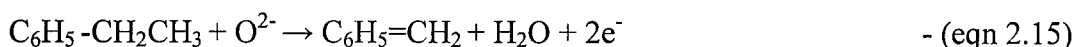
Table 2.7 - Different types of fuel cells of selected chemical electro cogeneration processes

FC reactor	Reactions	Anode	Cathode	Electrolyte	Power (W cm ⁻²)	Product yield (%)
SOFC	$4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$	Pt-Rh	Pt	YSZ	10-30 Wcm ⁻²	60
	$2\text{CH}_4 + 2\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{HCN} + 6\text{H}_2\text{O}$	Pt-Rh	Pt	YSZ	0.01 Wcm ⁻²	75
	$2\text{H}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O}$	Pt	Pt	YSZ	2.6 mWcm ⁻²	90
	$2\text{CH}_3\text{OH} + \text{O}_2 \rightarrow 2\text{H}_2\text{CO} + 2\text{H}_2\text{O}$	Ag	Ag	YSZ	1 mWcm ⁻²	90
	$2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$	Ag, Sm ₂ O ₃ -CaO-Ag	Ag	YSZ	-	88
	$4\text{CH}_4 + \text{O}_2 \rightarrow 2\text{C}_2\text{H}_6 + 2\text{H}_2\text{O}$	LaAlO ₃	La SrMnO ₃	YSZ	0.65 Wcm ⁻²	72
	$2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2$	Ni	LaSrCoO ₃	YSZ	0.53 Wcm ⁻²	20
Aqueous FC	$\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$	Pt	Rh	HCl	0.51 Wcm ⁻²	-
	$2\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow 2\text{CH}_3\text{CHO} + 2\text{H}_2\text{O}$	Pt-black	Pt-black	H ₂ SO ₄	8.7 mWcm ⁻²	-
PEMFC	$\text{C}_6\text{H}_5\text{NO}_2 + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}$	Pt	Pt	-	1.5 mWcm ⁻²	30-60
	$\text{CH}_2=\text{CHCH}_2\text{OH} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	Pt	Pt	Niafion 117	5.7 mWcm ⁻²	100
Molten salt FC	$2\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow 2\text{CH}_3\text{CHO} + 2\text{H}_2\text{O}$	Transition metal compound	Pt	Niafion	0.35 mWcm ⁻²	83

Chemical cogeneration in a solid oxide fuel cell is interesting as it works at higher temperatures. Many commercial inorganic and organic products could be cogenerated in SOFCs. The first cogeneration process was investigated by Farr and Vayenas with the production of nitric oxide from ammonia at the anode with other by-products being nitrogen and water [129]. The yield of nitric oxide exceeded 60% with simultaneous electrical power. The overall reaction is:



This reaction is highly exothermic ($\Delta G^\circ = -546 \text{ kJ/mol}$) at 1000K. Later, Michaels and coworkers studied the production of styrene in SOFCs [130]. Styrene was obtained by the electrochemical oxidative dehydrogenation of ethyl benzene. They found that the dehydrogenation rate increased with anodic current even though the total product conversion was less than 15%. The anodic reaction for styrene formation is as follows:



Ishihara *et al.* [131] studied the partial oxidation of methane to syngas ($\text{CO} + \text{H}_2$) on a platinum anode in a high temperature SOFC with YSZ electrolyte.

The anode reaction was suggested to be:



They found that an increase in current resulted in lower concentrations of CO , H_2 and CH_4 and higher concentration CO_2 in the outlet with respect to open circuit values.

Non oxidative methane coupling was studied by Chiang *et al.* [132] using a strontia-ceria based proton-conducting solid electrolyte with silver electrodes at 700-750°C to facilitate the dehydrogenation reactions:



The partial oxidation of methane has been studied using Ag, $\text{Bi}_2\text{O}_3\text{-Ag}$ and Fe anodes in an YSZ electrolyte cell at 900°C. High syngas selectivities were reported [133]. Vayenas

et al. [134] have reported formaldehyde production by partial oxidation of methanol in a SOFC at 547-697°C with YSZ electrolyte and Ag electrodes with the main by-products being CO and CO₂. Various investigators have studied HCN synthesis in fuel cells especially on platinum and rhodium catalysts [135-141]. They demonstrated cogeneration of electrical power ($\sim 0.01 \text{ W/cm}^2$) and HCN from methane and ammonia in a high temperature SOFC ($\sim 1000^\circ\text{C}$). Kiratzis and Stoukides investigated both the Andrussov (methane, ammonia and oxygen) and Degussa process (methane and ammonia) in an YSZ electrolyte cell with platinum electrodes at 750-1000°C [137,138]. The electrochemical reactions occurring at the two electrodes can be represented as:

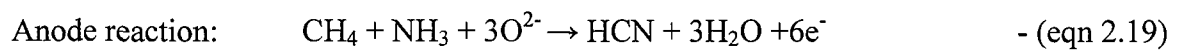


Table 2.8 - Possible reactions occurring during HCN synthesis using CH₄-NH₃ feed in a SOFC [137]

$\text{NH}_3 \rightarrow 3/2 \text{H}_2 + 1/2 \text{N}_2$
$\text{NH}_3 + \text{CH}_4 \rightarrow \text{HCN} + 3\text{H}_2$
$\text{NH}_3 + 5/4 \text{O}_2 \rightarrow \text{NO} + 3/2 \text{H}_2\text{O}$
$\text{NH}_3 + 3/2 \text{NO} \rightarrow 5/4 \text{N}_2 + 3/2 \text{H}_2\text{O}$
$1/2 \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}$
$\text{CH}_4 + 3/2 \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$
$\text{NO} + \text{H}_2 \rightarrow 1/2 \text{N}_2 + \text{H}_2\text{O}$
$\text{NO} \rightarrow 1/2 \text{N}_2 + 1/2 \text{O}_2$
$\text{NO} + \text{CO} \rightarrow 1/2 \text{N}_2 + \text{CO}_2$
$\text{CO} + 1/2 \text{O}_2 \rightarrow \text{CO}_2$
$\text{CH}_4 + \text{NO} \rightarrow \text{HCN} + 1/2 \text{H}_2 + \text{H}_2\text{O}$
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
$\text{HCN} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}$
$\text{CH}_4 + 3\text{NO} \rightarrow 3/2 \text{N}_2 + \text{CO} + \text{H}_2\text{O}$

Various kinetic models were proposed to explain the performance of the fuel cell with HCN production and it was found that HCN could be produced adiabatically without any external heat supply with methane and ammonia [137]. Fourteen chemical reactions were proposed to occur at the anode and are shown in Table 2.8. The selectivity to HCN in conventional Andrussov and Degussa processes was 90% whereas the cell selectivity to HCN in the SOFC was found to exceed 75% with power density of 0.01 Wcm^{-2} . The main advantages of the cogeneration process are that the process converts waste heat of exothermic reaction into useful electricity and produces HCN locally to avoid transport of dangerous chemical. Also, the operation temperature in the fuel cell was 100-200K less compared to the conventional Andrussov and Degussa reactors.

Kiratzis *et al.* [138] also concluded that neither electrochemical nor gaseous oxygen affected the rate of HCN formation significantly. The only slight difference being that the gaseous oxygen favoured CO over water formation.

2.6 Conclusions

Based on the reactions outlined above, an oxide ion conducting ceramic fuel cell reactor (CFCR) could be developed to produce HCN from CH_4 . However, both the Andrussov and Degussa processes, which normally take place at 1100°C or above, are difficult to accommodate in a ceramic fuel cell reactor. Instead, HCN could be produced from ammonia and methanol in a ceramic fuel cell reactor at much lower temperature (less than 600°C). The configurations using an oxide ion conducting SOFC are shown in Figure 2.5.

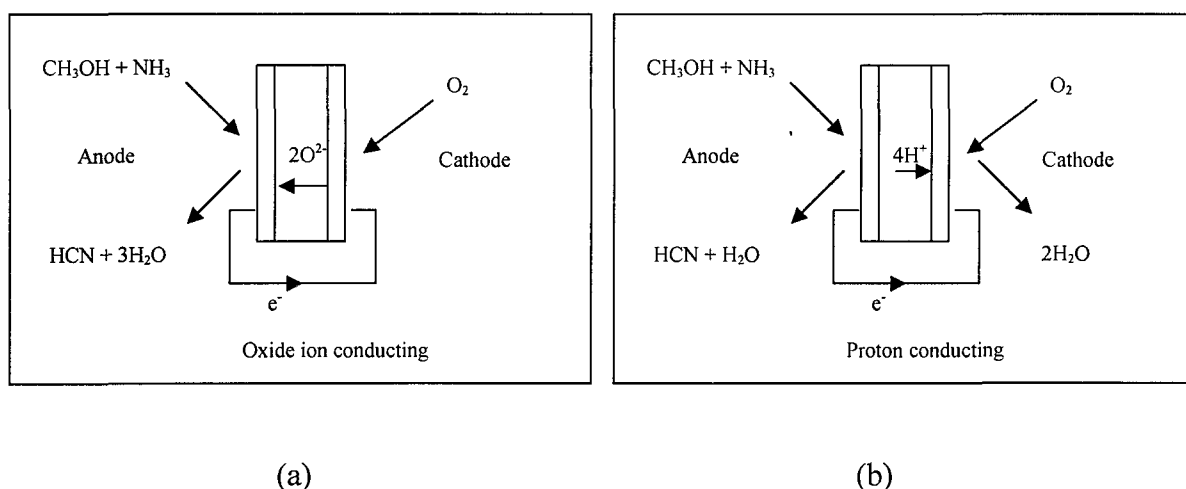
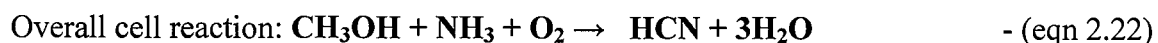


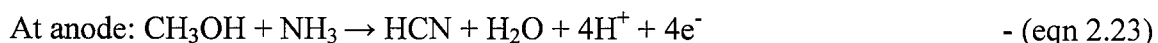
Figure 2.5 - Schematic of the synthesis of HCN in a CFCR

(a) oxide ion conducting SOFC and (b) PCFC

The HCN formation in the oxygen ion conducting electrochemical reactor could be stoichiometrically written as



And the stoichiometric representation of the HCN formation in the proton conducting electrochemical reactor could be written as



The main interest of this project is to develop anode materials appropriate for the ammoxidation or ammonolysis of methanol to produce HCN at the anode in a ceramic fuel cell reactor as explained schematically above. The electrolyte of choice for this study was gadolinium doped ceria (CGO), the anode electrocatalyst was a mixture of iron antimony oxide- (FSO) and nickel- gadolinium doped ceria (Ni-CGO) and the cathode being (La,Sr) (Co,Fe)O₃- CGO composite. The properties of each component were discussed in this chapter. The purpose of addition of the water vapour at the anode to avoid carbon deposition when using Ni catalyst has been explained.

The HCN synthesis in the PCFC has potential advantages in that less water is produced at the anode along with HCN and there is less possibility of formation of the oxidation products as CO₂ and CO. Unfortunately, HCN synthesis in the PCFC using Y: BaCeO₃ electrolyte was abandoned after initial experiments. During fabrication of the anode catalyst on the Y:BaCeO₃ and firing at 1300°C led to the development of cracks in the anode which was also not adherent to the electrolyte surface. SEM image analysis of the catalyst on the electrolyte confirmed the above. Therefore, the HCN synthesis in the SOFC was pursued using oxide ion conducting electrolyte.

2.7 Chapter 2 – References

- 1 The Columbia Encyclopedia, 6th edn. Columbia Univ. Press New York (2001)
- 2 C.N. Satterfield, Heterogeneous Catalysis in Industrial Practice, 2nd edn. McGraw-Hill New York (1991)
- 3 A.G. Dietz and L.D. Schmidt, Appl. Catal. A: Gen. 180 (1999) 287
- 4 J.R. Ebner, J.T. Gleaves, T.C. Kuechez and T.P. Li, AC Symposium series 328 (1987) 189
- 5 M. Diefenbach, M. Bronstrup, M. Aschi, D. Schroder and H. Schwarz, J. Amer Soc. 121 (1999) 10614
- 6 A.H. Tracy, Coordination Chemistry Reviews 248 (2004) 429
- 7 Y. Sasaki and M. Fukatsu, Catal. Surv. Jpn. 2 (1998) 199
- 8 Y. Sasaki, H. Yamamoto, K. Mori and K. Miyaki, Sci. Tech. Catal. 121 (1998) 335
- 9 J.F. Brazdil, Ammoxidation – Heterogeneous, Encyclopedia of Catalysis (2002)
- 10 J. Clayden, N. Greeves, S. Warren and P. Wothers, Organic Chemistry, Oxford University Press Inc. Oxford (2001)
- 11 W. Sedriks, PEP Reviews 76 (1977)
- 12 G B Patent 913, 836 (Dec. 28 1962), F.J Bellinger and F.C. Newman (to the Distillers Co. Ltd)
- 13 U S Patent 3,149,914 (Sept. 22 1964), F.J. Bellinger and F.C. Newman (to the Distillers Co. Ltd)
- 14 U S Patent 3,911,089 (Oct. 7 1984), T. Shiraishi, H. Ichihashi and R.F. Kato (to Sumitomo Chemical Co. Ltd)
- 15 U S Patent 4,485, 079 (Nov. 27 1984), J.F. Bradzil, T.G. Attig and R.K. Grasselli (to the Standard Oil Co. Ltd)
- 16 U S Patent 5,158, 787 (Apr. 3 1989), Y. Sasaki, H. Utsumi and M. Otani (to Nitto Chemical Industry Co. Ltd)
- 17 U S Patent 4,461,752 (Feb.22 1983), Y. Sasaki and H. Utsumi (to Nitto Chemical Industry Co. Ltd)
- 18 U S Patent 2,006,981 (Nov.25 1932), L. Andrussow (to I. G. Farben industrie, Germany)
- 19 B.Y.K. Pan, J. Catal. 21 (1971) 27
- 20 G B Patent 718,112 (Nov.10 1954), F.J. Bellringer (to the Distillers Co. Ltd)

- 21 G B Patent 913,836 (Dec. 28 1962), F.J. Bellringer (to the Distillers. Co. Ltd)
- 22 U S Patent 4,457,905 (Dec. 27 1982), J.R. Ebner (to Monsanto Company)
- 23 U S Patent 4,521,395 (Nov. 18 1983), T.C. Keuchler, J.R. Ebner and T.P. Li (to Monsanto Company)
- 24 U S Patent 4,511,548 (Aug.10 1983), T.G. Attig, R.K. Grasselli (to the Standard Oil Company)
- 25 PEP Reviews X-3-2, Hydrogen Cyanide Manufacture April (1975)
- 26 M.M. Gadgil and S.K. Kulshreshtha, J. Mol. Catal. A: Chem. 95 (1995) 211
- 27 J. Walczak, L. Filpek and M. Bosacka, Solid State Ionics 101 (1997) 1363
- 28 Y. Haung and P. Ruiz, J. Phy. Chem. B 109 (2005) 22420
- 29 J. Amador and I. Raisins, J. Appl. Cryst. 14 (1981) 348
- 30 K.T. Li, C. Yen and N. Shyu, Appl. Catal. A: Gen 156 (1997) 117
- 31 S. E. Golunski and D. Jackson, Appl. Catal. 48 (1989) 123
- 32 U S Patent 4,536,483 (Oct. 26, 1983), Y. Sasaki, Y. Kiyomiya, T. Nakamura, Y. Nakamura and M. Yamaguchi (to the Nitto Company)
- 33 Y. Sasaki, Appl. Catal. A: Gen 194 (2000) 497
- 34 G. Centi and F. Trifiro, Catal. Rev. Sci. Eng. 28 (1986) 165
- 35 M. Carbuicchio, G. Centi and F. Trifiro, J. Catal. 91 (1985) 85
- 36 N. Burriesci, F. Garbassi, M. Petrera and G. Petrini, J. Chem. Soc. - Faraday Trans. 1 78 (1982) 817
- 37 R.G. Teller, J.F. Brazdil, R.K. Grasselli and W. Yelon, J. Chem. Soc - Faraday Trans. 1 81 (1985) 1693
- 38 Y. Moro-oka and W. Ueda, Adv. Catal. 40 (1994) 233
- 39 M.D. Allen, G.J. Hutchings and M. Bowker, Appl. Catal. A: Gen 217 (2001) 33
- 40 U S Patent 5,094,990 (Jun. 20 1990), Y. Sasaki, M. Otani, H. Utsumi and K. Morishita (to the Nitto Company)
- 43 B.C.H Steele and A. Heinzl, Nature 414 (2001) 345
- 44 W.Z. Zhu and S.C. Deevi, Mater. Sci. Eng. A362 (2003) 228
- 45 M. Weller, F. Khelfaoui, M. Kilo, M.A. Taylor, C. Argirusis and G. Borchardt, Solid State Ionics 175 (2004) 329
- 46 O. Yamamoto, Electrochemi. Acta 45 (2000) 2423
- 47 R.M. Ormerod, Chem. Soc. Rev. 32 (2003) 17
- 48 S.P.S. Badwal and K. Foger, Ceram. Int. 22 (1996) 257

- 49 B.C.H. Steele, High Conductivity Solid Ionic Conductors, ed. T. Takahashi, World Scientific, Singapore (1989)
- 50 S.C. Singhal and K. Kendall, High Temperature Solid Oxide Fuel cells – Fundamentals, Design and Applications ed. Elsevier Adv. Tech. Oxford UK (2003)
- 51 J.A. Liu and S.A. Barnett, Solid State Ionics 158 (2003) 11
- 52 W. Vielstich, H.A. Gasteiger and A. Lamm; Handbook of Fuel cells – Fundamentals, Technology and Applications, John Wiley & sons New York (2003)
- 53 A. Weber, B. Sauer, A.C. Muller, D. Herbstritt and E. Ivers-Tiffée, Solid State Ionics 152 (2002) 543
- 54 R.T. Baker and I.S. Metcalfe, Appl. Catal. A: Gen. 126 (1995) 319
- 55 A. Atkinson, S. Barnett, R.J. Gorte, J.T.S. Irvine, A.J. Mcevoy, M. Mogensen, S.C. Singhal and J. Vohs, Nature materials 3 (2004) 17
- 56 M. Mogensen and K. Kammer, Annu. Rev. Mater. Sci. 33 (2003) 321
- 57 S. McIntosh and R.J. Gorte, Chem. Rev. 104 (2004) 4845
- 58 D.W. Dees, T.D. Claar, T.E. Easler, D.C. Fee and F.C. Mrazek, J. Electrochem. Soc. 134 (1987) 2141
- 59 B.C.H. Steele, Solid State Ionics, 86 (1996) 1223
- 60 B.C.H. Steele, Solid State Ionics, 129 (2000) 95
- 61 N.T. Yang, X.X. Meng, X.Y. Tan and Z.M. Li, J. Inorg. Mater. 21 (2006) 409
- 62 S. Baron, N.P. Brandon, A. Atkinson, B. Steele and R. Rudkin, J. Power Sources 126 (2004) 58
- 63 N. Oishi, A. Atkinson, N.P. Brandon, J.A. Kilner and B.C.H. Steele, J. Am. Ceram. Soc. 88 (2005) 1394
- 64 H. Timmermann, D. Fouquet, A. Weber, E. Ivers-Tiffée, U. Hennings and R. Reimert, Fuel cells 6 (2006) 307
- 65 B. Rosch, H.Y. Tu, A.O. Stormer, A.C. Muller and U. Stimming, Solid State Ionics 175 (2004) 113
- 66 E.V. Tsipis, V.V. Kharton and J.R. Frade, J. Eur. Ceram. Soc. 25 (2005) 2623
- 67 E. Ramirez-Cabrera, A. Atkinson and D. Chadwick, Appl. Catal. B: Environ. 47 (2004) 127
- 68 O.A. Marina, C. Bagger, S. Primdahl and M. Mogensen, Solid State Ionics 123 (1999) 199
- 69 S.J.A. Livermore, J.W. Cotton and R.M. Ormerod, J. Power Sources 86 (2000) 411

- 70 C.H. Lee, H.Y. Lee and S.M. Oh, *Solid State Ionics* 98 (1997) 39
- 71 D.J.L. Brett, A. Atkinson, D. Cumming, E. Ramirez-Cabrera, R. Rudkin and N.P. Brandon, *Chem. Eng. Sci.* 60 (2005) 5649
- 72 P.K. Cheekatamarla and C.M. Finnerty, *J. Power Sources* 160 (2006) 490
- 73 L.J.M. Blomen and M.N. Mugerwa, *Fuel Cell Systems*. ed.; Plenum Press: New York (1993)
- 74 L.W. Tai, M.M. Nasrallah, H.U. Anderson, D.M. Sparlin and S.R. Sehlin, *Solid State Ionics* 76 (1995) 259
- 75 J.M. Ralph, A.C. Schoeler and M. Krumpelt, *J. Mater. Sci.* 36 (2001) 1161
- 76 V. Dusastre and J.A. Kilner, *Solid State Ionics* 126 (1999) 163
- 77 B. Feng, C.Y. Wang and B. Zhu, *Electrochem. Solid- State Lett.* 9 (2006) 80
- 78 S. Assabumrungrat, W. Sangtongkitcharoen, N.Laosiripojana, A. Arpornwichanop, S. Charojrochkul and P. Prasertthdam, *J. Power Sources* 148 (2005) 18
- 79 L.M. Gomez-Sainero, R.T. Baker, I.S. Metcalfe, M. Sahibzada, P. Concepcion and J.M. Lopez-Nieto, *Appl. Catal. A: Gen* 294 (2005) 177
- 80 Y.H. Chin, R. Dagle, J.L. Hu, A.C. Dohnalkova and Y.Wang, *Catal. Today* 77 (2002) 79
- 81 F. Coutelieris, S. Douvartzides, S. Song and P. Tsiakaras, *Int. J. Green Energy* 1 (2004) 241
- 82 M. Sahibzada, B.C.H. Steele, K. Hellgardt, D. Barth, A. Effendi, D. Mantzavinos and I.S. Metcalfe, *Chem. Eng. Sci.* 55 (2000) 3077
- 83 S. Assabumrungrat, N. Laosiripojana, V. Pavarajarn, W. Sangtongkitcharoen, A. Tangjitmatee, P. Prasertthdam, *J. Power Sources* 139 (2005) 55
- 84 J.P. Breen and J.R.H. Ross, *Catal. Today* 51 (1999) 521
- 85 Y.T. Choi and H.G. Stenger, *J. Power Sources* 142 (2005) 81
- 86 Y.Y. Liu, T. Hayakawa, T. Tsunoda, K. Suzuki, S. Hamakawa, K. Murata, R. Shiozaki, T. Ishii and M. Kumagai, *Top. Catal.* 22 (2003) 205
- 87 Y. Jiang and A.V. Virkar, *J. Electrochem. Soc.* 148 (2001) 706
- 88 T. Takeguchi, Y. Kani, T. Yano, R. Kikuchi, K. Eguchi, K. Tsujimoto, Y. Uchida, A. Ueno, K. Omoshiki and M. Aizawa, *J. Power Sources* 112 (2002) 588
- 89 E. Ramírez-Cabrera, A. Atkinson, N.P. Brandon and B.C.H. Steele, *Proceedings of the Fifth European Solid Oxide Fuel Cell Forum*, vol. 1, Lucerne, Switzerland, (2002) 531

- 90 P. Aguiar, E. Ramirez-Cabrera, N. Laosiripojana, A. Atkinson, L.S. Kershenbaum and D. Chadwick, *Stud. Surf. Sci. Catal.* 145 (2003) 387
- 91 E. Ramirez-Cabrera, A. Atkinson and D. Chadwick, *Appl. Catal. B: Environ.* 36 (2002) 193
- 92 N. Laosiripojana, W. Sangtongkitcharoen and S. Assabumrungrat, *Fuel* 85 (2006) 323
- 93 E. Ramirez-Cabrera, N. Laosiripojana, A. Atkinson and D. Chadwick, *Catal. Today* 78 (2003) 433
- 94 K. Sasaki, K. Watanabe, K. Shiosaki, K. Susuki and Y. Teraoka, *J. Electroceram.* 13 (2004) 669
- 95 K. Sasaki and Y. Teraoka, *J. Electrochem. Soc.* 150 (7): (2003) 878
- 96 K. Eguchi, H. Kojo, T. Takeguchi, R. Kikuchi and K. Sasaki, *Solid State Ionics* 152 (2002) 411
- 97 G.J. Saunders, J. Preece and K. Kendall, *J. Power Sources* 131 (2004) 23
- 98 V.V Krishnan, S. McIntosh, R.J. Gorte and J.M. Vohs, *Solid State Ionics* 166 (2004) 191
- 99 C. Lu, W.L. Worrell, C. Wang, S. Park, H. Kim, J.M. Vohs and R.J. Gorte, *Solid State Ionics* 152 (2002) 393
- 100 A. Wojcik, H. Middleton, I. Damopoulos and J. Van Herle, *J. Power Sources* 118 (2003) 342
- 101 R. Metkemeijer and P. Achard, *J. Power Sources* 49 (1994) 271
- 102 C.H. Christensen, T. Johannessen, R.Z. Sorensen and J.K. Norskov, *Catal. Today* 111 (2006) 140
- 103 N. Dekkar and B. Rietveld, *European Symposium* (2004) 1524
- 104 T.V. Choudhary, C. Sivadinarayana and D.W. Goodman, *Catal. Lett.* 72 (2001) 197
- 105 J. Zhang, H.Y. Xu and W.Z. Li, *Appl. Catal. A* 296 (2005) 257
- 106 S.F. Yin, B.Q. Xu, X.P. Zhou, and C.T. Au, *Appl. Catal A: Gen* 277 (2004) 1
- 107 J. Zhang, H.Y. Xu, Q.J. Ge, and W.Z. Li, *Catal. Commun.* 7 (2006) 148
- 108 K.W. Kim, Y.J. Kim, I.T. Kim, G.I. Park and E.H. Lee, *Electrochim. Acta* 50 (2005) 4356
- 109 X.K. Li, W.J. Ji, J. Zhao, S.J. Wang and C.T. Au, *J. Catal.* 236 (2005) 181
- 110 H. Iwahara, T. Esaka, H. Uchida and N. Maeda, *Solid State Ionics* 3 (1981) 359
- 111 H. Iwahara, H. Uchida, K. Ono and K. Ogaki, *J. Electrochem. Soc.* 135 (1988) 529

- 112 K.D. Kreuer, *Annu. Rev. Mater. Res.* (2003) 333
- 113 G.L. Ma, T. Shimura and H. Iwahara, *Solid State Ionics* 120 (1999) 51
- 114 S. Yamaguchi, H. Yugami and S. Ikeda, *J. Alloys Compd.* 330 (2002) 911
- 115 H. Iwahara, H. Uchida and S. Tanaka, *J. Appl. Electrochem.* 16 (1986) 663
- 116 W.G. Coors, *J. Electrochem. Soc.* 151 (2004) 994
- 117 W.G. Coors, *J. Power Sources* 118 (2003) 150
- 118 J. Langguth, R. Dittmeyer, H. Hofmann and G. Tomandl, *Appl. Catal. A: Gen* 158 (1997) 287
- 119 H. Iwahara, Y. Asakura, K. Katahira and M. Tanaka, *Solid State Ionics* 168 (2004) 299
- 120 B. Zhu and S.W. Tao, *Solid State Ionics* 127 (2000) 83
- 121 E. Panagos, I. Voudouris and M. Stoukides, *Chem. Eng. Sci.* 51 (1996) 3175
- 122 N. Maffei, L. Pelletier, J.P. Charland and A. McFarlan, *J. Power Sources* 140 (2005) 264
- 123 F. Alcaide, P.L. Cabot and E. Brillas, *J. Power. Sources* 153 (2006) 47
- 124 X. Yuan, Z. Ma, H. Bueb, J.F. Drillet, J. Hagen and V.M. Schmidt, *Electrochimica Acta* 50 (2005) 5172
- 125 S.H. Langer and K.T. Pate, *Nature* 284 (1980) 434
- 126 M. Thomassen, B. Børresen, G. Hagen and R. Tunold, *J. Appl. Electrochem.* 33 (2003) 9
- 127 E.B. Anderson, E.J. Taylor, G. Wilemski and A. Gelb, *J. Power Sources* 47 (1994) 321
- 128 F. Alcaide, E. Brillas and P.L. Cabot, *J. Electroanal. Chem.* 566 (2004) 235
- 129 R.D. Farr and C.G. Vayenas, *J. Electrochem. Soc.* 127 (1980) 478
- 130 J.N. Michaels and C.G. Vayenas, *J. Electrochem. Soc.* 131 (1984) 2544
- 131 T. Ishihara, T. Yamada, T. Akbay and Y. Takita, *Chem. Eng. Sci.* 54 (1999) 1535
- 132 P.H. Chiang, D. Eng, H. Alqahtany and M. Stoukides, *Solid State Ionics* 53 (1992) 135
- 133 Y. Jiang, I.V. Yentekakis and C.G. Vayenas, *Science* 264 (1994) 1563
- 134 C.G. Vayenas and S. Neophytides, *J. Catal.* 127 (1991) 645
- 135 E.A. McKenna, A. Othoneos, N. Kiratzis and M. Stoukides, *Ind. Eng. Chem. Res.* 32 (1993) 1904
- 136 E. A. McKenna and M. Stoukides, *Chem. Eng. Sci.* 47 (1992) 2951
- 137 N. Kiratzis and M. Stoukides, *J. Electrochem. Soc.* 134 (1987) 1925

- 138 N. Kiratzis and M. Stoukides, *J. Catal.* 132 (1991) 257
- 139 N. Waletzko and L.D. Schmidt, *AIChE J.* 34 (1988) 1146
- 140 A.S. Bodke, D.A. Olschki and D. Schmidt, *Appl. Catal. A: Gen* 201 (2000)13
- 141 D. Hasenberg and L.D. Schmidt, *J. Catal.* 104 (1987) 441

Chapter 3

Experimental Procedures and Characterisation Techniques

3.1 Introduction

As mentioned in the introduction of this thesis, the aim of the research project is to develop anode materials for simultaneous production of hydrogen cyanide (HCN) and electricity using methanol and ammonia in a fuel cell reactor. Initial work concentrated on designing and developing an experimental set up for HCN synthesis in a micro reactor in order to evaluate the catalytic properties of the anode. This chapter outlines the experimental set up, and the procedures employed in the preparation and characterisation of the catalysts used for the HCN synthesis. X-ray diffraction (XRD) was used to confirm the phase purity and structure of the materials. Microstructure and elemental analysis studies were carried out by scanning electron microscopy (SEM-EDX). Nitrogen gas adsorption was used to investigate the physical properties of the catalysts.

3.2 Sample preparation

HCN synthesis from ammonia and methanol is catalysed by iron antimony oxide (FSO). Iron antimony oxide catalyst precursor was purchased from Catal International UK. It was a mixture of oxides of iron and antimony with a weight composition of 76% Fe_2O_3 , 15% FeSbO_4 , 8% Sb_2O_3 and 1% Cr_2O_3 . No other information about the catalyst was supplied by the company. The catalyst was characterised and evaluated at Imperial College, UK. This catalyst was first used as received without any pre treatment. The experiments were carried out in the temperature range of 450 - 650°C. $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO-10) was purchased from Rhodia and nickel (II) oxide (NiO) from Aldrich. The abbreviation of the catalyst constituents are shown in Table 3.1.

Table 3.1 - Materials used as a catalyst in the experiments

Material	Representation
Iron antimony oxide	FSO
$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$	CGO -10
Nickel(II)oxide	NiO

3.2.1 High temperature calcination

HCN synthesis had to be tested over the temperature range 450 - 650°C with the iron antimony oxide powder calcined to 1300°C, since temperatures of this magnitude are often required to sinter the anode to the electrolyte in a SOFC. Iron antimony oxide powder was placed in an alumina crucible and the heated in an Elite Thermal Systems box furnace under static air with a heating rate of 120°C /h up to 1300°C for a dwell time of 2h and cooled slowly to ambient temperature.

3.2.2 Ni-CGO anode preparation

The Ni-CGO is a common anode precursor material in the fuel cell. Extra care was taken in its preparation focusing on its performance in the fuel cell. Low cost nickel has been a popular component of the anode for SOFCs using YSZ or CGO electrolytes [1, 2]. The Ni-CGO cermet was prepared by mixing NiO and CGO powders. The NiO was mixed with solid electrolyte CGO-10 powder. The CGO-10 helps to prevent the sintering of Ni during operation, is an essential support for the catalytic activity of the nickel anode and provides oxygen ion conductivity [1- 4].

The anode slurry preparation procedure followed those given by Livermore *et al.* [5] and Baron [6]. The objective is to produce NiO and CGO powders with similar particle sizes and mix them homogeneously. Black NiO powder (Aldrich) was pre treated by ball milling for 7 days and CGO-10 powder was pre calcined to 1300°C for 5h followed by ball milling for 3 days. Ball milling reduces the particle size whereas precalcining leads to increase particle size. Ball milling also produces a narrower particle size distribution. A 60-40 wt% Ni-CGO-10 mixture was prepared for this study. The composition 60-40 wt% represents the final composition of Ni and CGO-10 but not NiO and CGO-10 in the precursor. NiO will reduce to metallic Ni in the SOFC fuel stream to conduct electronically. Therefore, the appropriate weights of NiO and CGO-10 were used to obtain the final desired composition.

30g of 60- 40 wt% Ni-CGO (as Ni-CGO precursor) was mixed with 18g of ethanol and 0.5g of KD1 dispersant (Hypermer) and ball milled together in a 250ml polyethylene bottle with milling media of 2 different sizes i.e. 12 large (3.3g each) and 24 small (1.4g each) MgO stabilised zirconia balls for 24h. The dispersant prevents formation of agglomerates which hinder fabrication and also promotes a homogeneous mixture. At this stage, 4.5g of polyvinyl butyral (PVB) binder was added to the mixture along with the addition of a further 20g

ethanol to reduce the viscosity, thus allowing a free and uniform mixing. Binders were added to give strength to the slurry when it is applied as a coating on the electrolyte. 1.1g of PEG400 additional binder and dibutyl phthalate plasticizer were added followed by another 24h milling.

3.2.3 FSO- Ni/CGO preparation

Since Ni-CGO is unlikely to catalyse the HCN synthesis, iron antimony oxide (FSO) was added to the Ni-CGO slurry to catalyse HCN synthesis in the fuel cell anode. Iron antimony oxide was ground to a fine powder using a mortar and pestle and subsequently ball milled for 24h. 10g of FSO-Ni/CGO mixture was mixed with 0.5g of KD1 dispersant and 25g of ethanol and ball milled for approximately 24h followed by the addition of PVB binder and a further milling for half an hour. Three different final weight percent compositions of FSO-Ni/CGO (40:60, 50:50 and 60:40) were prepared and tested for mechanical stability and room temperature conductivity after reduction in humidified 10% H_2/N_2 . The composition 40- 60 wt % FSO-Ni/CGO satisfied these requirements and was used for further studies.

The resultant slurry was dried in an oven at 30°C and the dry powder was used for structural characterisation by X-ray diffraction, micro structural and elemental analysis by SEM-EDX, and physical properties by nitrogen gas adsorption. Finally, its catalytic performance for HCN synthesis was evaluated.

3.3 Characterisation Techniques

The various characterisation techniques used in this study are discussed in this section.

3.3.1 X-Ray Diffraction

The X-ray diffraction (XRD) technique is a common tool for characterisation of crystalline materials and the determination of their crystal structure. Powder X-ray diffraction is useful in qualitative phase analysis because every crystalline material has its own characteristic powder pattern. This pattern is determined by the size and the shape of the unit cell, the atomic number and position of the various atoms in the cell. Samples for the XRD analysis must contain a random arrangement of crystal orientations.

On a fundamental level, there are three main variables in XRD studies – X-ray source, the sample and a detector. An electron beam, provided by a heated tungsten filament, is

accelerated towards an anode by a potential difference of ~ 40 kV. The electrons strike the target- a piece of copper fixed to the anode. The incident electrons have sufficient energy to ionise some of the copper 1s (K shell) electrons. An electron ion in an outer orbital immediately drops down to occupy the vacant 1s level and the energy released in the transition appears as X-radiation. For copper, the 2p to 1s transition is called $K\alpha$ and has a wavelength of $1.5418\text{\AA}$ and the 3p to 1s transition, $K\beta$ has a wavelength of $1.3922\text{\AA}$.

The $K\alpha$ transition occurs much more frequently than the $K\beta$ transition and for this reason; $K\alpha$ radiation is used in diffraction experiments [7]. For most diffraction experiments, in order to achieve a monochromatic beam of X-rays (i.e. intense $K\alpha$ lines for copper), all other wavelengths are filtered out using a sheet of nickel foil. After the X-rays hit the surface of the sample crystals and penetrate inside, the atoms or ions act as secondary point sources and scatter the X-rays. The most common approach of treating diffraction by crystals is by applying Bragg's law (eqn 3.1 and Figure 3.1). Bragg's law regards crystals as built-up layers or planes of atoms such that each acts as a semi-transparent mirror. Some of the X-rays are reflected off a plane with the angle of reflection equal to the angle of incidence, but the rest are transmitted through one plane and then partially reflected by the next planes. The perpendicular distance between pairs of adjacent planes is denoted by the letter d , and is also referred to as the d -spacing.

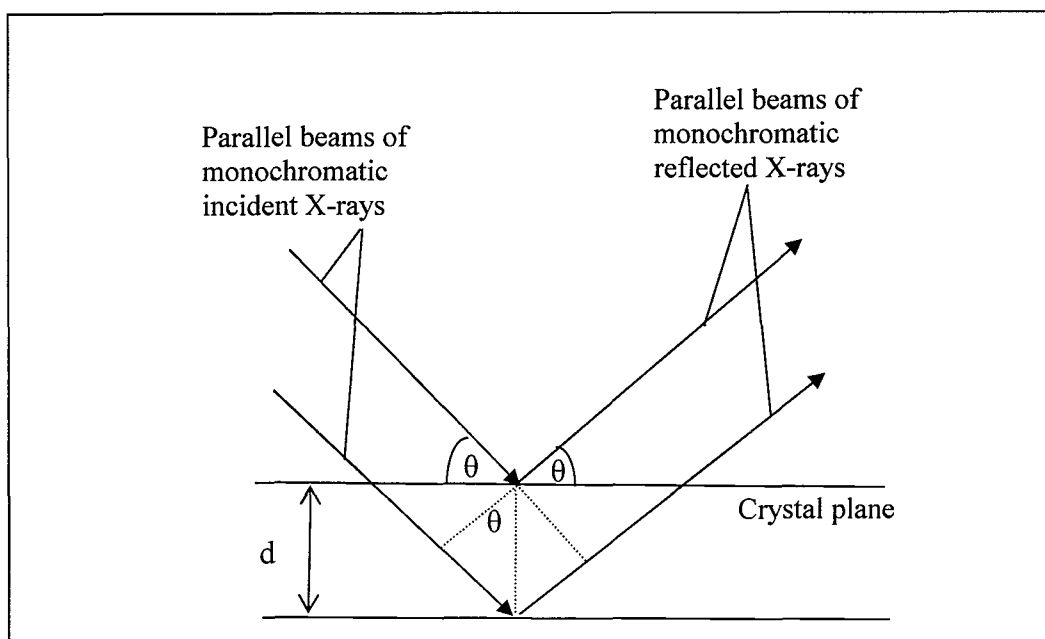


Figure 3.1 - Pictorial representation of Bragg's law for XRD

The Bragg angle is the angle of incidence, θ and λ is the X-ray wavelength.

$$2d \sin \theta = n\lambda \quad \text{- (eqn. 3.1)}$$

The diffraction order, n is usually kept equal to one in all cases. In cases where n is not unity, the d - spacing is adjusted to take this into account. A Philips PW1700 Series Automated Powder Diffractometer using Cu- $K\alpha$ radiation with a secondary crystal monochromator was used to determine phase and structure of catalyst powders.

3.3.2 Nitrogen gas adsorption

The specific surface area of the powders was determined by the nitrogen gas adsorption technique (Quanta Chrome Autosorb AS6). A known mass of powder was submitted to evacuation and pre-treatment at 150°C for 15h to remove moisture and contaminants. Nitrogen gas molecules (adsorptive, of known cross-sectional area) were passed over the degassed sample (adsorbent), at 77.4K (boiling point of nitrogen gas), and physically adsorbed to the entire surface both internally and externally [8]. Nitrogen molecules physically adsorb on the clean surface as a consequence of the van der Waals forces at the surface of the solid. Due to the weak nature of these bonds, physisorption is reversible without any disruptive structural changes occurring at the surface. This enables both the adsorption and desorption processes to be studied [9]. Physisorption also leads to surface coverage by more than one layer of adsorbate, allowing pores to be filled with layers of nitrogen adsorbate and hence measurement of pore volume, modal pore diameters and pore distribution [9]. The volume of nitrogen adsorbed and desorbed at different relative pressure was measured thereby generating adsorption isotherm curves. A small change in temperature changes the saturation vapour pressure considerably. Data points of the adsorption isotherm were measured and the BET equation used to give specific surface area from the volume of gas needed to form a monolayer on the surface of the sample. The actual surface area can be calculated from the size and number of the adsorbed gas molecules. Each isotherm comprised a minimum of 20 adsorption and 20 desorption points measured at equilibrium. The specific areas were estimated in relation to the masses of the degassed samples, assuming the cross-sectional area of a nitrogen molecule to be 0.162nm² [10].

The specific surface area is defined as the accessible (or detectable) area of solid surface per unit mass of material. The most widely used theory for specific surface area calculation is that

of Brunauer, Emmett and Teller known as BET theory, which is a modification of Langmuir's adsorption kinetic theory, expanded for multilayer adsorption [11, 12]. The BET model is based on the measurement of quantities of gas adsorbed onto a surface at equilibrium pressure. It assumes that adsorbed molecules in one layer can act as adsorption sites for molecules in the next layer and, at any pressure below the saturation vapour pressure (P_0) fractions of the surface are covered by layers of adsorbed molecules. Therefore the adsorbed layer can consist of random stacks of molecules and be of non-uniform thickness.

The model leads to the BET equation:

$$\frac{P}{n^a(P_0 - P)} = \frac{1}{n_m^a C} + \frac{(C-1)}{n_m^a C} \left(\frac{P}{P_0} \right) \quad - \text{(eqn 3.3)}$$

where n^a is the amount adsorbed at the relative pressure P/P_0 , n_m^a is the monolayer capacity and C is the BET constant. The standard BET procedure requires the measurement of at least three (preferably five or more) points in the monolayer adsorption region ($0.05 < P/P_0 < 0.30$) of the isotherm.

The surface area, S_{BET} , of the specimen is estimated using:

$$S_{\text{BET}} = n_m^a N A_{cs} \quad - \text{(eqn 3.4)}$$

where N is the Avogadro's constant and A_{cs} the molecular cross-sectional area of the adsorbate molecule in a complete monolayer 0.162nm^2 .

At saturated vapour pressure ($P/P_0 = 1$), pores are filled with condensed liquid adsorbate [9]. The total pore volume is derived from the amount of nitrogen adsorbed at ($0.994 < P/P_0 < 0.999$). As high a relative pressure as possible is required to include the largest macropores in this measurement. The total pore volume (V_p) is determined by the volume of liquid nitrogen contained in the pores, which is obtained from the volume of nitrogen adsorbed (V_{ads}) using:

$$V_p = \frac{P_a V_{ads} V_m}{RT} \quad - \text{(eqn 3.5)}$$

where P_a and T are pressure and temperature at which the volume of adsorbed nitrogen is measured as gas, V_m is the molar volume of the liquid adsorbate ($34.7\text{cm}^3\text{mol}^{-1}$ for N_2) and R is the universal gas constant [13]. The Barrett, Joyner and Halenda (BJH) method was used to obtain the pore size distribution of the electrode catalysts in the mesoporous range in this work. The BJH method is based on the desorption of liquid nitrogen from within the pores by the step-wise reduction of relative pressure from $P/P_o = 1$.

3.3.3 Scanning Electron Microscopy / Energy Dispersive Spectrometry

Scanning electron microscopy (SEM) provides a detailed knowledge of the topography of the surfaces or edges of solids on a sub-micrometer scale. SEM uses a beam of electrons to scan the surface of the sample and to build an image of the specimen. An electron gun generates the beam of electrons usually from a tungsten filament. The column is kept under vacuum to ensure that electrons reach the sample, because they can be easily deflected by gas molecules in air. The beam of electrons is focussed on the sample and is scanned in a rectangular TV-type raster across the surface of the specimen. A raster pattern means that the beam of electrons initially sweeps across the surface in a straight line, then returns to its starting position and is shifted downwards by a standard increment [14]. Once the electron beam hits the sample, a variety of signals are generated. Depending on the sample these include secondary electrons (electrons from the sample), backscattered electrons (electrons that bounce off the nuclei of atoms in the sample), X-rays, light, heat, and even transmitted electrons (electrons that pass through the sample). These emitted radiations may be detected and the signals amplified and displayed. The first two signal types are the most commonly used signals in SEM imagery. Secondary electrons have energies $< 50\text{eV}$, which are emitted as a result of inelastic collisions between the atoms in the sample and the electrons and these originate within a few nanometres of the surface. Any variation in surface topography will greatly affect the emission efficiency. For back scattered electrons, the probability of a large angular deflection taking place increases with the atomic number of the target atom with respect to the number of incident beam electrons [14]. In general, to ensure good imaging of samples, the specimen must be electrically conductive and devoid of water and solvent that could vaporise.

In this study, SEM was used to characterise the microstructure of the polished and fractured surfaces of the sintered electrolyte/cathode and electrolyte/anode samples. The samples were fractured and then attached using double-sided carbon tabs, onto an aluminium stub. In the

case of polished cross-sections, the sample was vertically cut into two using a diamond saw and immersed in epoxy resin before being dried under vacuum for 10 minutes. The embedded sample was allowed to cure for 24h and then polished on a polishing machine using a sequence of grinding papers and diamond impregnated pastes to a $1\mu\text{m}$ finish. Subsequently, the samples were sputter-coated with gold or carbon so as to aid electrical conduction and thus prevent charging of the samples by the electron beam. Backscattered electrons, energy $>50\text{eV}$, were used to detect contrast between areas with different chemical compositions or densities. Elements that are of a higher atomic number will produce more backscattered electrons and will therefore appear brighter than neighbouring elements. The region of the specimen from which backscattered electrons are produced is considerably larger than it is for secondary electrons. For this reason, the resolution of a backscattered electron image is considerably less ($1.0\mu\text{m}$) than it is for a secondary electron image (e.g. 10nm). Because of their greater energy, backscattered electrons can escape from much deeper regions of the sample than can secondary electrons hence the larger region of excitation.

Energy Dispersive Spectrometry (EDS) also known as Energy Dispersive X-ray analysis (EDX) is a technique used for identifying the elemental composition of an area of interest in the specimen. Interaction of the primary electron beam with the specimen, apart from secondary and backscattered electrons, also produces characteristic X-rays [15]. When the incident electron beam strikes the sample creating secondary electrons, it leaves many of the sample atoms with vacancies in the electron shells where the secondary electrons used to be. If these vacancies are in their inner shells, electrons from outer shells will drop into the inner shells. Energy is emitted during this transition in the form of X-rays. The X-rays emitted from the sample atoms are characteristic in energy and wavelength of, not only the type of element of the parent atom, but which shells lost electrons and from which shells the electrons replaced them. These X-rays can also be used to form an image of the sample that shows where atoms of a given element are localized. The resolution of these X-ray maps is on the order of greater than $1\mu\text{m}$. Chemical composition analyses by EDX were performed with an EDX analyser associated to a scanning electron microscope (JSM 840). Incident electron beam energies from up to 10keV were used. In all cases, the beam was at normal incidence to surface. All the EDX spectra were corrected by using the ZAF correction, which takes into account the influence of the matrix material on the obtained spectra.

3.4 GC Instrumentation

A Shimadzu 14B gas chromatograph was used this project and incorporated the features common to all forms of chromatography, namely a mobile phase, sample introduction system, a stationary phase and a detection system. The column temperature, instrument variables and signal processing were controlled by a microprocessor.

The main components are now described.

3.4.1 Carrier gas and controls

The main purpose of the carrier gas is to carry the sample through the column. It is the mobile phase and it should be inert and not interact chemically with the sample. A secondary purpose is to provide a suitable matrix for the detector to sense the sample components. For a thermal conductivity detector, helium is the most popular carrier. With a flame ionization detector, either nitrogen or helium may be used. Nitrogen provides slightly more sensitivity, but a slower analysis than helium. For an electron capture detector, very dry, oxygen-free nitrogen, or a mixture of argon with 5% methane is recommended. Selection of the carrier gas is important, because it affects both the column separation process and detector performance. Gases with a small molecular weight (e.g. hydrogen and helium), will give better separation delays for analytes than higher molecular weight gases such as nitrogen, carbon dioxide and argon [16]. Dry helium carrier gas of 99.99% purity was used in the experiment and GC analysis in this work.

A constant flow rate should be maintained to achieve reproducible separations. Pressure regulators and flow controllers were built into the carrier gas lines at the cylinder and in the instrument to obtain a pulse – free supply at pre-set pressures and flow rates. An outlet pressure of 7 bar was set at helium gas cylinder.

3.4.2 Flow controllers

A flow controller model CFC-14PM (incorporating a pressure regulator and a mass flow controller) for the carrier gas flow line. This flow controller regulates the flow rate of carrier gas (mass flow control) and is most suitable for the packed column single flow line system used here. An inlet pressure of 7 bar of helium carrier gas was set.

3.4.3 Sample introduction

The introduction of a sample into a GC is the first stage in the chromatographic process and it should enter the column with the minimum of dispersion in the mobile phase, as a narrow band containing all the sample components. Gaseous samples were introduced to the column using a multiport switching valve (Figure 3.2a and 3.2b). There is essentially no dead volume with gas sample valves and their repeatability is very good.

The sample was introduced into the sample loop while the valve was in the LOAD position. It is important that excess volume of sample is used to ensure that the sample loop is completely flushed through. When the valve is turned to the INJECT position, carrier gas is directed on to the column via the sample loop. A 10 port sample valve was configured for analyzing the SOFC reactor gas streams.

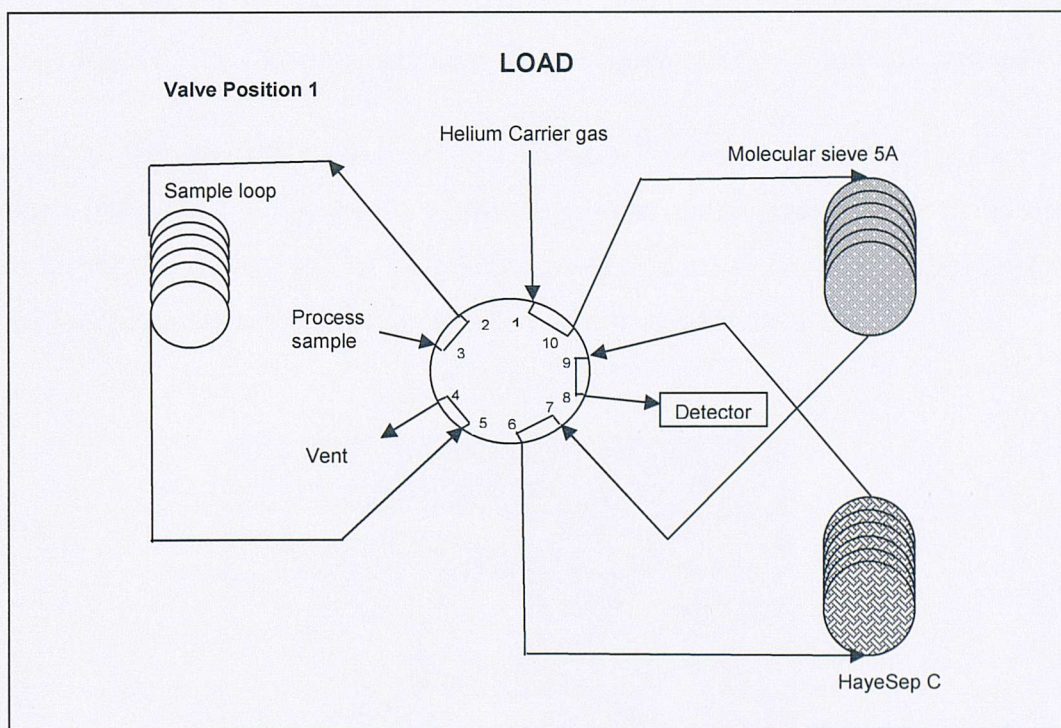


Figure 3.2a - 10 port switching valves: loading sample loop

In valve position 1, the process sample flows through the sample loop then to vent. Meanwhile the helium carrier gas flows through the GC columns, firstly through the molecular sieve 5A column then the HayeSepC column before reaching the detector.

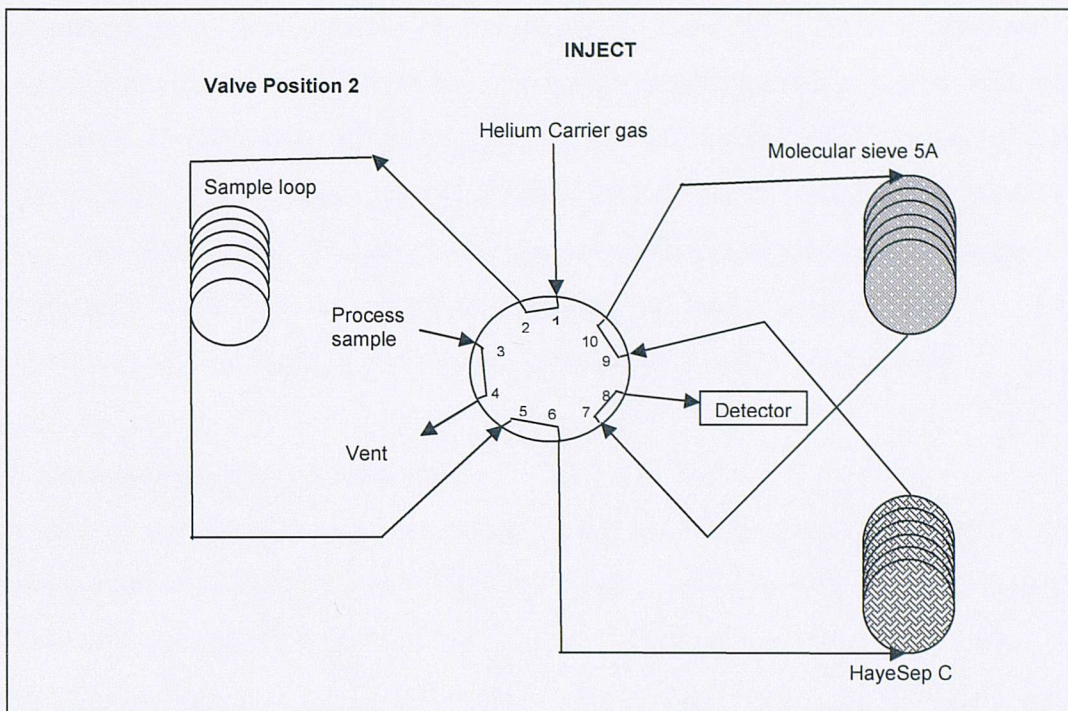


Figure 3.2b - 10 port switching valves: injecting sample onto the column

On sampling, the valve moves to position 2 allowing the carrier gas to transfer the contents of the sample loop onto the HayeSepC, whilst the process sample goes directly to the vent. After a short interval, sufficient for the permanent gases to elute from the HayeSepC column and onto the molecular sieve 5A column, the valve returns to position 1.

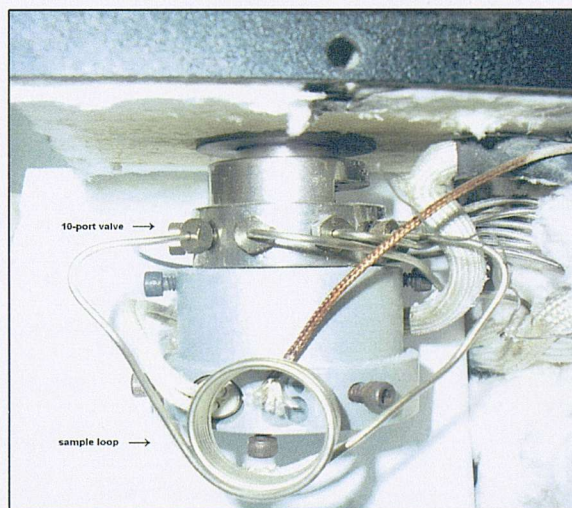


Figure 3.3 - Picture of 10-port valve and the sample loop

The permanent gases then separate on the molecular sieve 5A column before passing once more through the HayeSepC column, which is itself separating the HCN, ammonia, water and carbon dioxide components. Advantages of this method are that only one valve is required and that the sample loop is always filled ready to start another analysis as soon as one is complete. The disadvantage is that passing the separated permanent gas components through the HayeSepC column for a second time sometimes leads to some peak broadening in addition to making it difficult to prevent co-elution with the other components.

3.4.4 Chromatographic column

The column is perhaps the most important feature of a GC system. The key to good GC separations is to use the most appropriate stationary phase (column) at the optimum mobile phase velocity and column temperature. A gas chromatograph may have either a packed column or a capillary column. The characteristics of packed columns that make them ideal for gas analysis are [17]:

- Adsorbents provide high surface areas for maximum interaction with gases that may be difficult to retain on liquid stationary phase;
- Large samples can be accommodated, providing lower absolute detection limits;
- Some packed column GCs can be configured to run below ambient temperature which will also increase the retention of the gaseous solutes; unique combinations of multiple columns make it possible to optimize for a particular sample.

Packed columns are normally three, six, or twelve feet in length and the outside diameter is usually 1/4 or 1/8 in. The glass or metal tubing is packed with either adsorbent particles or stationary phase-coated particles. Stainless steel is used most often for the tubing, primarily because of its strength. Copper and aluminium are conveniently soft for easy bending, but are not recommended due to their reactivity. Common adsorbent solids like silica gel and alumina are sometimes used in GC, but most of the solids used as stationary phases have been developed for specific applications. Molecular sieve 5A (2m x1mm steel) and HayeSepC (1m x1mm steel) columns were used for the analysis in this work (Figure 3.4).

3.4.4.1 HayeSepC

HayeSep porous polymers are macro porous, spherical, ultra pure resins for performing specific separations in gas chromatography [17, 18]. HayeSepC is a porous copolymer of divinyl benzene (DVB) and acrylonitrile (ACN). The DVB content controls pore size through cross linking to produce surface area of approximately $440\text{m}^2/\text{g}$ and a bulk density of 0.33 g/ml . It has strong affinity for polar molecules such as hydrogen cyanide, ammonia, hydrogen sulphide, and water and also separates methylamine, dimethyl ether and methanol. It exhibits no shrinkage and minimum column bleed thus giving good baseline stability. This requires conditioning at $200\text{-}250^\circ\text{C}$ for 4-6h under nitrogen or helium before packing into a column.

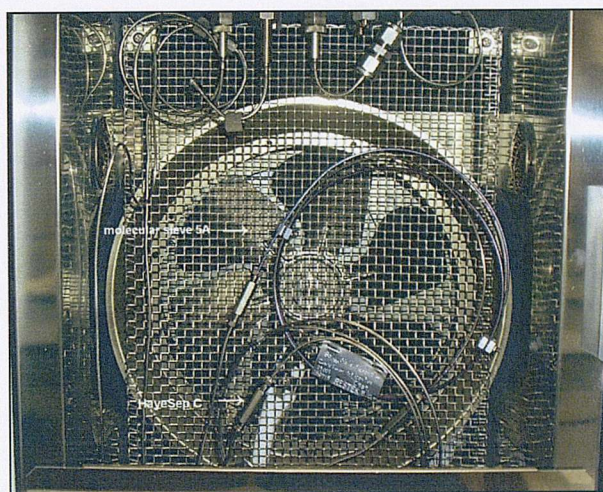


Figure 3.4 - Picture of the two columns (molecular sieve 5A and HayeSepC) installed in the oven

3.4.4.2 Molecular sieve 5A

It is easy to separate hydrogen, oxygen and nitrogen using solids known as molecular sieves, which are naturally occurring zeolites and synthetic materials like alkali metal aluminosilicates [17, 18]. These sieves are named in accordance with their approximate effective pore sizes, e.g. 5A has $5\text{\AA}$ pores and 9A has $9\text{\AA}$ pores. The atomic structure consists of an aluminum silicate skeleton with pores of regular size and shape formed by linking polyhedra made up from $-\text{SiO}_4$ and $-\text{AlO}_4$ tetrahedra.

3.4.5 Injection port temperature

The columns are fixed in between a heated injection port and a heated detector. The injection port should be hot enough to prevent condensation of any sample components so that no loss

in efficiency results from the injection technique. On the other hand, the injection port temperature must be low enough so that thermal decomposition or chemical rearrangement is avoided. An optimum temperature of 200°C was selected to avoid unwanted chemical reactions.

3.4.6 Column oven temperature

The separation process occurring in the column involves an equilibrium established by the component between the stationary and the mobile phases. The column is thermostated so that a good separation will occur in a reasonable amount of time. Column temperature of 200°C was maintained in this analysis. The distribution coefficient and hence the retardation is dependent on vapour pressure and retention properties of the stationary phase and is a function of temperature. The column temperature should be high enough so that sample components pass through it at a reasonable speed. It is usually preferable if the column temperature is below the normal boiling point of the sample constituents. Accurate control of column temperature is important in order to obtain reproducible chromatograms, retention times and peak area to height ratios. The oven temperature could be set to operate from about 10°C above ambient, up to 450°C with reproducibility of better than 0.1°C. Accurate control is important in isothermal analyses where retention times are being measured. The temperature control circuit monitors the ambient temperature and compensates for its fluctuation automatically, thus maintaining the column temperature at the set point.

3.4.7 Detector

The detector senses the effluent from the column and provides a record of the chromatography in the form of chromatogram. The detector signals are proportional to the concentration of each analyte making possible quantitative analysis. Most widely used detectors are the Flame Ionisation Detector (FID), Thermal Conductivity Detector (TCD) and Electron Capture Detector (ECD). Since TCD was used in this analysis, it is discussed here. Gas chromatographs used for gas analysis usually are fitted with thermal conductivity detectors (TCD), which are stable and moderately sensitive. TCD is used mainly for packed columns and inorganic analytes like water, carbon monoxide, carbon dioxide and hydrogen. The TCD is a differential detector that compares the thermal conductivity of the analyte in carrier gas to the thermal conductivity of pure carrier gas.

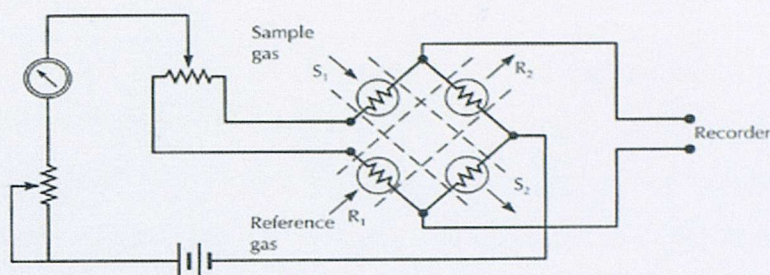


Figure 3.5 - Thermal Conductivity Detector, balanced in a Wheatstone bridge [19]

When the metallic filaments are heated with an electric current in a high thermal conductivity carrier gas such as helium, the sample components which have lower thermal conductivity than the carrier gas raise the filament temperature when they pass through the detector. The chromatogram is obtained by measuring a change in the filament resistance caused by the temperature rise. Tungsten rhenium filaments (approx. 100Ω each at ambient temperature) were used in a Wheatstone bridge which is shown in Figure 3.5. With pure carrier gas passing over all four elements, the bridge circuit is balanced to give a 'zero' control. When an analyte elutes, the thermal conductivity of the gas mixture in the two sample cavities is decreased, their filament temperatures increase slightly, causing the resistance of the filaments to increase and the bridge becomes unbalanced – that is a voltage develops across opposite corners of the bridge. That voltage is dropped across a voltage divider (the so-called attenuator) and then all or part of it is fed to a recorder and integrator.

One type of sample that cannot be analyzed with a TCD and helium carrier gas is hydrogen in a gas mixture. Hydrogen's thermal conductivity is so close to helium's that either the peak shapes are irregular or do not appear at all and thus quantitative results are not possible [16]. The carrier gas used with the TCD must have a thermal conductivity that is very different from the samples to be analysed (Table 3.2), so the most commonly used carrier gases are helium and hydrogen which have the highest values.

Thermal conductivity detectors have the advantage of stability, simplicity and recovery of the separated materials, but the disadvantage is the low sensitivity relative to that of flame ionization detectors. Because of their low sensitivity they cannot be used with capillary columns.

3.4.8 Detector temperature

The detector temperature depends on the type of detector employed. However, the detector and its connection from the column exit must be hot enough to prevent condensation of the sample. If the temperature is too low and condensation occurs, peak broadening and even the total loss of peaks is possible. The thermal conductivity detector temperature must be controlled to $\pm 0.1^{\circ}\text{C}$ or better for baseline stability and maximum sensitivity. 200°C was set as a default detector temperature for the analysis.

Table 3.2 - Thermal conductivity for selected gases at STP

Species	Thermal conductivity (W/ (mK))
Helium	0.152
Hydrogen	0.182
Nitrogen	0.026
Argon	0.018
Carbon dioxide	0.017

3.4.9 Data processing

Data processing in chromatography involves collecting and processing the detector signals to produce chromatograms and extract major parameters such as retention time, peak area and peak width.

Table 3.3 - Parameters set for GC analysis

Parameters	Set value
Column initial temperature ($^{\circ}\text{C}$)	70
Column final temperature ($^{\circ}\text{C}$)	200
Detector temperature ($^{\circ}\text{C}$)	200
Heating rate ($^{\circ}\text{C}/\text{min}$)	2.5
Injection port temperature ($^{\circ}\text{C}$)	200
¹ Polarity of the detector	1
² Detector current (mA)	100

¹ The signal output from the detector on the flow 1 side will be positive.

² Current set to be allowed to flow through the detector.

Chromatograms are produced by plotting the continuously varying signal from the detector against time. The area under each peak is proportional to the measure of the amount of that component in the sample. The parameters set for the GC analysis are shown in Table 3.3.

Figure 3.6 shows the photograph of the gas chromatograph Shimadzu 14B installed and connected to the rest of the experimental set up.

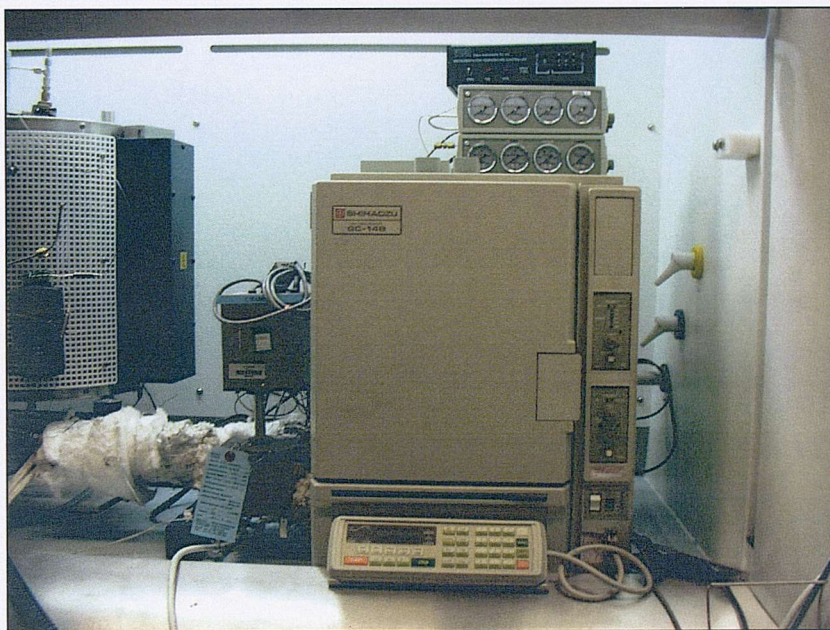


Figure 3.6 - Photograph of installed GC-Shimadzu 14B

3.5 Micro reactor design and fabrication

The objective of these experiments was to characterise the catalytic properties of the materials used in the SOFC anode. Using the knowledge gained from the literature survey, a micro reactor was constructed for the kinetic experiments. The work was split into three sections:

- Construction and preparation of the micro reactor
- Operation of the reactor
- Analysis of reaction products

3.5.1 Construction and Preparation of the micro reactor

A gas phase flow micro reactor was designed and constructed. A tubular silica glass reactor was used for the kinetic experiments. The catalyst bed length was < 1 cm. The use of a long entrance length, in which the reactant gas mixture was heated to the reaction temperature, and a very short catalyst bed length ensured that the reacting system was isothermal and its temperature was measured by the thermocouple just above the catalyst bed. The simplest way to describe the equipment layout and connections is via the P & ID (piping and instrumentation diagram) is shown in Figure 6.4 (Chapter 6).

The complete reactor system included the following features:

- ❖ Construction: Most of the construction other than the reaction tube was stainless steel. The maximum design operating temperature was 750°C . Pressure sealing of the reactor tube was by stainless steel gaskets and the majority of fittings used were SS316 purchased from Swagelok. All the fittings were either $1/4''$ or $1/8''$. The feed gases entering the reactor were through stainless steel tubes and the connections between the gas lines were made using union tees (316) and union crosses (316).
- ❖ Reactor and catalyst support: The reactor tube was a 1.19cm o.d., 0.97cm i.d., and 45.7cm long silica glass tube. To connect the glass tube and the stainless steel fittings, graphite ferrules (SF800) were used. The reactor was operated vertically with the gas in down flow. The catalyst was placed two-thirds along the length from the top of the reactor tube, supported on inert material (silica glass wool). The micro reactor was located with the catalyst at the centre of the furnace hot zone. The small openings on the top and bottom of the furnace and the rest of the micro reactor exposed outside the furnace were covered with high temperature insulating alumina wool to prevent escape of heat and wrapped with aluminium foil to keep it in position.
- ❖ Reactant inlet gas manifold: Dry helium carrier gas and the reactant gases (research grade A) were purchased from BOC Gases Ltd. Gases were supplied pressure regulated from cylinders to a bank of four mass flow controllers for methanol/helium and water/helium (8-400ml/min), oxygen (2-100ml/min) and ammonia (2-100ml/min) and various switching valves. This provided flexibility in the choice of gas composition for

the kinetic experiments. Two separate temperature-controlled water baths (Grant) were used to maintain constant temperature of the saturators.

- ❖ Reactor effluent: The reactor effluent was piped directly to the sampling valve of the gas chromatograph (GC) and then to vent. All lines and valves were fully heated to 70°C to minimise condensation of products.
- ❖ Process control: Flow control was by four Brooks high pressure mass flow valves. A Brooks microprocessor-based flow controller (model 0154) with four channels for oxygen, methanol, ammonia and water was used to control the mass flow valves. The gas flow was limited using plug valves wherever necessary (Swagelok). Bellows-sealed valves were used for the helium carrier gas which was taken from a high pressure cylinder. Check valves (SS Poppet Check Valve 1/8" Swagelok) were used in conjunction with mass flow valves where the direction of flow must not be allowed to reverse itself. They are sometimes referred to as one-way directional valves. The detailed flow control set up is shown in Figure 3.7.
- ❖ Temperature control: Temperature control was by use of a high stability temperature controller (Type 2416) controlling a cylindrical split furnace surrounding the reactor. A vertical split tube furnace from Elite Thermal systems Ltd. with a maximum rated temperature up to 1000°C was used. The furnace temperature was located against the set temperature prior to the experiment. A K-type thermocouple was placed near the catalyst bed and the catalyst temperature (reaction temperature) was assumed to be equal to the temperature of the thermocouple.
- ❖ Leak gas detection: Two Crowcon Gasman II personal gas detectors were used during the experiment to continuously monitor the level of HCN (0-25ppm) and CO (0-500ppm). Another detector (Crowcon TRIPLE PLUS+ microprocessor controlled portable gas detector) monitored up to four gas types ammonia (0-50ppm), CH₄ (0-500ppm) CO (0-500ppm), NH₃ (0-500ppm) and H₂ (0-2000ppm) simultaneously to provide warning of any hazardous levels.

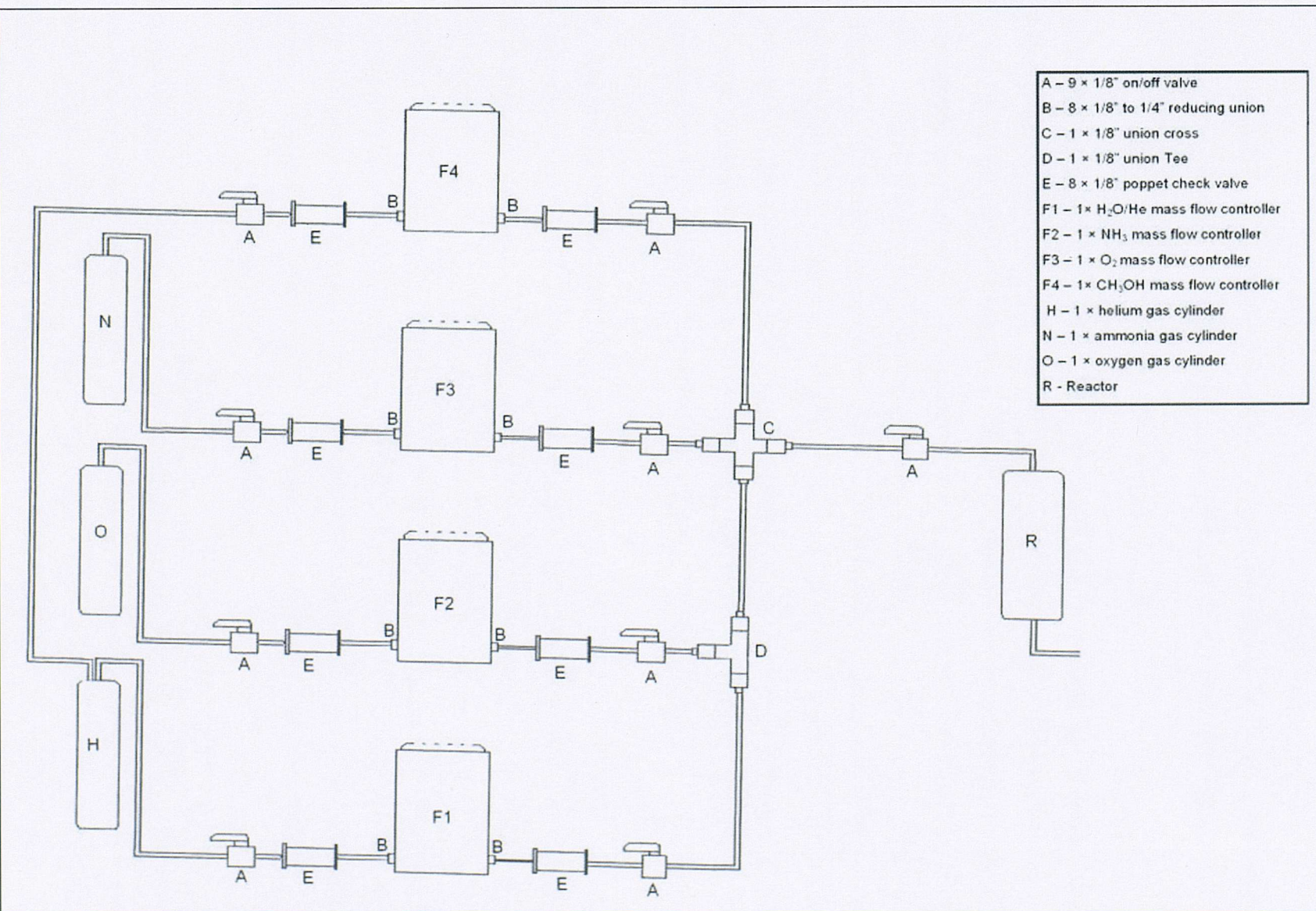


Figure 3.7 - Illustration of mass flow controller set up

3.5.2 Operation of the reactor

The procedure for the kinetic experiment was follows:

- ❖ Catalyst loading: The catalyst (particle size $\sim 10\mu\text{m}$) was placed in the lower 1/3 reactor length supported on silica glass wool. A constant mass of approximately 2g of catalyst was used in all experiments.
- ❖ Experimental reaction: The reaction was carried out at atmospheric pressure and at temperatures in the range 450°C to 650°C . The temperature controller was set to ramp at $2^{\circ}\text{C}/\text{min}$. to the desired temperature and then held for 20 to 30 minutes at the reaction temperature for every run. The reactants methanol (VWR Ltd., 99.6% purity) in helium (BOC Ltd., 99.995% purity), ammonia (BOC Ltd., 99.8% purity) and oxygen (BOC, Ltd., 99.96% purity) were delivered by the mass flow controller system and the total flow was in the range of 50-100ml/min (All gas volumes are quoted at standard temperature and pressure). A flow of helium was allowed through a Dreschel bottle containing methanol at room temperature. The lines between the outlet of the bubbler and the inlet of the microreactor were heated using heating tape (70°C) to avoid condensation.

3.5.3 Analysis of reaction products

The analysis of the product stream was carried out by a gas chromatograph (GC Shimadzu 14B). A continuous bleed of the effluent from the tubular reactor was taken through a heated line to minimise condensation of products (70°C). The automated injection valve was capable of taking a sample every 20 to 30 minutes. 0.5ml samples were taken by the gas sampling valve. Two chromatographic columns were used to separate the condensable and non-condensable products. The samples were injected into molecular sieve 5A and HayeSepC columns using helium as a carrier gas. The columns were maintained at 200°C and allowed separation of compounds through their retention times.

Detection of products was performed using the thermal conductivity detector. Response factors were determined for the compounds thought to be likely to be detected. This was done using pre-calibrated gas mixtures purchased from Cryoservice Ltd. The minimum detectable amount of all the analytes was found to be in the range 100- 500ppm. Both the retention time and peak area were reproducible with $\pm 0.01\%$ error. The chromatograms were recorded on a chart recorder. The overall experimental procedure is shown in Table 3.4.

Table 3.4 - Operation procedure of micro reactor for HCN synthesis

Stage	Description
System Conditioning	• Turn on extraction fan inside laboratory and fume cupboard. • Turn on the micro reactor furnace and ramp (2°C/min) to temperature. • Turn on helium carrier gas, then the GC. • Switch on the TCD detector. • Connect the detector to the chromatogram recorder. • Check the carrier gas flow in GC using soap solution. • Insure a flow of <10ml/min helium into the reactor during ramping.
Feed preparation	• Once the operating temperature is reached, use GC to detect any presence of O₂, CO or CO₂. If any of the mentioned gases are detected terminate the experiment and ramp down the temperature of furnace otherwise continue. • Check furnace reached set temperature and GC registering none. • Adjust flow of gases into the reactor via mass flow controllers to required flow rates.
Reaction	• Check the flow rates in the mass flow controllers. • Adjust the valve positions to analyse composition of feed and the product stream via GC. • Repeat the experiment by injecting the product stream into the GC for concordance. • Adjust the temperature for next run.
Shut down	• Reduce the flow of source gases to 0ml/min using the mass flow controllers. • Close ball valves prior to the mass flow controller (excluding helium). • Close valves on cylinder (excluding helium). • Switch off the detector and disconnect the detector from recorder. • Turn off GC and recorder. • Turn off furnace when operating temperature reaches 30°C. • Turn off helium gas supply using mass flow controller. • Turn off mass flow controller. • Close valves on helium cylinder. • Log duration of operation.

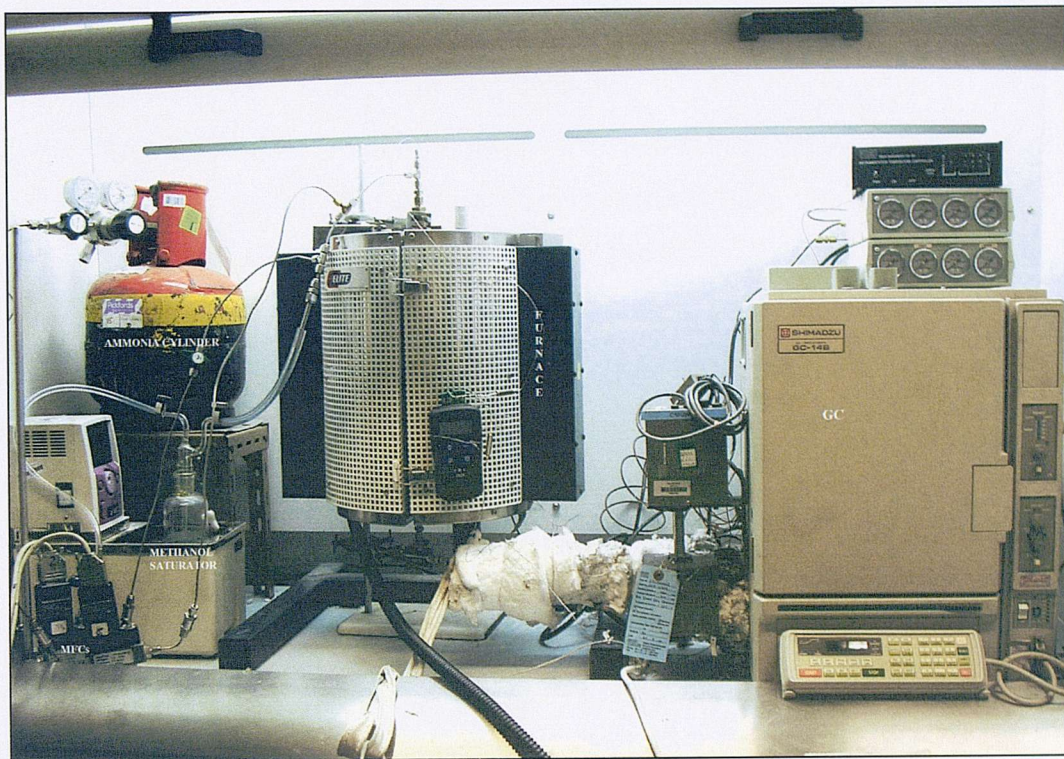


Figure 3.8 - Photograph of the experimental set up

3.6 Conclusions

This chapter outlined the experimental procedures for the HCN synthesis in a micro reactor and characterisation techniques to study the performance of the electrodes. FSO- Ni/CGO anode catalyst preparation was explained. It has been concluded that 60-40 wt% Ni-CGO is the preferred composition for the study as it has a good lateral electronic conductivity. Physical characterisation techniques such as X-ray diffraction (XRD), nitrogen gas adsorption and scanning electron microscopy/ energy dispersive spectrometry (SEM/EDX) were explained. These techniques were used to study the phase changes, surface area and microstructure of the electrocatalyst. This was followed by the GC instrumentation which was one of the main aspects of the project for the product analysis. Each component which was specifically installed for this project was well defined. Finally, the design, construction and operation of the micro reactor for the catalytic studies of the reaction kinetics of the HCN synthesis were described. The micro reactor rig set up was complex and time consuming.

3.7 Chapter 3 – References

- 1 N.Q. Minh, J. Am. Ceram. Soc. 76 (1993) 563
- 2 N.P. Brandon, S. Skinner and B.C.H. Steele, Annu. Rev. Mater. Res. 33 (2003) 183
- 3 B.C.H. Steele, Solid State Ionics 86-8: Part 2 (1996) 1223
- 4 B.C.H. Steele and A. Heinzl, Nature 414 (2001) 345
- 5 S.J.A. Livermore, A.M. Diskin, J.W. Cotton and R.M. Ormerod, Fourth European Solid Oxide Fuel Cell Forum, Switzerland, 1 (2000) 95
- 6 S. A. Baron, Anodes for Solid Oxide Fuel Cells with Ceria Electrolytes, Ph.D. Thesis Imperial College London (2004)
- 7 A.R. West, Solid State Chemistry and its Applications, Wiley New York (1984)
- 8 K.S.W. Sing, Advances in Colloid and Interface Science 76 (1998) 3
- 9 S. Lowell and J.E. Shields, Power Surface area and Porosity, Chapman and Hall, London (1984)
- 10 N.J. Coleman and L.L. Hench, Ceramics International 26 (2000) 171
- 11 F. Rouquerol, J. Rouquerol and K.S.W. Sing, Adsorption by Powders and Porous Solids – Principles, Methodology and Applications, Academic Press New York (1999)
- 12 S.J. Gregg and K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press London (1982)
- 13 J. Rouquerol, D. Avnir, C.W. Fairbridge, D.H. Everett, J.H. Haynes, N. Pernicone, J.D.F. Ramsay, K.S.W. Sing and K.K. Unger, Pure and Appl. Chem. 66 (1994) 1739
- 14 D. Skoog and J.J. Leary, Principles of Instrumental Analysis, Saunders College Publishing Philadelphia (1992)
- 15 J.I. Goldstein, Scanning Electron Microscopy and X-ray Microanalysis, Plenum New York (2003)
- 16 H.M. McNair and J.M. Miller, Basic Chromatography, John Wiley New York (1998)
- 17 A. Braithwaite, Chromatographic Methods, 4th ed. Chapman and Hall London (1985)
- 18 J.M. Miller, Chromatography: Concepts and Contrasts, 2nd ed. John Wiley New York (2004)
- 19 I.A. Fowles, Gas Chromatography, 2nd ed. Wiley Chichester (1995)

Chapter 4

Catalyst Characterisation Results and GC Calibration

4.1 Characterisation results

4.1.1 X-ray Diffraction

Initial characterisation of the iron antimony oxide catalyst (FSO) was performed by XRD analysis. XRD analysis was carried out initially on as received FSO catalyst to find the phases existing. The weight composition of the as received FSO catalyst was 76% Fe_2O_3 , 15% FeSbO_4 , 8% Sb_2O_3 and 1% Cr_2O_3 . The technique indicated the coexistence of FeSbO_4 and Fe_2O_3 (Figure 4.1) in the as received catalyst. Fe_2O_3 exists in three polymorphic forms; α - Fe_2O_3 , β - Fe_2O_3 and γ - Fe_2O_3 . It was found that the bulk of the FSO material comprised of α - Fe_2O_3 and FeSbO_4 (squawcreekite), a schematic of which is shown in Figure 4.2.

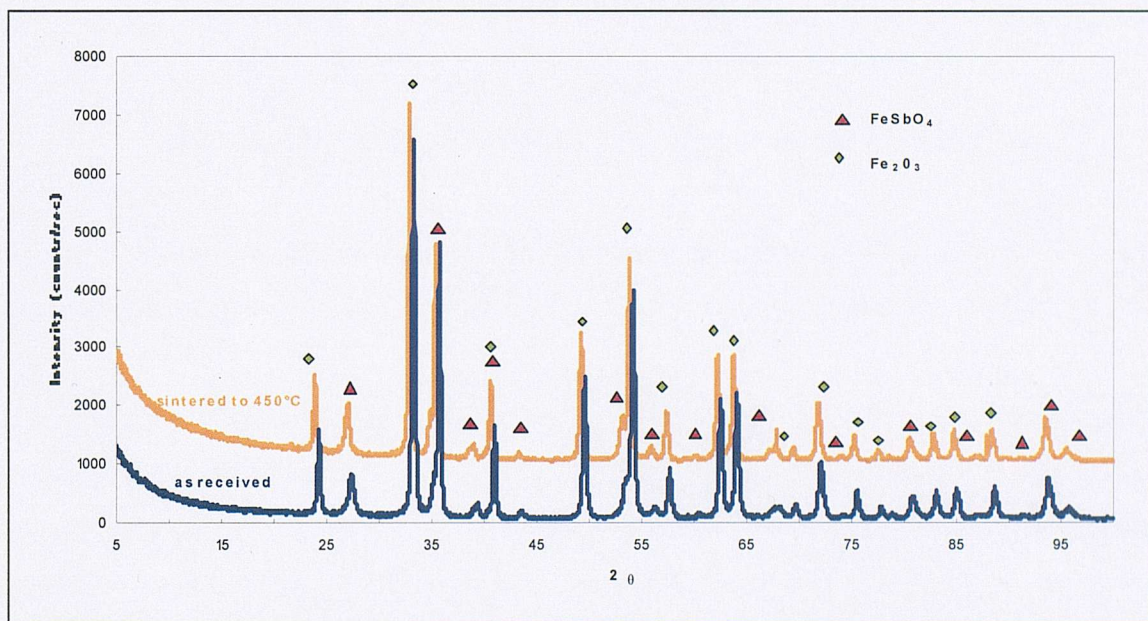


Figure 4.1 - XRD pattern of as received FSO catalyst and after being calcined to 450°C

According to the literature data, FeSbO_4 crystallises in the tetragonal system and has a structure related to rutile [1-5]. The structure is described in terms of a rutile-like framework, with Fe and Sb cations distributed in the octahedral sites between the oxygen lattice. However, the extent of ordering of Fe and Sb in these sites is still unclear.

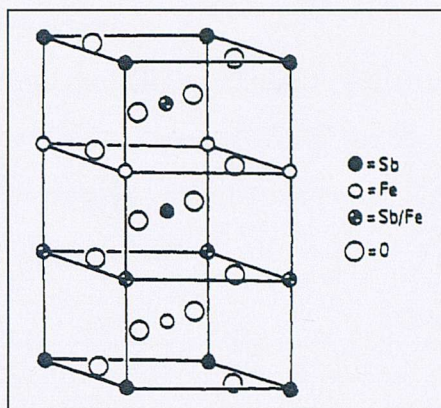


Figure 4.2 - Diagram illustrating the positions of the iron, antimony and oxygen atoms in the tripled unit cell of ordered iron antimonate [6]

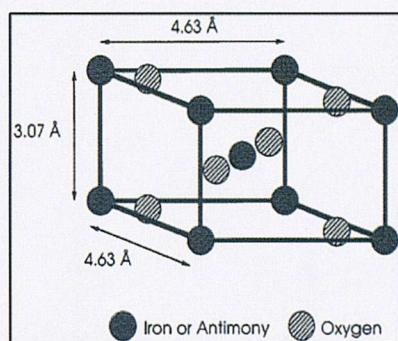


Figure 4.3 - Schematic of ideal rutile type structure of FeSbO_4 [4]

No Sb_2O_3 peaks were detected in the XRD due to its low concentration in the catalyst and the fact that its main peaks (at 2θ values of 24, 32, 35, 41, and 55°) coincide with Fe_2O_3 peaks.

The promoter Cr_2O_3 in the catalyst was undetectable by XRD due to its very low concentration (approximately 1%). The effect of including antimony oxide in catalysts used for selective partial oxidation is well known [8]. Sb (III) ions appear to act as sites for trapping gaseous oxygen and for generating mobile oxide ions, especially in oxidation and ammoxidation reactions [9]. Iron-antimonate catalysts having excess Fe_2O_3 (i.e., iron-rich catalysts) have shown significantly better catalytic performances than the corresponding stoichiometric FeSbO_4 oxide catalysts [10, 11]. Mixed metal oxide catalysts containing iron have been widely used for the selective oxidation hydrocarbons [12, 13]. Antimony exists in +5 oxidation number in FeSbO_4 and iron at +3 in both Fe_2O_3 and FeSbO_4 phases. However, during catalytic reactions both Sb and Fe are capable of changing oxidation states which is believed to assist electron transfer to and from adsorbed gas molecules.

4.1.2 Calcination behaviour

Figures 4.4 and 4.5 show the XRD diffraction patterns of FSO catalyst calcined at different temperatures in air. The FSO calcined at 450°C for 5h gives a diffraction pattern similar to the as received pattern. The sample does not show any significant change in the intensity of the peaks, especially in the Fe_2O_3 peaks.

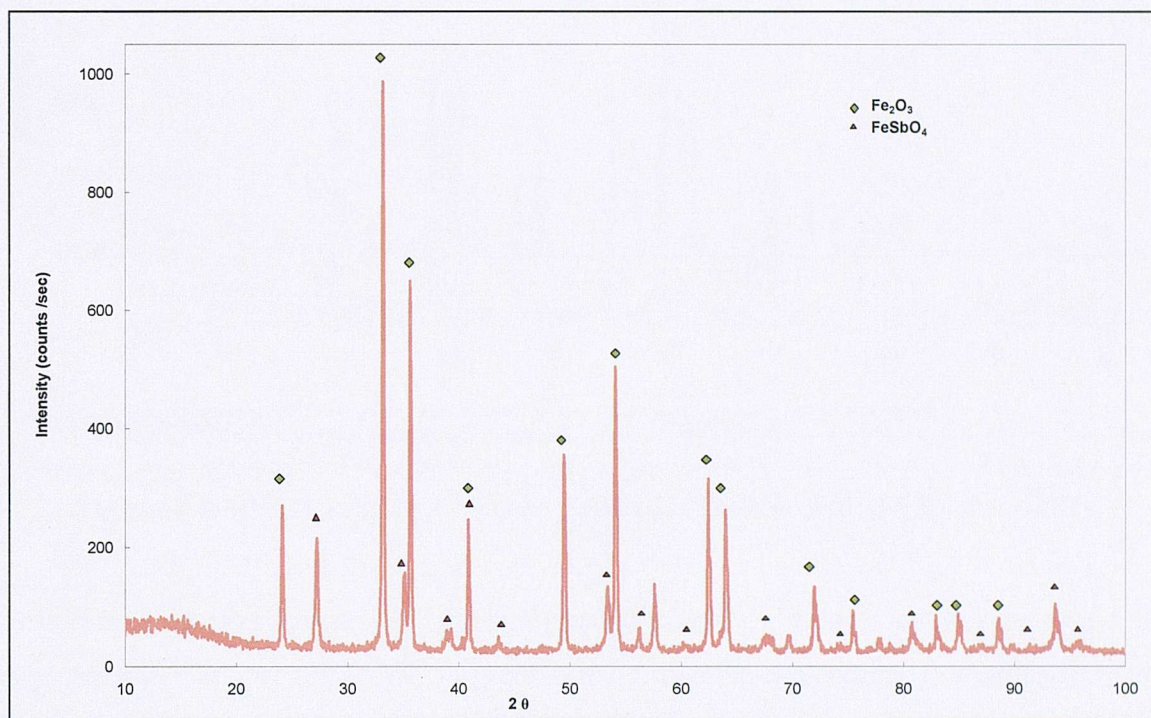


Figure 4.4 - XRD pattern of FSO calcined to 900°C

Heating the FSO material at 900°C for 5h led to the improved crystallinity. The sample also showed a corresponding increase in the intensity of Fe_2O_3 and FeSbO_4 peaks as seen in Figure 4.4. Carbucicchio *et al.* [14] also reported that the increase of the calcination temperature of FSO from 350°C to 900°C resulted in a dramatic increase in the intensity of the FeSbO_4 XRD characteristic peaks as a result of increased crystallinity.

The XRD pattern for FSO calcined at 900°C reveals that the same two phases of Fe_2O_3 and FeSbO_4 are stable. Also increasing the calcination to 1300°C led to further increase in the FeSbO_4 content of the mixed oxide catalyst. Peaks at $2\theta = 35, 42, 57$ and 66° are characteristic of FeSbO_4 , and these peaks were either weak or absent in the as received material.

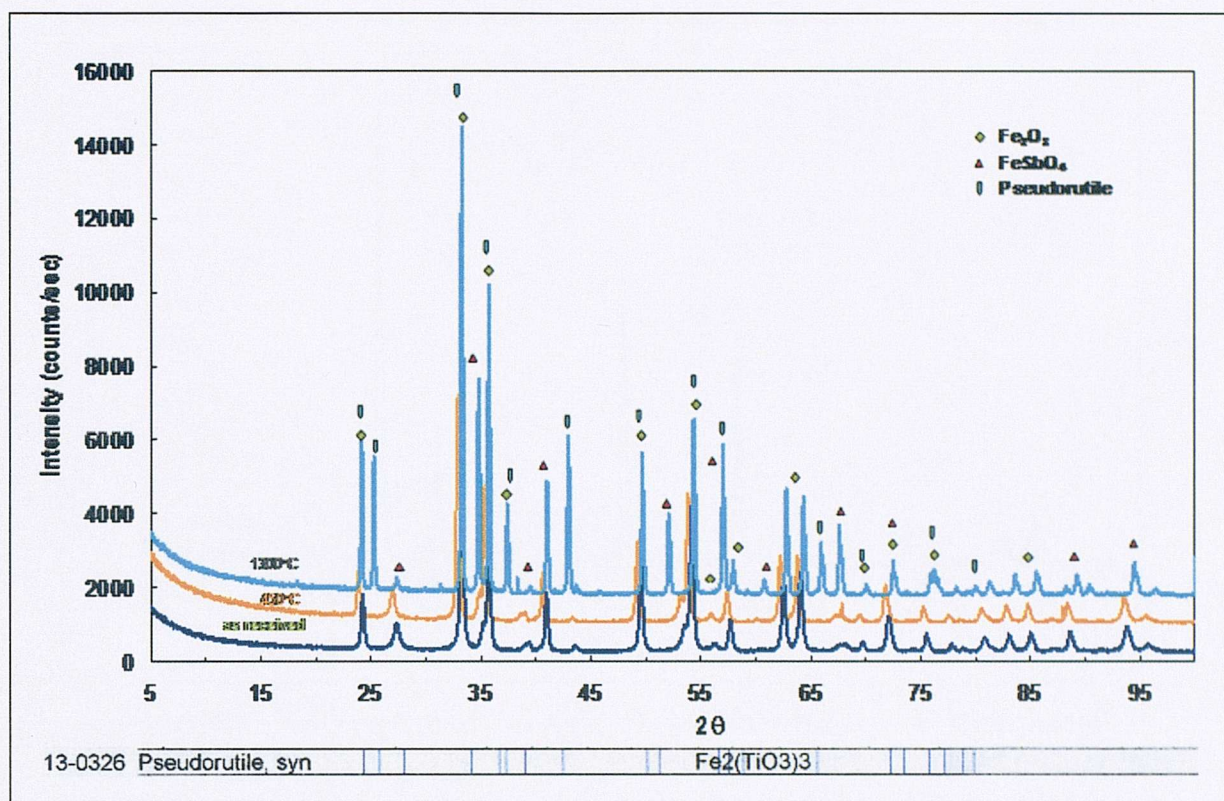


Figure 4.5 - XRD pattern of FSO as received, FSO calcined to 450 and 1300°C

In addition to the presence of crystalline Fe_2O_3 and FeSbO_4 , Bragg reflections characteristic of the pseudorutile structure $\text{Fe}_2(\text{TiO}_3)_3$ were also noticed from the sample calcined at 1300°C. These extra peaks appear at 2θ values of 25.3 and 37.5°.

X-ray diffraction was also performed on $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO - 10) obtained from Rhodia (Figure 4.6). The material was single phase and crystalline. The XRD pattern of CGO was fitted to a cubic fluorite structure. The presence of cubic fluorite structure of CGO was also confirmed in the XRD pattern of 60-40 wt% Ni-CGO composite (Figure 4.7). The peaks at 2θ value of 37.4, 43.3, 63.4, 75.6 and 79.2° correspond to NiO.

Figure 4.8 shows the XRD pattern of the full 40-60 wt% FSO-Ni/CGO composite after calcinations at 1300°C. All the phases Fe_2O_3 , FeSbO_4 , NiO and CGO required for the electrocatalytic anode are present and no new phases are evident. It is interesting to note that the pseudorutile detected when FSO was calcined at 1300°C does not appear in the composite.

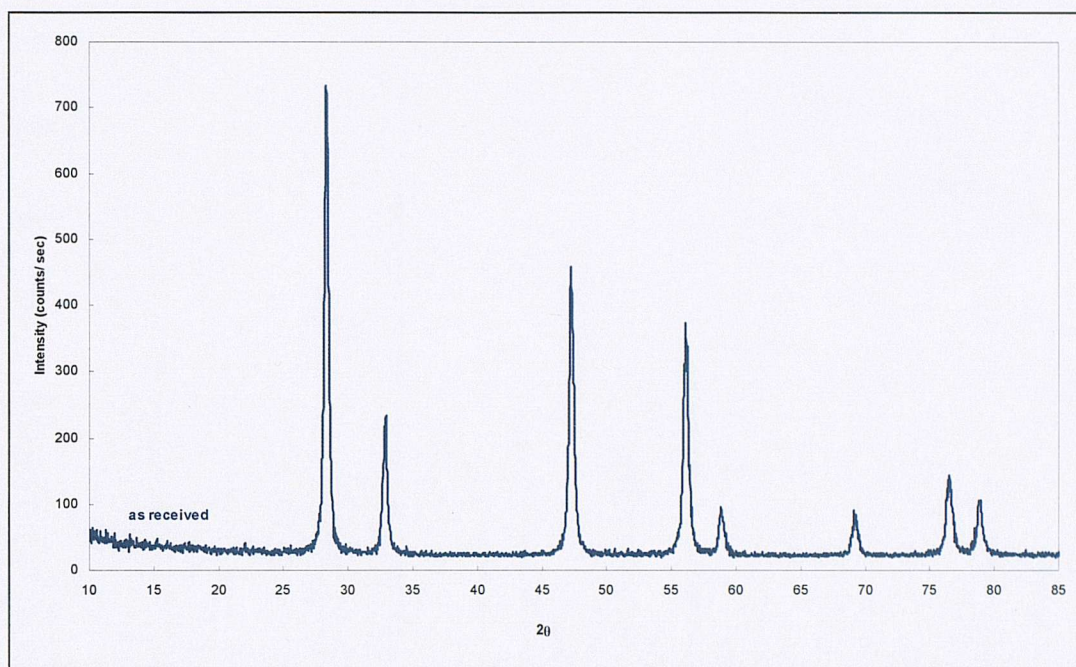


Figure 4.6 - XRD pattern of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO -10) at room temperature

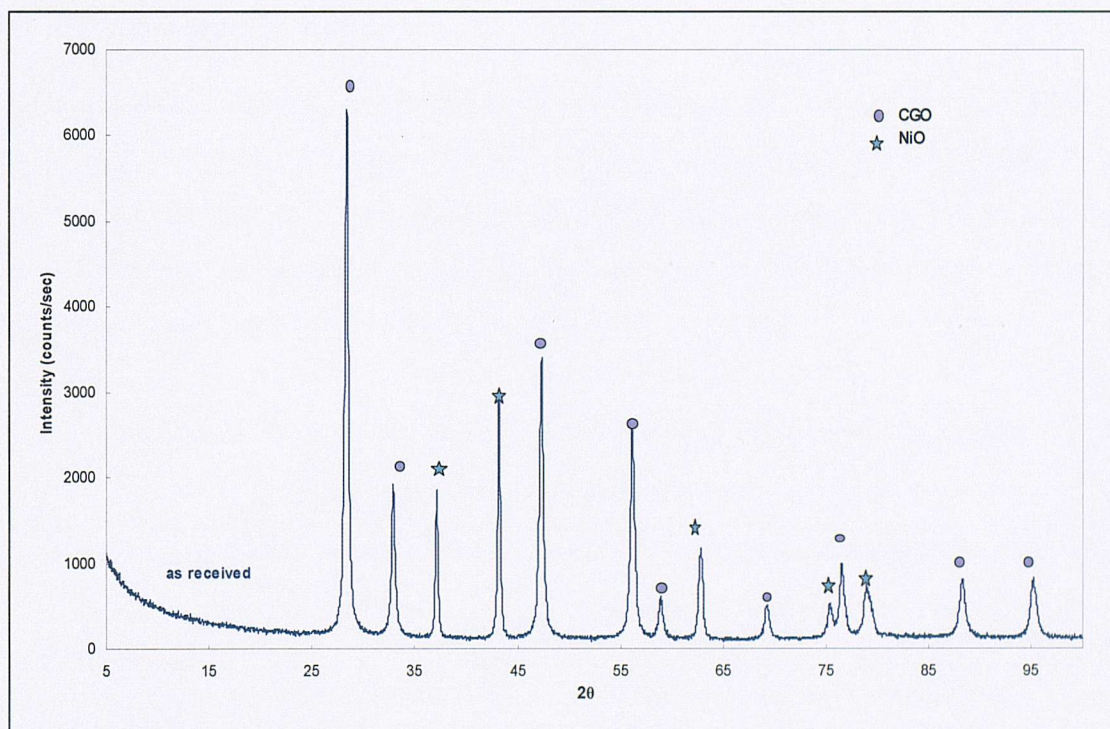


Figure 4.7 - XRD pattern of 60-40 wt% Ni-CGO mixture

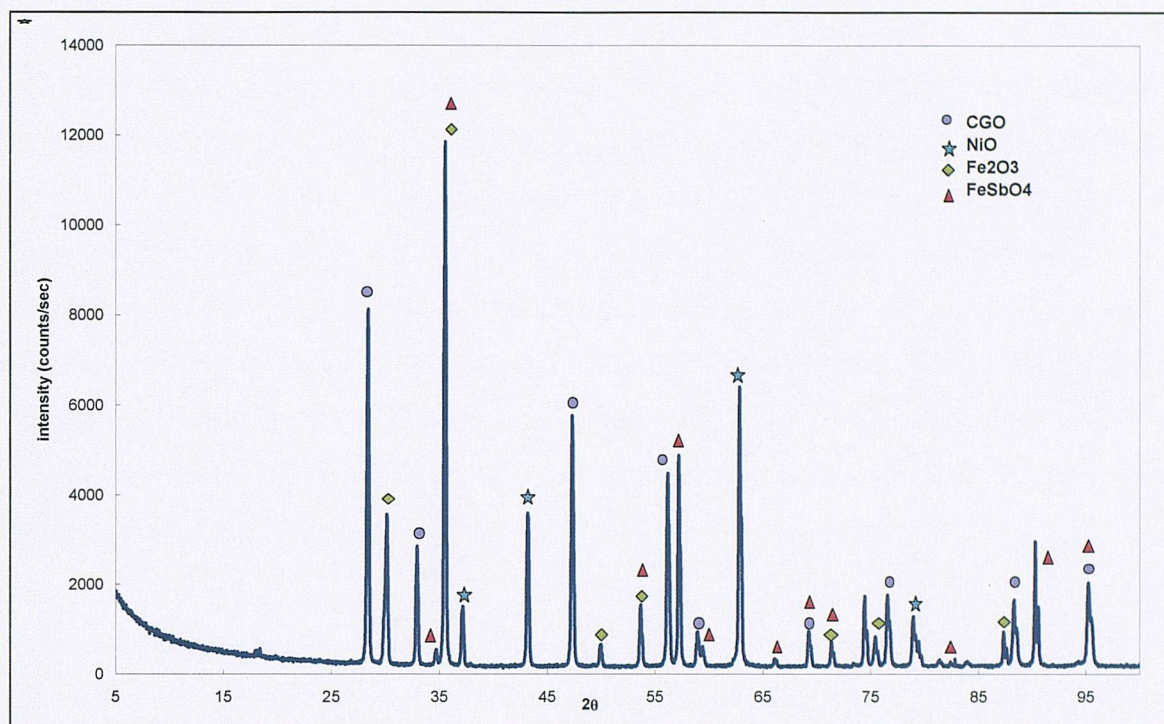


Figure 4.8 - XRD pattern of 40-60 wt % FSO-Ni/CGO composite calcined to 1300°C

4.1.3 Nitrogen gas adsorption

Nitrogen gas adsorption was performed at 77.4K with a sample weight of 0.1 and 0.5g of as received FSO and sintered 40–60 wt% FSO-Ni/CGO respectively. The FSO-Ni/CGO anode slurry was then deposited on both sides of an alumina plate acting as a substrate and sintered to 1300°C for 5h. The anode material was then scraped of the alumina plate and analysed using nitrogen gas adsorption.

Table 4.1 - Typical physical properties of electrode catalyst materials
from nitrogen gas adsorption

Electrode	BET surface area (m ² /g)	Total pore volume (cc/g)	Average pore diameter (Å)
FSO-Ni/CGO fired at 1300°C	30.02 ± 0.1	0.10 ± 0.01	140.6 ± 0.2
FSO as received	122.5 ± 0.1	0.25 ± 0.01	79.5 ± 0.2

The particle size of NiO-CGO was 1.2 μm [15]. The particle size of FSO was in the range of 10-50 μm obtained from Catal International, UK. The specific surface area obtained from nitrogen adsorption is given in the Table 4.1. The Brunauer, Emmett and Teller (BET) method was applied to derive the surface area from the physisorption isotherm data. As received FSO has a very high surface area (122.5 m^2/g). Table 4.1 also gives a summary of pore size measured by the Barrett, Joyner and Halenda (BJH) method using liquid nitrogen. The catalyst particles contained pores mainly within the range of 70 to 150 $\text{\AA}$, confirming that the mixed oxide powder catalysts were mesoporous with good porosity and high surface areas. Mesopores have widths between 20 and 500 $\text{\AA}$, micropores are smaller than 20 $\text{\AA}$ and macropores are larger than 500 $\text{\AA}$ [16, 17].

4.1.4 Scanning Electron Microscopy - X-Ray Microanalysis (SEM -EDX)

To determine the composition of the individual crystallites in the catalyst and the anode cermet FSO-Ni/CGO, SEM-EDX measurements were performed. SEM micrographs and point analysis EDX spectra of FSO catalyst as received and 40-60 wt% FSO-Ni/CGO after calcination are shown in Figure. 4.9 and 4.10. Characteristic (EDX) X-ray spectra confirmed the presence of elements such as Fe, Sb and Cr. The strength of the Fe peak in each spectrum shows that iron is the main constituent (other than oxygen). The low concentration of Cr is consistent with its use as a promoter for FSO in HCN synthesis. The peaks at about 1 and between 6 and 8keV correspond to Fe and those between 3 and 4keV correspond to Sb respectively. The images show that the distribution of elements is uniform (to the resolution of the EDX method).

Figure 4.10 shows the SEM-EDX of 40-60 wt% FSO-Ni/CGO catalyst calcined to 1300 $^{\circ}\text{C}$ for 2h. This confirms the presence of the Fe, Sb, Ce, Gd, and Ni. The Cr composition was less than the detection limit of the EDX. From the results, it is clear that the contents of Fe and Ce are significantly higher than that of antimony. The distribution of the different phases is not uniform.

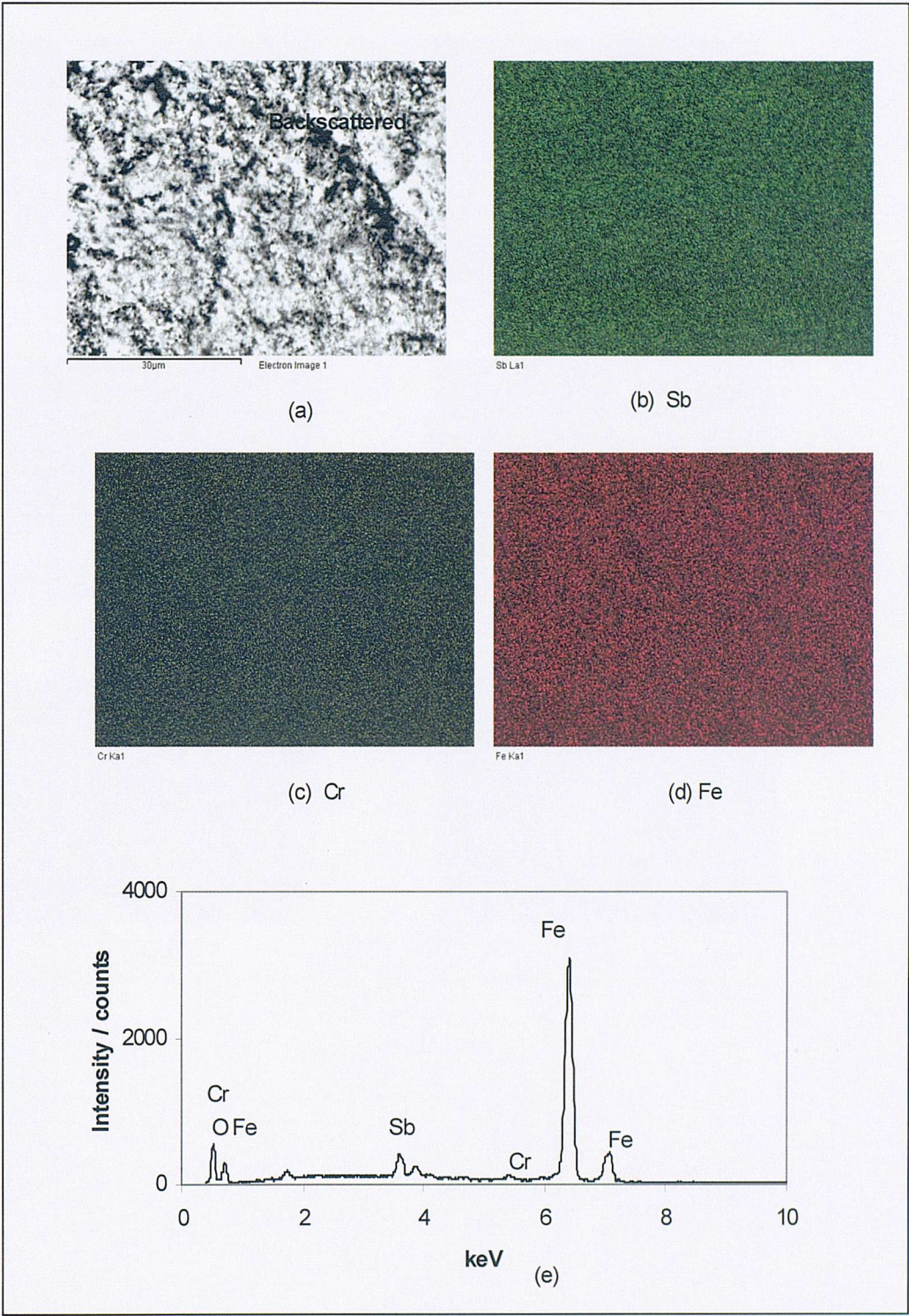


Figure 4.9 - SEM-EDX analysis of as received FSO (a) backscattered image (b)-(d) element maps (e) EDX spectrum

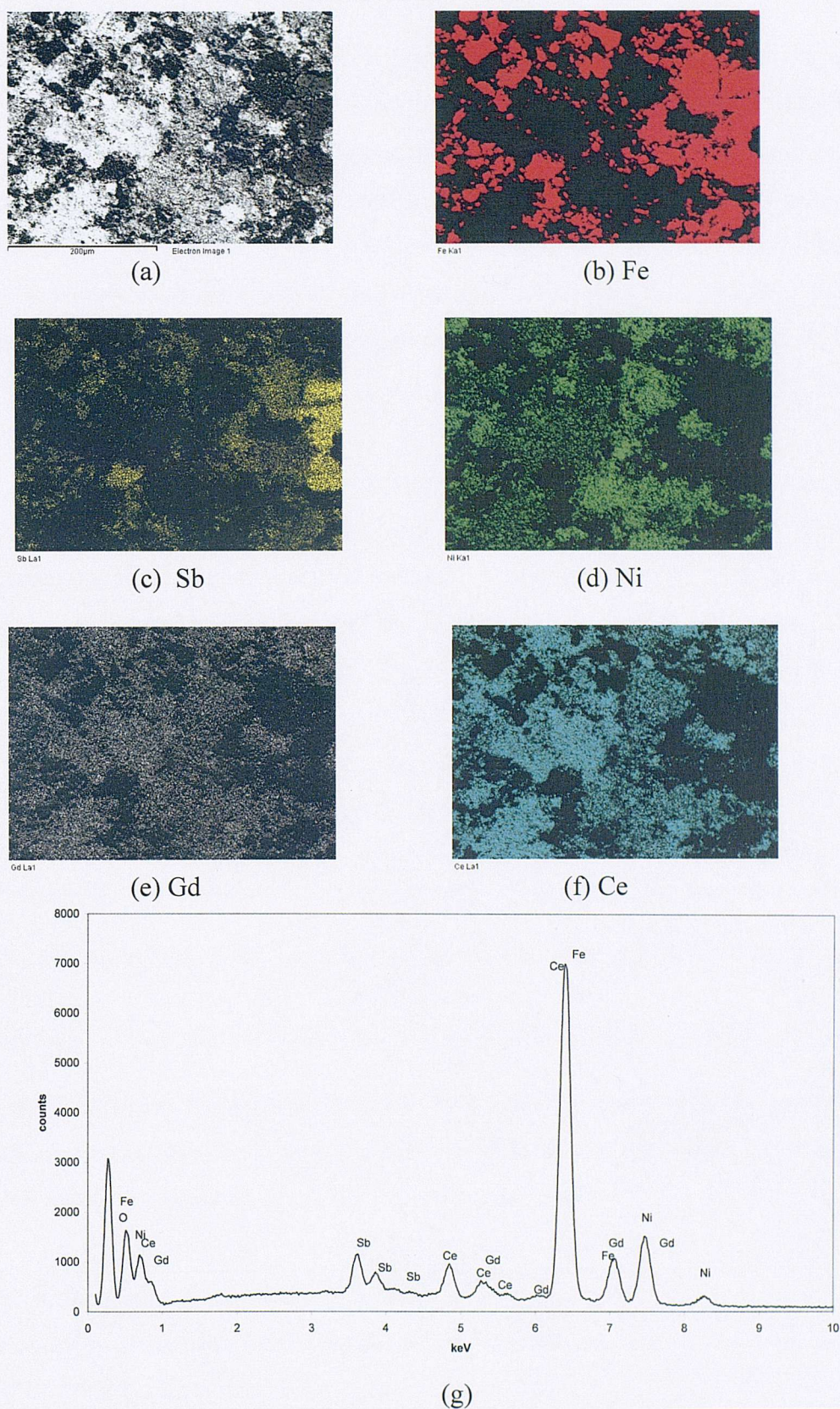


Figure 4.10 - SEM-EDX analysis of 40-60 wt% FSO-Ni/CGO calcined to 1300°C (a) backscattered image (b)-(f) element maps (g) EDX spectrum

4.2 Calibration of Gas Chromatograph

A GC can separate the gaseous compounds, but cannot identify them or measure their quantity without calibration. By calibrating the GC, the retention time for identifying specific compounds can be determined. Furthermore the area under the peak for each compound may be expressed in terms of its concentration by calibration with standards of known concentration. The calibration of the GC was carried out to determine the retention time and response factors of all the reactants and likely products of the HCN synthesis. Calibration was carried out with calibration gas mixtures obtained from Cryo Services, UK in 58L cylinders with helium balance. HCN was supplied in a 2L cylinder by Linde gas, Germany.

Each gas cylinder was connected through a regulator to the injection port of the gas chromatograph. Calibrations were repeated several times over a period of 30 to 40 minutes. The retention time and the peak area were noted for each gas and the response factor (concentration/area) was calculated for each compound. Molecular sieve 5A separates hydrogen, methane, oxygen, nitrogen, and carbon monoxide whereas HayeSepC separates hydrogen cyanide, ammonia, carbon dioxide, methanol, formaldehyde, dimethyl ether, methyl amine and water [18, 19]. The order of elution of compounds in the analysis using molecular sieve 5A and HayeSepC is shown below (CO₂ being the first to elute):

CO₂ > NH₃ > CH₃NH₂ > O₂ > N₂ > H₂O > CH₄ > CO > CH₃OCH₃ > HCHO > CH₃OH > HCN

The chromatograms for each calibration gas mixture are now presented and followed by a tabulation of retention time and response factors. These data were used for the product analysis of HCN synthesis.

4.2.1 Calibration of GC using CO, CO₂, N₂ and O₂

Figure 4.11 shows the chromatogram of the calibration gas mixture of carbon dioxide, oxygen, nitrogen and carbon monoxide with concentrations of 502.3, 530.9, 502.3 and 522.7 ppm respectively. Helium did not show any peak as it was the carrier gas in the GC analysis. Peaks at 0.4, 0.9, 1.08, and 2.6 minutes correspond to CO₂, O₂, N₂, and CO respectively.

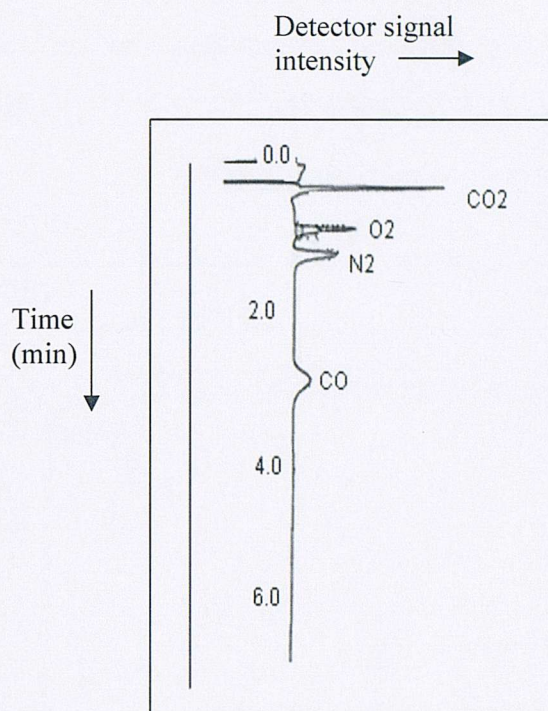


Figure 4.11 - Chromatogram of CO₂, O₂, N₂ and CO

4.2.2 Calibration of GC using CH₃OH, CH₃-O-CH₃ and N₂

Nitrogen, dimethyl ether and methanol of 500ppm concentration each with balance helium were separated in the order seen in Figure 4.12.

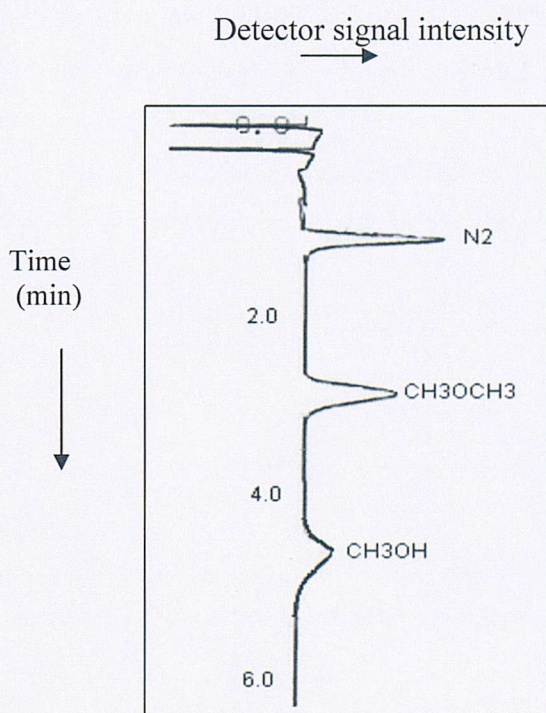


Figure 4.12 - Chromatogram of CH₃OH, CH₃-O-CH₃ and N₂

4.2.3 Calibration with O₂, N₂, CH₄ and CO

Oxygen, nitrogen, methane and carbon monoxide of concentration 150000, 834550, 15000 and 450ppm respectively gave the chromatogram shown in Figure 4.13.

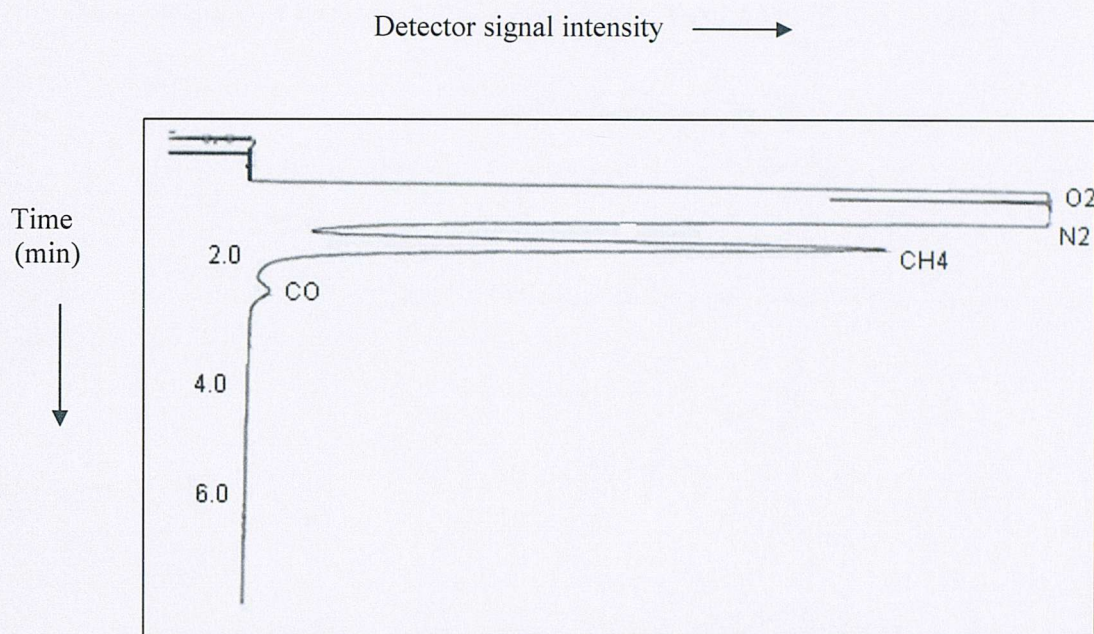


Figure 4.13 - Chromatogram of O₂, N₂, CH₄ and CO

4.2.4 Calibration with methylamine

Since methylamine was one of the possible products in the HCN synthesis especially in the ammonolysis reaction, calibration was carried out with 1000ppm of methylamine and balance helium (Figure 4.14). The methylamine was found to appear prior to oxygen at 0.7 minutes.

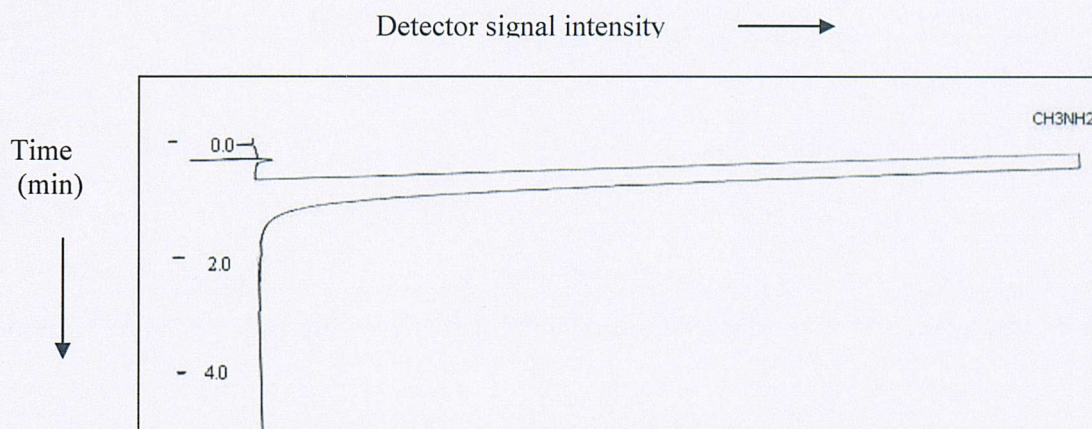


Figure 4.14 - Chromatogram of 1000ppm methylamine and helium balance

4.2.5 Calibration with HCN

846ppm of HCN gave a peak at 4.2 minutes close to methanol. This was found to be the last peak to appear in all calibration mixtures as well as in the subsequent synthesis experiment. The chromatogram of 846ppm HCN with nitrogen balance is shown in Figure 4.15.

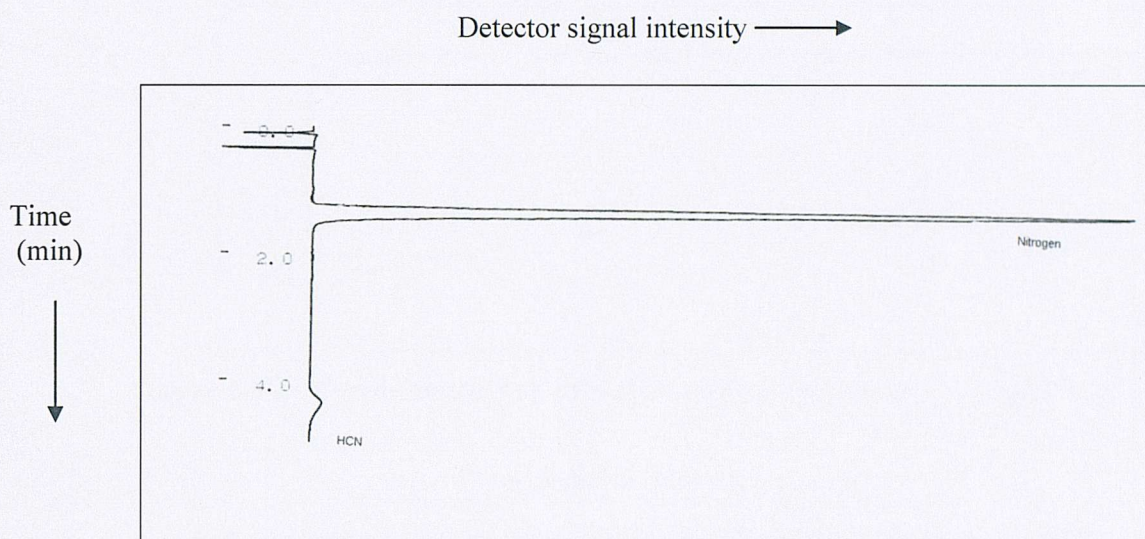


Figure 4.15 - Chromatogram of 846ppm HCN and balance nitrogen

4.2.6 Calibration of GC with ammonia, oxygen and methanol

Further the calibrations were carried out with appropriate compositions of the reactants.

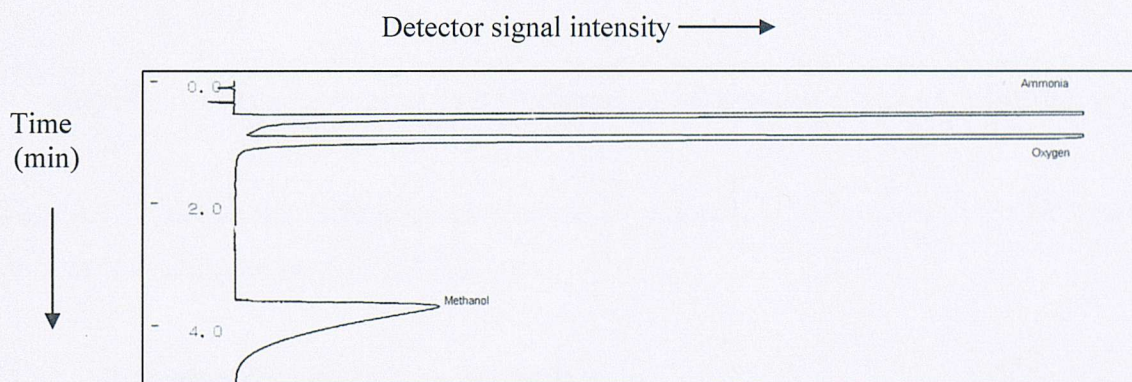


Figure 4.16 - Chromatogram of 13% ammonia, 15% oxygen, 10% methanol and helium

~13ml/min of ammonia, ~15ml/min of oxygen and ~70ml/min of helium were passed through methanol in a saturator and the mixture injected into the GC. Peaks at 0.5, 0.9 and 3.7 minutes correspond to ammonia, oxygen and methanol (Figure 4.16). This calibration was conducted before each HCN synthesis experiment. Similarly, calibration was done with methanol and

ammonia at a molar ratio of 1:1.3 prior to ammonolysis experiments. The corresponding chromatogram is shown in Figure 4.17.

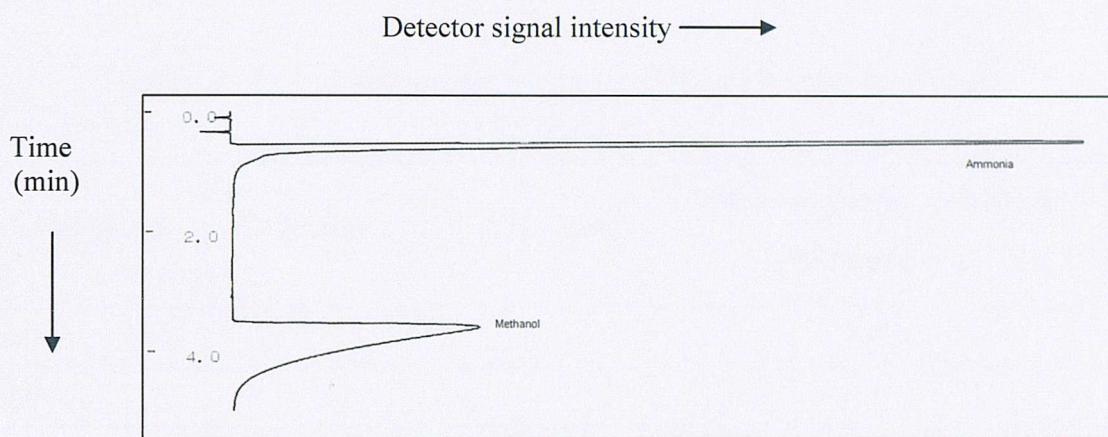


Figure 4.17 - Chromatogram of 13% ammonia, 10% methanol and helium

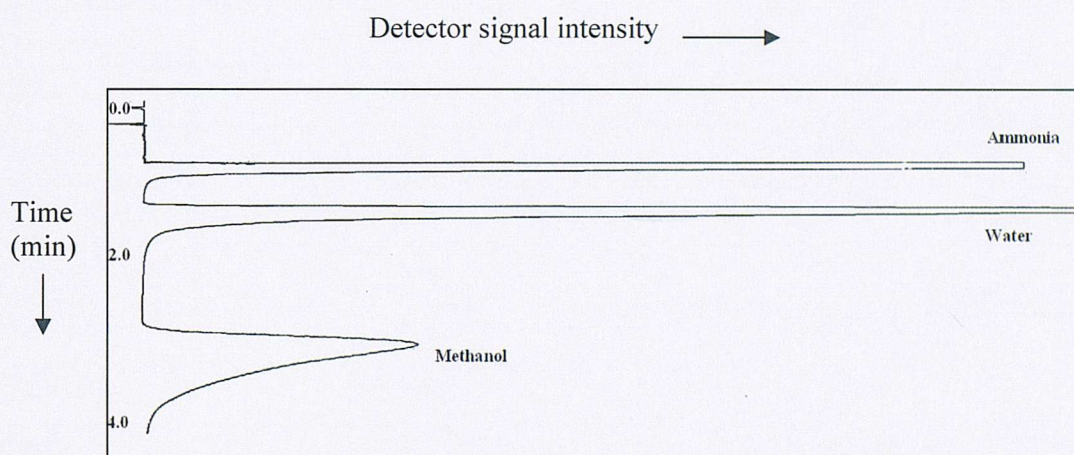


Figure 4.18 - Chromatogram of 13% ammonia, 20% water, 10% methanol and helium

Figure 4.17 shows the calibration plot of 10% methanol, 13% ammonia with 20% water and helium at a set molar ratio of 1:1.3:2.

4.2.7 Retention time and Response factors

The response factor is obtained experimentally by analyzing a known quantity of the substance with the GC and measuring the area of the relevant peak. No detector responds equally to different compounds. Results using one detector will differ from results obtained using another detector. The response factor is independent of temperature and carrier flow rate.

The retention time and the calculated response factor of each compound are tabulated in Table 4.2 and used in all the experiments. The errors are those associated with the repeatability of the measurement.

Table 4.2 - Retention time and the response factor relative to nitrogen

Compound	Retention time ± 0.01 (min)	Response factor relative to nitrogen ± 0.01
CO ₂	0.4	0.96
NH ₃	0.5	1.01
N ₂	1.3	1.00
CH ₃ OH	3.7	0.95
CO	2.8	0.72
HCN	4.2	1.12
CH ₃ NH ₂	0.7	0.47
O ₂	0.9	1.15
H ₂ O	1.6	0.55
CH ₄	1.8	1.34
CH ₃ OCH ₃	3.0	0.84
HCHO	3.2	0.66

4.3 Conclusions

The XRD analysis confirmed the presence of FeSbO₄ and Fe₂O₃ phases in the as received iron antimony oxide (FSO) powder catalyst required to catalyse the methanol ammoxidation. On calcination to higher temperatures (450, 900 and 1300°C) these phases were found stable and the material had become more crystalline. Catalyst calcined at 1300°C resulted with a new peaks appeared characteristic of Fe₂(TiO₃)₃ pseudorutile phase similar to Fe₂O₃. The XRD pattern of the 40-60 wt % FSO-Ni/CGO anode composite after calcination at 1300°C showed no phase changes ideal for the electro catalytic synthesis in SOFC. Further, the SEM/EDX measurement confirmed the presence of the elements with the appropriate composition in the catalysts. The GC calibration with the reactants and all the possible products were performed and their retention time and the response factors were tabulated for the experiments.

4.4 Chapter 4 – References

- 1 J. Walczak, E. Filipek and M. Bosacka, *Solid State Ionics* 101 -103 (1997) 1363
- 2 A.F. Wells, *Structural Inorganic Chemistry*, 4th edn. Claredon Press, (1975)
- 3 Y. Sasaki, *Appl. Catal. A: Gen* 194 (2000) 497
- 4 M. D. Allen, S. Poulston, E. G. Bithell, M. J. Goringe and M. Bowker, *J.Catal.* 163 (1996) 204
- 5 J. Amador and I. Rasines, *J. Appl. Cryst.* 14 (1981) 348
- 6 X. Obradors, J. Bassas, J. Rodriguez, J. Pannetier, A. Labarta, J. Tejada and F.J. Berry, *J. Phys.: Condens. Matter* 2 (1990) 6801
- 7 CELREF V3, LMGP suite for Windows by J. Laugier and B. Bochu
- 8 Y. Haung, G. Wang and V.C. Corberan, *Surf. Sci.* 547 (2003) 55
- 9 M.M. Gadgil and S.K. Kulshreshtha, *J. Mol. Catal. A: Chem.* 95 (1995) 211
- 10 E.V. Steen, M. Schnobel, R. Walsh and T. Riedel, *Appl Catal A: Gen* 165 (1997) 349
- 11 Y. Haung, G. Wang, R.X. Valenzuela and V.C. Corberan, *Appl. Surf. Sci* 210 (2003) 346
- 12 G.A. Zenkovets, G.N. Kryukova and S.V. Tsybulya, *Kinet. Catal.* 43 (2002) 731
- 13 K. T. Li, C. Yen and N. Shyu, *Appl. Catal. A: Gen* 156 (1997) 117
- 14 M. Carbucicchio, G. Centi and F. Trifiro, *J. Catal.* 91 (1985) 85
- 15 S. A. Baron, *Anodes for Solid Oxide Fuel Cells with Ceria Electrolytes*, Ph.D. Thesis Imperial College London (2004)
- 16 J. Rouquerol, D. Avnir, C.W. Fairbridge, D.H. Everett, J.H. Haynes, N. Pernicone, J.D.F. Ramsay, K.S.W. Sing and K.K. Unger, *Pure and Appl. Chem.* 66 (1994) 1739
- 17 P. Saravanapavan and L.L. Hench, *J. Non-Cryst. Solids* 318 (2003) 14
- 18 A. Braithwaite, *Chromatographic Methods*, 4th edn. Chapman and Hall London (1985)
- 19 J.M. Miller, *Chromatography: Concepts and Contrasts*, 2nd edn. John Wiley New York (2004)

Chapter 5

Synthesis of HCN in micro reactor - Results and Discussion

5.1 Introduction

Nitto made the first attempt at HCN synthesis by methanol ammoxidation to satisfy the increasing demand for HCN and other related speciality chemicals. Methanol, ammonia and air were introduced into a fixed bed reactor containing a promoted iron antimony oxide catalyst. The optimised process had >80% hydrogen cyanide yield, with by-products in only small amounts. In our present work, the process was carried out with the iron antimony oxide catalyst purchased from Catal International, UK. The catalyst was a mixture of iron and antimony oxide with a weight composition of 76% Fe_2O_3 , 15% FeSbO_4 , 8% Sb_2O_3 and 1% Cr_2O_3 .

Table 5.1 - List of the main experiments for HCN synthesis performed in the micro reactor

Catalyst	Condition	Experiment
Iron antimony oxide (FSO)	as received	ammoxidation
FSO	as received	ammonolysis
FSO	precalcined to 1300°C/2h	ammoxidation
60-40 wt % Ni-CGO	as prepared	ammoxidation
CGO	as received	ammoxidation
40-60 wt% FSO- Ni/CGO	precalcined to 1300°C/ 2h	ammonolysis
40-60 wt% FSO- Ni/CGO	precalcined to 1300°C/ 2h	ammonolysis with steam

Table 5.1 shows the list of the main experiments for HCN synthesis carried out in the project and each experiment is discussed in detail. The reaction temperature range was 450-650°C at atmospheric pressure. The catalysts were characterised by XRD after each experiment to determine any phase changes.

5.2 Synthesis of HCN by methanol ammoxidation using FSO

In a typical experiment, the powder form of the catalyst weighing approximately 2g was loaded in the quartz tube and supported on quartz wool in the micro reactor. Before the experiment, the system was purged with helium gas to remove the impurity gases in the reactor and GC. A reactant mixture of 10 volume % methanol, 13 volume % ammonia and 15 volume % oxygen approximately with a molar ratio of 1:1.3:1.5 and a balance of helium were passed through the catalyst bed which was maintained at the desired reaction temperature. Oxygen and anhydrous ammonia were fed from high pressure cylinders to the microreactor through the digital mass flow controllers. The reaction temperatures were in the range from 450- 650°C and at atmospheric pressure. The temperature was slowly increased at a steady rate of 2°C/min and once the reaction temperature was reached, it was held constant for few minutes until the reaction products were recorded in the GC. Then the experiment was continued to higher temperatures. The target concentrations of the reactants are listed in Table 5.4. ~10% methanol was obtained by flushing helium through the saturator containing methanol at 19°C. The methanol vapour pressure was calculated using Antoine equation as follows:

Vapour pressure:

$$\ln(P) = a - \frac{b}{T + c} \quad - \text{(eqn 5.1)}$$

$a = 18.5875$; $b = 3626.55$ and $c = -34.29$

P in mmHg; T in °K

$$\% \text{ methanol} = \frac{P}{760} \times 100 \quad - \text{(eqn 5.2)}$$

P is vapour pressure of methanol in mmHg.

The calculated methanol concentrations at three different temperatures are listed below in Table 5.2 and these were used in all the experiments.

Table 5.2 - Calculated concentration of methanol

T (°C)	T(K)	T+c	b/T+c	a- b/T+c	P (mmHg)	P (bar)	Methanol (%)
18	292	258	14.1	4.4	84.2	0.111	11.1
19	293	259	14.0	4.5	88.9	0.117	11.7
20	294	260	14.0	4.5	93.8	0.123	12.3

The reactant concentrations were confirmed by allowing the reactant mixture to the GC directly before and after the experiment and were found to be close to the target values. These values are listed in Table 5.4.

For ammoxidation, the flow rate of ammonia was set approximately to 11 ml/min, oxygen to 13 ml/min and the helium gas carrying the methanol to 78 ml/min to give a total flow rate of 102 ml/min. Literature reports that the required molar ratio of the reactants methanol, ammonia and oxygen for ammoxidation is 1:1.3:1.5 i.e. a slight excess of both ammonia and oxygen is necessary [1-3]. The same reactant molar ratios of 1:1.3:1.5 was used in these experiments. Table 5.3 gives the molecular fluxes of reactants into the micro reactor.

Table 5.3 - Set composition of the reactant feed for methanol ammoxidation using as received FSO (total pressure = 1atm)

Components	Pressure (atm) before mixing	Flow rate (ml/min)	Flow rate (E-06 moles/min)
Helium	0.89	78.65	3125
Methanol	0.11	78.65	386
Oxygen	1.00	13	580
Ammonia	1.00	11	491

The values given in Table 5.3 were calculated as follows:

1 mole of an ideal gas has a volume of 22.4 litres at STP. The number of moles/min of each component at the reactor at STP was calculated using the formula

$$N_{Gas} (mol / min) = \frac{p_{Gas} \times flowrate(ml / min at STP)}{22400} \quad - (eqn 5.3)$$

where p_{Gas} is the partial pressure of the gas in atmospheres.

Using the above formula, $N_{\text{CH}_3\text{OH}}$, N_{NH_3} and N_{O_2} can be calculated as follows and summarised in Table 5.3.

Partial pressure of helium after the bubbler to the reactor is $1 - 0.11 = 0.89\text{atm}$

Total flow rate of helium plus methanol is $70/0.89 = 78.65\text{ml/min}$.

$$N_{\text{CH}_3\text{OH}} = (0.1 \times 70) / 0.89 \times 22400 = 3.86 \text{ E-04 mol/min or } \mathbf{386\mu\text{mol/min}}$$

$$N_{\text{NH}_3} = (1.013 \times 11) / 22400 = 4.91\text{E-04 mol/min or } \mathbf{491\mu\text{mol/min}}$$

$$N_{\text{O}_2} = (1.013 \times 13) / 22400 = 5.8\text{E-04 mol/min or } \mathbf{580\mu\text{mol/min}}$$

The total flow rate was found to be $4582 \text{ E-06 mol/min}$. The composition of the reactant gas stream was verified experimentally by performing a blank test. The reactants were allowed into GC instead of the micro reactor and the reactant flow rate was slightly adjusted so that the appropriate peak area of required theoretical initial concentration was obtained.

Table 5.4 - Measured concentrations of the reactant components of methanol ammoxidation using as received FSO

Reactants	Target conc. (mol %)	Measured conc. (mol %)
Methanol	10	9.8 ± 0.1
Ammonia	13	12.6 ± 0.1
Oxygen	15	14.7 ± 0.1

A very small difference less than 5% relative i.e. 9.6 to 9.8% CH_3OH was seen between the measured concentration and the target value of 10% CH_3OH . Similarly, the measured concentration of ammonia was 12.5 to 12.8% NH_3 compared with the target value of 13%. Chromatogram of reactants before the experiment is shown (Figure 4.16) in the previous Chapter 4.

5.2.1 Product analysis of methanol ammoxidation using as received FSO

The measured concentration of the products is given in Table 5.5 as a function of the reaction temperature. Apart from the target product HCN, the total oxidation products carbon dioxide and water were seen. Oxygen had been completely consumed in the reactor as no unreacted oxygen was seen whereas small amounts of unreacted ammonia and methanol were present in the off-gas. The HCN yield was maximum at 450°C. HCN was optimally synthesised by the Nitto group in the temperature range of 400 to 450°C [1, 2, and 4]. In the lab, the reaction was conducted in a wide range of temperatures 450 to 650°C at intervals of 50°C and there was no significant amount of HCN formed at or below 400°C. The main reason to run the present experiments at higher temperatures (to 650°C) was to verify whether HCN could be produced at a typical fuel cell operating temperature using FSO.

Table 5.5 - Product concentrations of methanol ammoxidation using as received FSO

Temp (°C)	HCN (mol %)	CO ₂ (mol %)	N ₂ (mol %)	H ₂ O (mol %)	CH ₄ (mol %)	CH ₃ NH ₂ (mol %)	CO (mol %)	CH ₃ OH (mol %)	NH ₃ (mol %)	O ₂ (mol %)	C _{TOTAL} (mol %)	N _{TOTAL} (mol %)
450	5.2	2.0	2.7	1.2	0.3	0.6	0.50	1.0	1.3	ND*	9.6	12.2
500	4.3	2.8	3.2	1.3	0.6	0.1	0.61	0.8	1.3	ND*	9.2	12.1
550	1.7	5.9	4.1	1.6	0.2	0.2	0.31	1.3	2.1	ND*	9.6	12.2
600	1.2	6.7	4.6	2.0	0.5	0.0	0.11	1.2	1.5	ND*	9.7	11.9
650	0.8	7.0	5.2	2.1	0.3	0.1	0.20	0.8	1.2	ND*	9.2	12.5

*ND – not detectable, below limit of detection

The mass balances of carbon and nitrogen showed no obvious trend with reaction temperature. For carbon, the average output concentration was 9.5 ± 0.2 mol% compared with the input concentration of 9.8 ± 0.1 mol%. For nitrogen, the average output concentration was 12.2 ± 0.2 mol% compared with the input of 12.6 ± 0.1 mol%. Therefore there were probably some minor concentrations of carbon and nitrogen containing products unaccounted for.

The order of product elution is seen in the chromatogram (Figure 5.1). The attenuation was adjusted in the integrator such that the small peaks like methylamine, methane, carbon monoxide and methanol were more significant.

The maximum yield of HCN was found at 450°C and decreased at higher temperatures. The carbon source, CH₃OH had been used partly for the production of HCN but also in

other carbon by-products like (CH_4 , CO and CH_3NH_2). Neither dimethyl ether nor formaldehyde was detected.

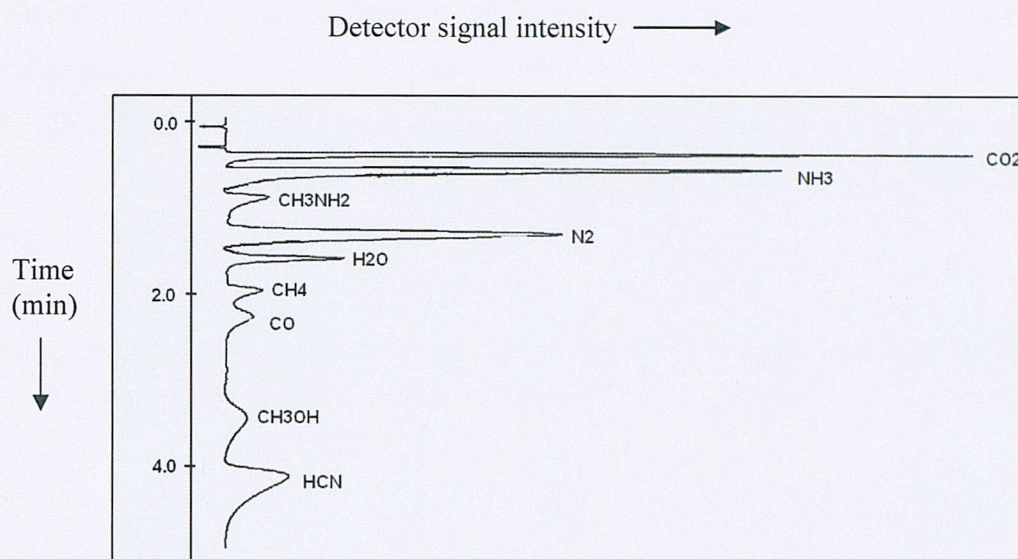


Figure 5.1 - Chromatogram of methanol ammoxidation using as received FSO at 450°C

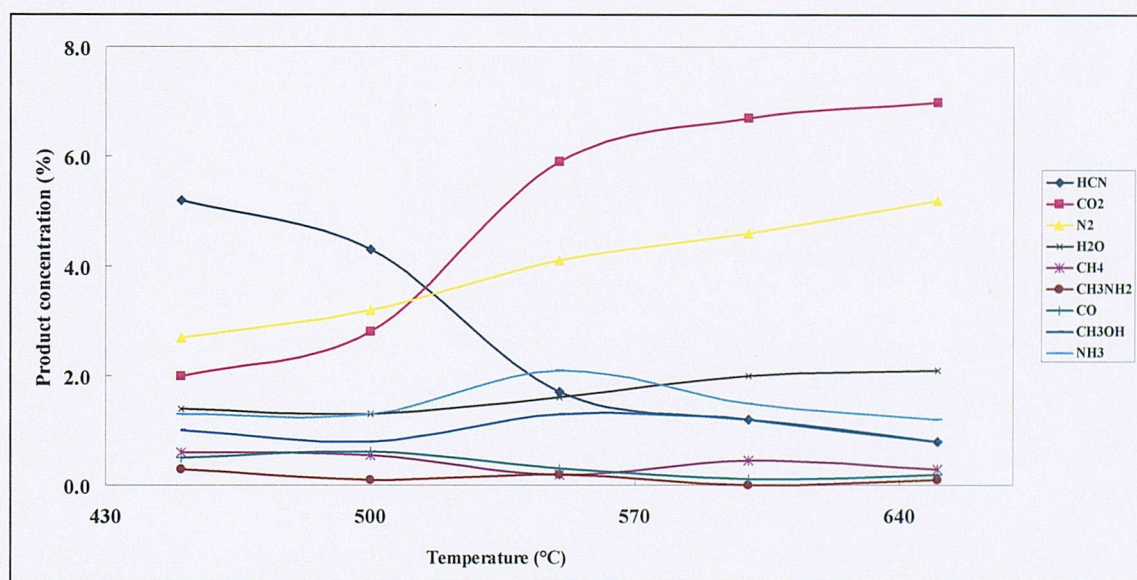


Figure 5.2 - Product concentration plot of ammoxidation of methanol to HCN using as received FSO

Methanol conversion was around 90% in the experiments and ammonia conversion 81-90%. Ammonia was consumed in the formation of HCN, N_2 , and CH_3NH_2 . Some of the other reactions that compete in parallel with methanol ammoxidation include ammonia

oxidation, methanol partial or total oxidation, ammonia decomposition and methane generation. Oxides of nitrogen were not detected in the experiment.

Characterisation of the catalyst after HCN synthesis was carried out using X-ray diffraction. On ammoxidation of methanol using methanol, ammonia and oxygen in the molar ratio of 1:1.3:1.5 over the FSO mixed oxide catalyst in the temperature range of 450 to 600°C, Fe_2O_3 was found to be partially reduced to Fe_3O_4 . The formation of Fe_3O_4 is evident in Figure 5.3.

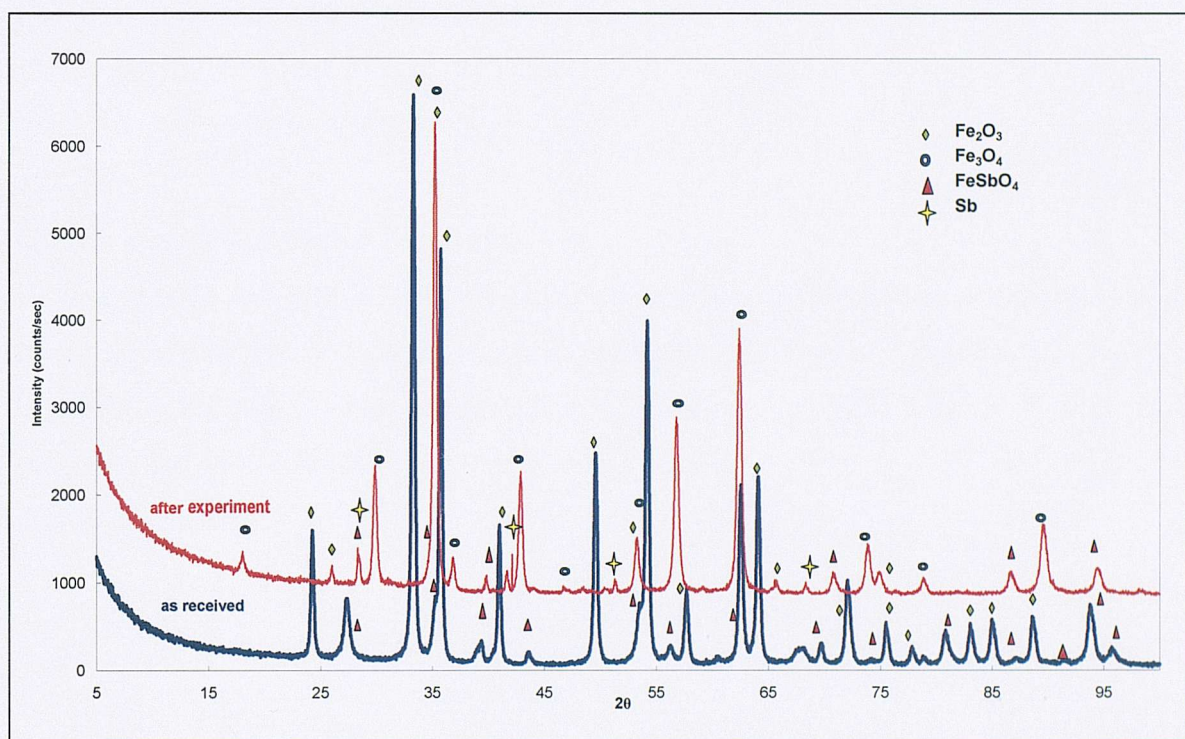


Figure 5.3 - Combined XRD pattern of FSO as received and after methanol ammoxidation reaction

In addition, there is an indication for the formation of metallic Sb on the catalyst along with the Fe_3O_4 phase. Although antimony was not observed by XRD very significantly, a metallic precipitation on the reactor outlet was observed. Since the reactant mixture has at net excess of oxygen this implies that the reduction reactions are faster than the oxidation reactions. When the ammoxidation was repeated on this partially reduced catalyst, no HCN was detected. Therefore the activity of the catalyst for HCN production depends on its degree of reduction and hence time in the micro reactor. In order to obtain reproducible

results, the experiments were always conducted with fresh catalyst and the same time sequence for starting the reaction and analysing the products.

5.2.2 Possible product formation reactions

Hydrogen cyanide:

The desired route for HCN production is the ammoxidation reaction:



However, some could also produced by ammonolysis:



Carbon dioxide and carbon monoxide:

Carbon dioxide was one of the main oxidation products in the ammoxidation reaction and found to elute first in chromatographic analysis. The carbon dioxide concentration increased as the reaction temperature increased from 450 to 650°C. Carbon dioxide can be produced by partial or complete oxidation of methanol [5-11] and by the oxidation of carbon monoxide:



CO can be generated by methanol decomposition, the water-gas shift equilibrium [5-11] or by oxidation of methane:



Nitrogen:

Nitrogen was observed as a major product in the experiment. Like carbon dioxide, the formation of nitrogen increased with increasing temperature. A slight excess of ammonia in

the molar ratio of 1:1.3 of methanol was used in the reaction. Catalytic cracking of ammonia (eqn 5.11) readily takes place in the presence of Fe- containing catalysts [12, 13].



Ammonia could burn in oxygen atmosphere resulting in the formation of nitrogen and water.



Methylamine:

Methylamine was formed in minor amounts probably by ammonolysis of methanol according to:



Methane:

Methane was also produced in small amounts possibly through the reverse steam reforming reaction [14]:



Steam:

Water was a major total oxidation product observed in the experiment. Many of the reactions mentioned contribute to water formation. The fraction of steam in the product mix increases with temperature as expected for a total oxidation product.

Hydrogen:

Ammonia and methanol reactants are rich sources of hydrogen [15-17]. According to the possible reactions discussed above, it is evident that hydrogen would have been produced in the experiments. Unfortunately, hydrogen could not be detected by the GC due to the poor sensitivity of the TCD.

Ammonia:

A slight excess of ammonia (1:1.3) was used in the experiment. The fact that very little was detected in the reaction product stream indicates that reactions involving ammonia had proceeded almost to completion.

5.2.3 Mars Van Krevelen redox mechanism (MVK)

Literature on the mechanism by which iron antimony oxide catalyses ammoxidation to HCN is very limited. The ammoxidation of methanol probably proceeds via a Mars-van-Krevelen (MVK) redox mechanism on metal oxide catalyst systems [18]. In a MVK catalytic reaction the reacting species chemisorb on the catalyst surface and are oxidised by lattice oxygen. The adsorbed species then react followed by desorption of the products and reoxidation of the catalyst. Since the catalyst is an oxide of variable valency cations, the oxygen is supplied by local reduction of the oxide, which can be reoxidised later by gaseous oxygen.

5.3 Synthesis of HCN by ammonolysis of methanol using as received FSO

Ammonolysis of lower alcohols is an industrially important reaction and work on this type of reaction has been carried out mainly on zeolite catalysts especially to synthesise di- and tri- methylamines. The process of dimethylamine synthesis using a zeolite catalyst has commercialized by Nitto Chemical and Mitsui Toatsu in Japan [2]. There is no report in the literature of HCN synthesis using iron antimony oxide from methanol in the absence of oxygen. In an oxide ion conducting fuel cell reactor, the source of oxygen is air from the cathode side of the SOFC. Therefore it was necessary to verify whether iron antimony oxide could catalyse HCN production with ammonia and methanol in the absence of oxygen. Fresh iron antimony oxide catalyst was loaded into the quartz micro reactor and following the same procedure as for the ammoxidation reaction.

Table 5.6 - Set composition of the reactant feed for methanol ammonolysis using as received FSO (total pressure = 1 atm)

Components	Pressure (atm) before mixing	Flow rate (ml/min)	Flow rate (E-06 moles/min)
Helium	0.89	78.65	3125
Methanol	0.11	78.65	386
Ammonia	1.00	11	491

The only difference compared with ammoxidation was the absence of oxygen flow in this experiment. The initial concentration of reactants is shown in Table 5.6 and Table 5.7 and the total flow rate was 4002 E-06 mol/min.

Table 5.7 - Measured concentrations of the reactant components of methanol ammonolysis using as received FSO

Reactants	Target conc. (mol %)	Measured conc. (mol %)
Methanol	10	9.8 ± 0.1
Ammonia	13	12.6 ± 0.1

The reaction was carried out in the temperature range of 450 to 650°C in steps of 50°C and the products were analysed by GC. The product concentrations of the ammonolysis reaction are listed in Table 5.8.

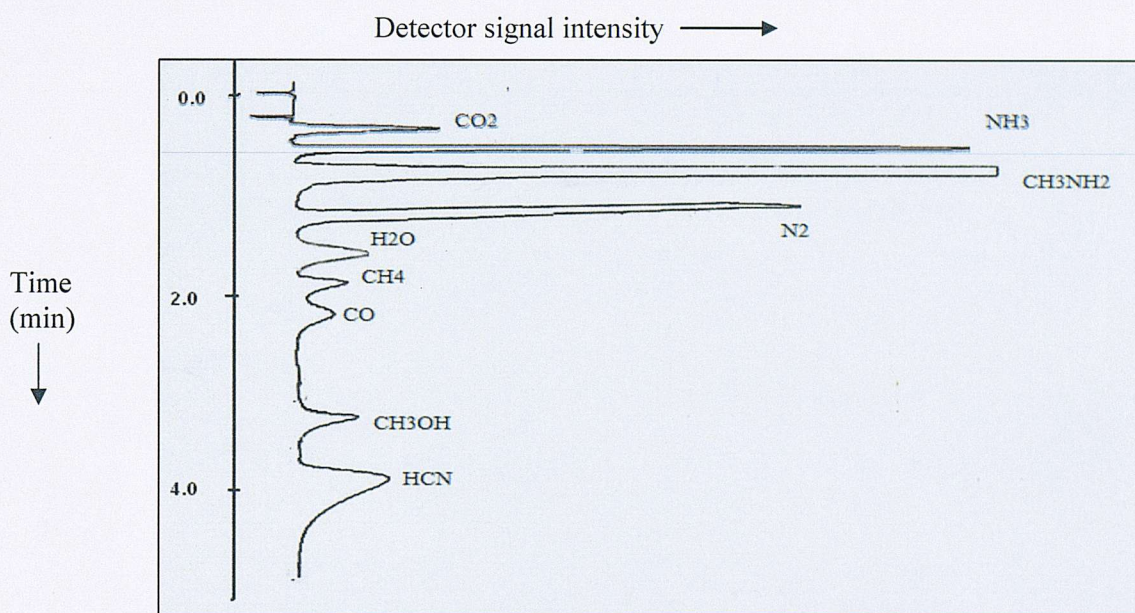


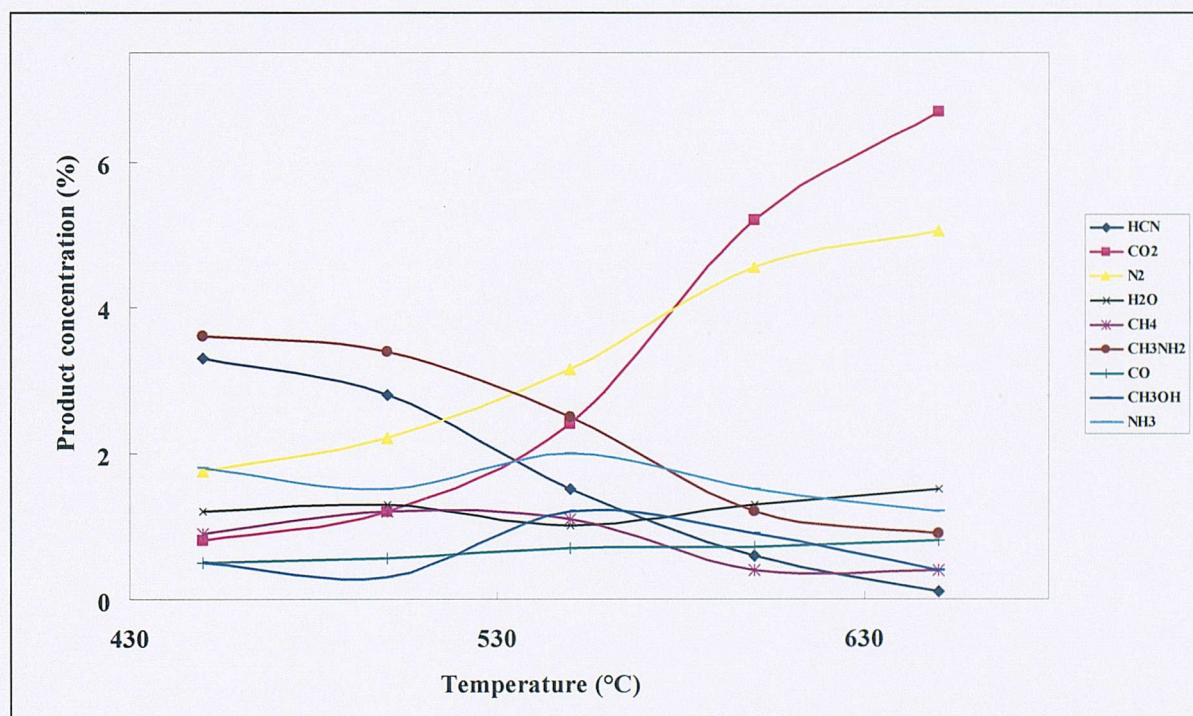
Figure 5.4 - Chromatogram of methanol ammonolysis using as received FSO at 450°C
HCN was produced in a smaller amount than in the ammoxidation reaction. The same products formed in the ammoxidation experiment also appeared in the ammonolysis reaction but in different proportion. At 450°C, methylamine was the main product followed by HCN, carbon dioxide, nitrogen, methane, carbon monoxide and water.

Table 5.8 - Product concentrations of methanol ammonolysis using as received FSO

Temp (°C)	HCN (mol %)	CO ₂ (mol %)	N ₂ (mol %)	H ₂ O (mol %)	CH ₄ (mol %)	CH ₃ NH ₂ (mol %)	CO (mol %)	CH ₃ OH (mol %)	NH ₃ (mol %)	O ₂ (mol %)	C _{TOTAL} (mol %)	N _{TOTAL} (mol %)
450	3.3	0.8	1.8	1.2	0.9	3.6	0.50	0.5	1.8	ND*	9.6	12.2
500	2.8	1.2	2.2	1.3	1.2	3.4	0.56	0.3	1.5	ND*	9.5	12.1
550	1.5	2.4	3.2	1.0	1.1	2.5	0.70	1.2	2	ND*	9.4	12.3
600	0.6	5.2	4.6	1.3	0.4	1.2	0.71	0.9	1.5	ND*	9.0	12.4
650	0.1	6.7	5.1	1.5	0.4	0.9	0.80	0.4	1.2	ND*	9.3	12.3

*ND – not detectable, below limit of detection

The methylamine and HCN concentrations slowly decreased with increase in temperature and the carbon dioxide increased. It is evident that the HCN concentration in ammonolysis was lower than in the ammoxidation reaction mainly due to the absence of oxygen whereas the formation of carbon monoxide and methane were higher. Also the total oxidation products (carbon dioxide and water) were lower as expected. The trend of product formation with increase in reaction temperature was similar to that of the ammoxidation reaction.

**Figure 5.5** - Product concentration plot of methanol ammonolysis using as received FSO

5.4 Synthesis of HCN by ammoxidation of methanol using FSO calcined to 1300°C

It is evident from previous experiments, that iron antimony oxide purchased from Catal International, UK could catalyse both ammoxidation and ammonolysis of methanol to HCN. Since the fuel cell anode would be sintered at 1300°C, it was necessary to establish the effect of this on the FSO catalyst. As received iron antimony oxide was calcined to 1300°C for 2h at the ramp rate of 5°C/ min. It was then characterised by XRD to verify that the required phases necessary for the HCN synthesis Fe_2O_3 , FeSbO_4 , and Sb_2O_3 still existed (refer to earlier chapter 4). The phases were stable and the sintered catalyst contains more FeSbO_4 than did the as received catalyst. The calcined catalyst was more crystalline but the surface area was lower. The ammoxidation of methanol was then carried out with this precalcined catalyst. The experimental condition was same as for the as received iron antimony oxide catalyst with methanol, ammonia and oxygen in the molar ratio of 1:1.3:1.5 in the temperature range of 450 to 650°C at the same flow rate. The measured initial concentrations were methanol 9.8 ± 0.1 mol %, ammonia 12.7 ± 0.1 mol% and oxygen 14.6 ± 0.1 mol%.

Table 5.9- Product concentrations of methanol ammoxidation using calcined FSO to 1300°C

Temp (°C)	HCN (mol %)	CO ₂ (mol %)	N ₂ (mol %)	H ₂ O (mol %)	CH ₄ (mol %)	CH ₃ NH ₂ (mol %)	CO (mol %)	CH ₃ OH (mol %)	NH ₃ (mol %)	O ₂ (mol %)	C _{TOTAL} (mol %)	N _{TOTAL} (mol %)
450	5.4	2.2	2.3	1.6	0.6	0.3	0.50	0.3	2.1	ND*	9.3	12.4
500	4.6	2.3	3.0	1.7	0.7	0.2	1.10	0.6	2	ND*	9.5	12.8
550	1.9	5.6	4.5	2.1	0.2	0.1	0.31	1.2	1.4	ND*	9.3	12.4
600	1.7	6.2	4.8	2.0	0.5	0.0	0.11	1.0	1.3	ND*	9.5	12.6
650	1.0	7.2	5.1	2.1	0.3	0.1	0.20	0.8	1.2	ND*	9.6	12.5

*ND – not detectable, below limit of detection

The highest yield of HCN of all the experiments was seen with this calcined catalyst. This may be due to the higher FeSbO_4 content in the calcined catalyst. The formation of methylamine was low as observed for ammonolysis using as-received FSO. HCN was the major product at 450°C (Table 5.9).

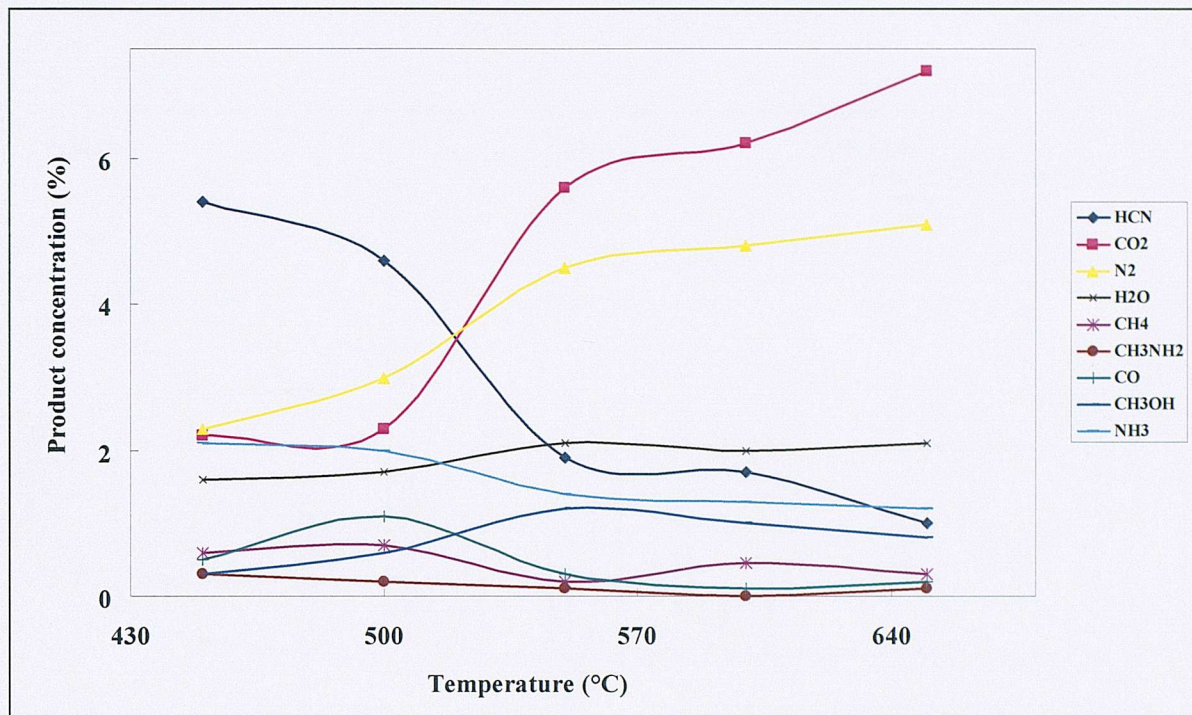


Figure 5.6 - Product concentration plot of methanol ammoxidation using calcined FSO to 1300°C

The trend product concentrations with temperature were similar to that observed with the as received FSO. By-product formation was also quite similar to that observed for as received FSO. Oxygen was again found to be consumed completely as no unreacted oxygen was seen in the product.

Figure 5.7 shows the XRD of the FSO catalyst calcined to 1300°C before and after ammoxidation. The presence of Fe_2O_3 and FeSbO_4 confirms that the catalyst was not completely reduced by the ammonia and methanol reactant mixtures.

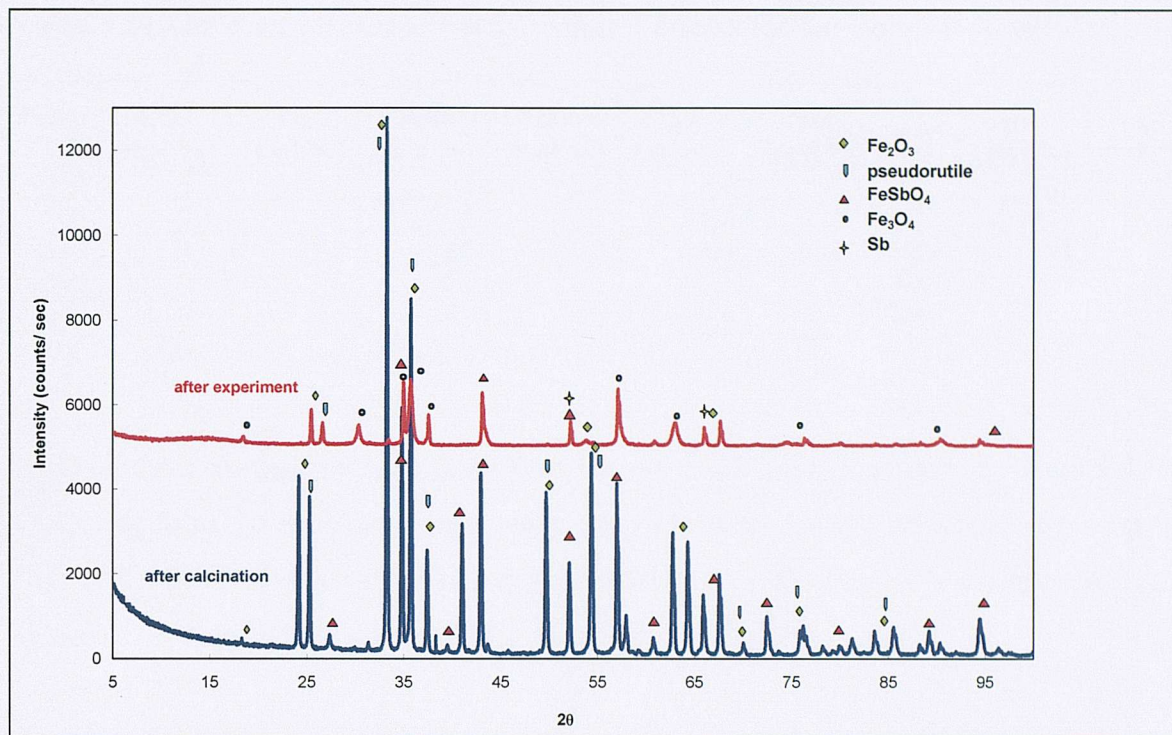


Figure 5.7 - Combined XRD pattern of FSO calcined to 1300°C and after ammoxidation reaction

5.5 Ammoxidation of methanol with CGO and 60-40 wt% Ni-CGO

The ammoxidation reaction was tested with CGO and 60-40wt % Ni-CGO as these were intended components of the anode material in the fuel cell. The experimental procedure described previously was followed with CGO powder and Ni-CGO in the same temperature range.

No HCN was detected in either case. With CGO, only carbon dioxide, water and nitrogen were detected as products (Table 5.10) and Ni-CGO produced a small quantity of methylamine in addition (Table 5.11).

Table 5.10 - Product concentrations of methanol ammoxidation using CGO -10

Temp (°C)	CO ₂ (mol %)	N ₂ (mol %)	H ₂ O (mol %)	CH ₃ OH (mol %)	NH ₃ (mol %)	O ₂ (mol %)	C _{TOTAL} (mol %)	N _{TOTAL} (mol %)
450	7.8	5.3	5.4	1.8	2	ND*	9.6	12.5
500	8.1	5.1	5.3	1.4	2.3	ND*	9.5	12.5
550	7.9	5.1	5.6	1.3	2.1	ND*	9.2	12.3
600	8.3	5.4	6.2	1.2	1.6	ND*	9.5	12.4
650	9.1	5.3	6.1	0.4	1.6	ND*	9.5	12.1

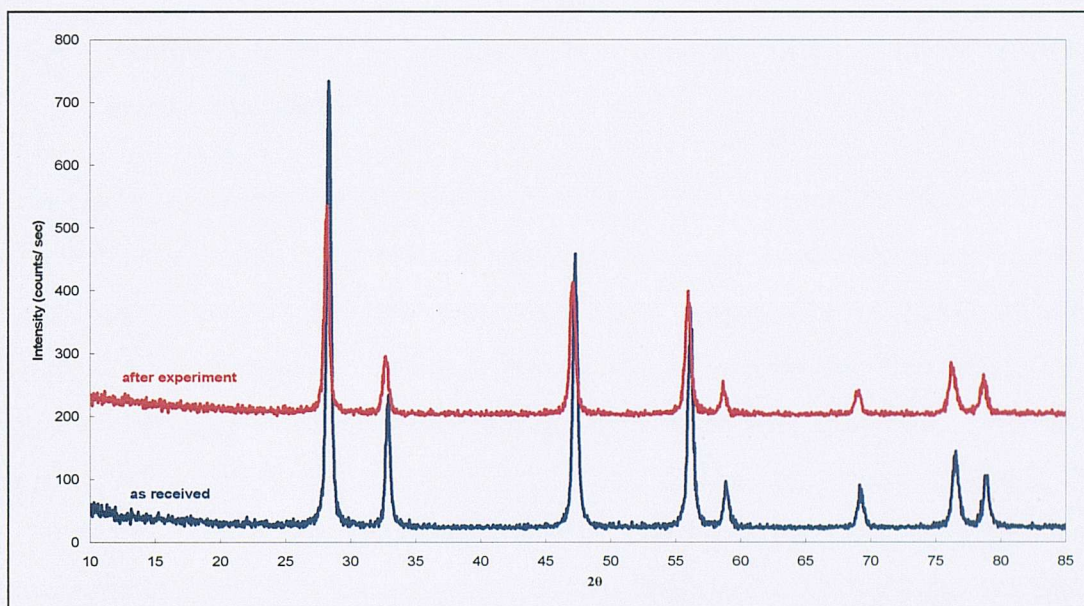
*ND – not detectable, below limit of detection

Table 5.11 - Product concentrations of methanol ammoxidation using 60-40 wt% Ni-CGO

Temp (°C)	CO ₂ (mol %)	N ₂ (mol %)	H ₂ O (mol %)	CH ₃ NH ₂ (mol %)	CH ₃ OH (mol %)	NH ₃ (mol %)	O ₂ (mol %)	C _{TOTAL} (mol %)	N _{TOTAL} (mol %)
450	7.1	5.2	3.2	0.8	1.6	1	ND*	9.5	12.2
500	7.1	5.3	3.3	0.7	1.6	1.1	ND*	9.4	12.4
550	7.2	5.2	3.5	0.7	1.3	1.2	ND*	9.2	12.3
600	7.4	5.6	4.2	0.1	1.5	1.1	ND*	9.0	12.4
650	8.1	5.4	4.3	0.5	0.6	1.2	ND*	9.2	12.5

*ND – not detectable, below limit of detection

XRD analysis showed no detectable change in the CGO catalyst as seen in Figure 5.8. The CGO was found to remain a single phase with the cubic fluorite structure. However, the NiO in the Ni-CGO composite was partially reduced to Ni. The Ni peaks appeared at 2θ values of 44.4, 51.7, 92.8 and 98.7 (Figure 5.9).

**Figure 5.8** - Combined XRD pattern CGO catalyst before and after ammoxidation

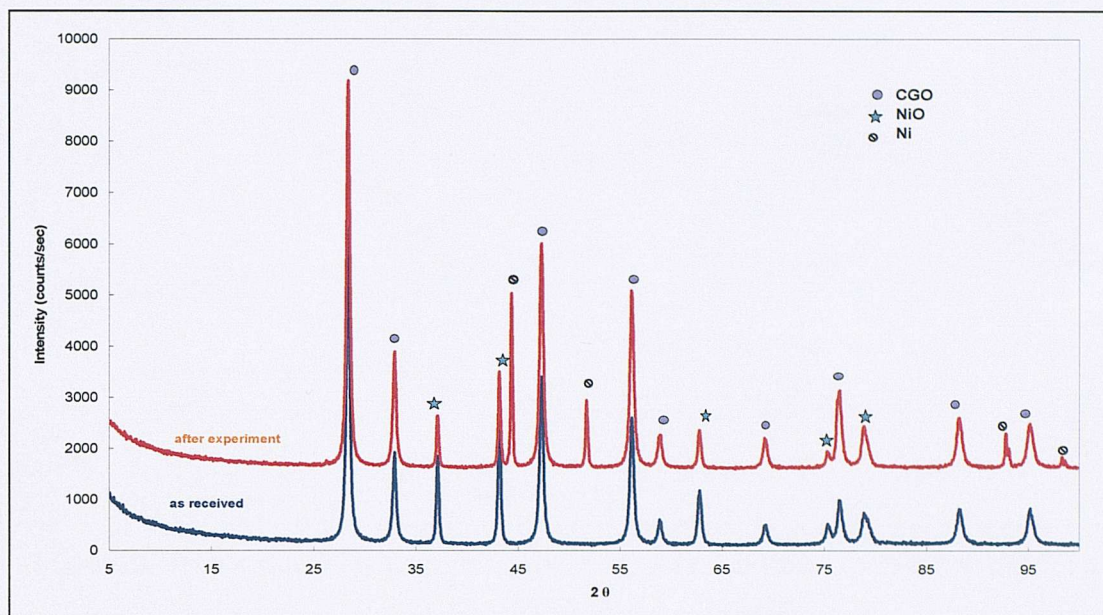


Figure 5.9 - Combined XRD pattern 60- 40 wt% Ni-CGO catalyst
before & after experiment

5.6 Synthesis of HCN by ammonolysis of methanol using 40-60 wt% FSO-Ni/CGO calcined to 1300°C

The catalytic properties of the 40-60 wt% FSO-Ni/CGO anode composite were then studied. Since HCN synthesis in the fuel cell would not involve gaseous oxygen, the anode was first tested only with methanol and ammonia without oxygen. The calculation of the reactant concentrations was shown earlier in this section. A flow rate of 78ml/min of helium was bubbled through the methanol saturator and then mixed with 11ml/min of ammonia to give a methanol: ammonia molar ratio of 1:1.3 and total flow rate of approximately 89ml/min. The composition of the product gas stream is listed in the Table 5.12 and the product concentration plot with respect to temperature is shown in Figure 5.10. The results show appreciable HCN production by the ammonolysis using this anode composite.

Table 5.12 - Product concentrations of methanol ammonolysis using
40-60 wt% FSO-Ni/CGO calcined to 1300°C

Temp (°C)	HCN (mol %)	CO ₂ (mol %)	N ₂ (mol %)	H ₂ O (mol %)	CH ₄ (mol %)	CH ₃ NH ₂ (mol %)	CO (mol %)	CH ₃ OH (mol %)	NH ₃ (mol %)	O ₂ (mol %)	C _{TOTAL} (mol %)	N _{TOTAL} (mol %)
450	3.8	2.2	3.0	1.8	1.8	0.7	0.80	0.2	2	ND*	9.5	12.4
500	3.6	2.1	3.3	2.0	1.5	0.2	0.80	0.8	1.8	ND*	9.0	12.1
550	1.7	3.1	4.3	2.0	2.2	0.4	0.90	0.4	1.8	ND*	8.7	12.5
600	1	3.8	4.4	1.9	2.4	0.5	1.10	0.2	1.6	ND*	9.0	11.9
650	0.3	4.2	4.9	2.3	1.9	0.3	1.10	0.3	1.9	ND*	8.1	12.2

*ND – not detectable, below limit of detection

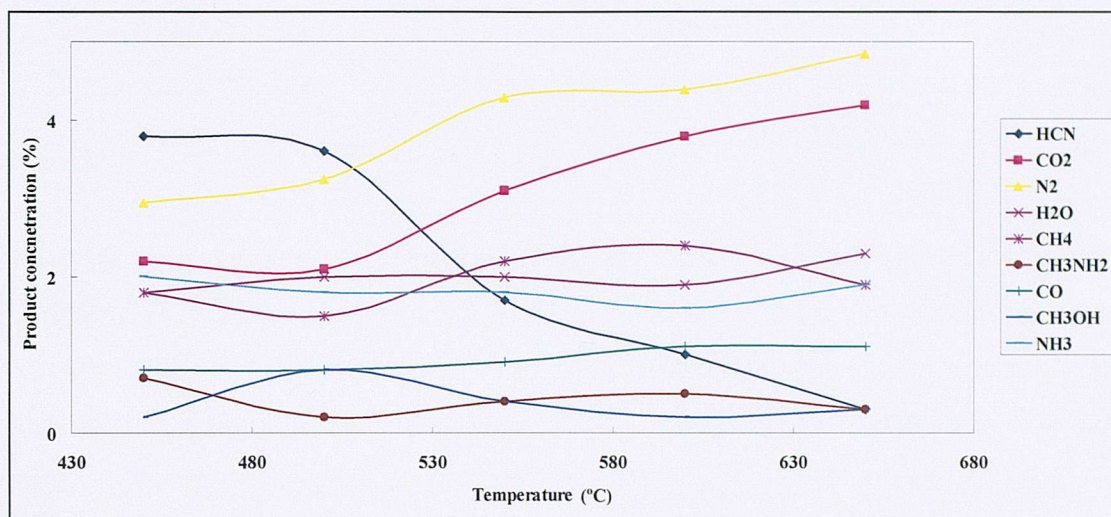


Figure 5.10 - Product concentration plot of methanol ammonolysis using calcined 40-60 wt% FSO-Ni/CGO at 1300°C

The anode catalysed ammonolysis is in a similar way to as received iron antimony oxide but produced larger concentrations of methane and carbon monoxide and less methylamine. The methylamine concentration in this experiment was approximately 5 times lower than in ammonolysis using as received FSO. The enhanced methane formation in the reaction can be understood since Ni supported on Al_2O_3 is a known catalyst for the methanation reaction [19-21]:



The by-product formation in this experiment can be explained by the same reactions as for FSO. However, with the anode composite carbon deposition was seen on the catalyst surface and on the interior of the micro reactor after the experiment. Carbon deposition is also evident from the deficit in the total carbon in the product stream compared with the inlet stream. The nickel in the anode composite would have been the main cause of the carbon deposition. This is very common with SOFCs using nickel anodes and leads to deactivation and poor durability [22- 25].

Carbon deposition could be due to the following reactions; hydrocarbon pyrolysis [26] (eqn 5.17), carbon monoxide disproportionation (the Boudouard reaction [27, 28] (eqn 5.18) or reduction of carbon monoxide by hydrogen (eqn 5.19).



In order to avoid carbon deposition in the fuel cell, it was decided to add water to the methanol and ammonia reactant mixtures. From the thermo chemical calculations, a steam to carbon ratio of 2 is required to thermodynamically prevent carbon deposition with the methanol feed in the fuel cell experiment [29-31]. Therefore it was decided to investigate a reactant mixture of methanol, ammonia and water vapour in the molar ratio of 1:1.3:2.1 with FSO-Ni/CGO composite as catalyst. A water/methanol molar ratio of approximately 2 was set to avoid carbon deposition. 2g of the dried FSO-Ni/CGO composite was loaded in the micro reactor and the catalytic reaction was studied in the temperature range of 450 to 650°C at intervals of 50°C as before.

Table 5.13 - Set composition of the reactants of humidified methanol ammonolysis using 40-60 wt% FSO-Ni/CGO calcined to 1300°C (total pressure = 1atm)

Components	Pressure (atm) before mixing	Flow rate (ml/min)	Flow rate (E-06 moles/min)
Helium 1(F1)	0.890	26.40	1049
methanol	0.110	26.40	129
Helium 2(F2)	0.800	36.25	1294
Water	0.200	36.25	323
ammonia	1.000	4.00	179

Two separate helium gas streams were bubbled through water and methanol saturators situated in thermostatic water baths. The flow rate of ammonia was set approximately at 4 ml/min and the helium gas was 26 ml/min for the methanol and 36 ml/min for the water vapour. 10% CH₃OH in one helium stream was obtained based on the calculation mentioned earlier (Table 5.2). 20% water vapour was obtained in the second helium stream by setting its water bath temperature to 60°C [32]. The temperature of the water inside the bubble column was checked with a thermometer. The calculated initial concentrations of methanol, ammonia and water are listed in Table 5.13.

Table 5.14 - Measured concentration of the reactant components of humidified methanol ammonolysis using FSO-Ni/CGO calcined to 1300°C

Reactants	Target conc. (mol %)	Measured conc. (mol %)
Methanol	10	9.6 ± 0.1
Ammonia	13	12.7 ± 0.1
Water vapour	20	18.6 ± 0.1

The total flow rate of the reactants was 2975×10^{-6} mol/ min. A blank was conducted to check the initial concentration before entering the micro reactor by passing the reactants to the GC (Figure 4.18). It was found that the theoretical and the experimental initial concentration values obtained through GC analysis were closer with an experimental error less than 5% (Table 5.14).

Table 5.15 - Product concentrations of humidified methanol ammonolysis using FSO-Ni/CGO calcined to 1300°C

Temp (°C)	HCN (mol %)	CO ₂ (mol %)	N ₂ (mol %)	H ₂ O (mol %)	CH ₄ (mol %)	CH ₃ NH ₂ (mol %)	CO (mol %)	CH ₃ OH (mol %)	NH ₃ (mol %)	O ₂ (mol %)	C _{TOTAL} (mol %)	N _{TOTAL} (mol %)
450	4.1	2.8	2.8	19.1	0.9	0.4	0.30	1	2.1	ND*	9.5	12.2
500	3.7	3.0	3.7	20.2	1.0	0.3	0.50	1.12	1.8	ND*	9.6	13.3
550	1.7	4.5	4.1	19.6	1.2	0.2	0.34	1.13	1.6	ND*	9.0	11.7
600	1.0	5.7	5.2	19.4	1.1	0.1	0.22	1.2	1.2	ND*	9.4	12.7
650	0.3	7.1	5.1	21.0	1.0	0.2	0.24	0.4	1.5	ND*	9.2	12.2

*ND – not detectable, below limit of detection

In this experiment, a large fraction of water was seen as a result of the high water vapour concentration in the feed. The concentration of carbon dioxide was high and increased with increase of temperature while the concentration of carbon monoxide was much lower and decreased with temperature. These phenomena indicate that the water gas shift reaction was effective. The concentration of HCN, N₂ and NH₃ are very similar to those observed in dry conditions (Table 5.12). However, the concentrations of CH₄, CO, and CH₃NH₂ are all lower in the presence of water vapour, reflecting the less reducing conditions overall.

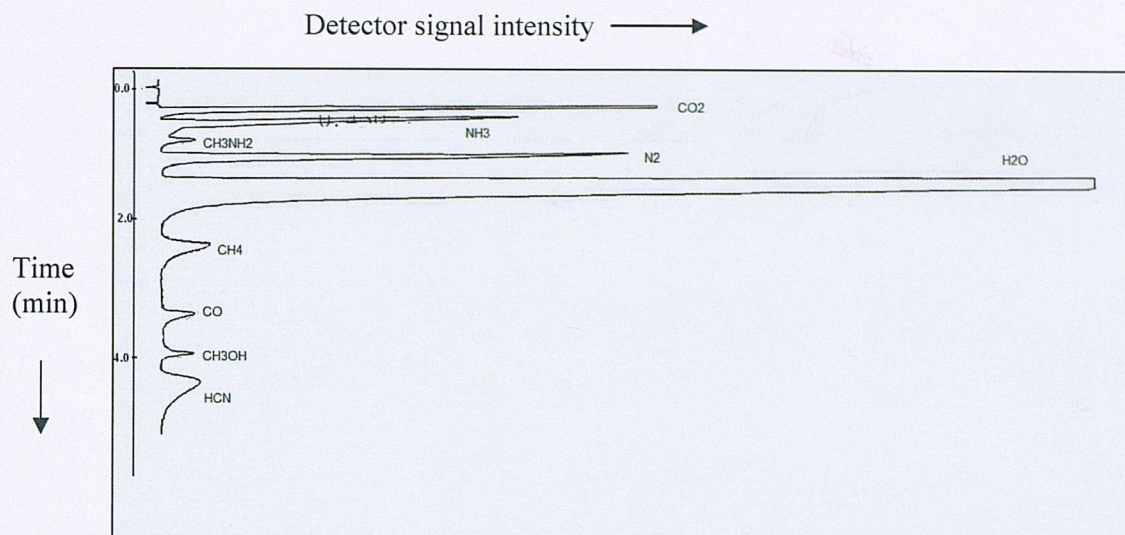


Figure 5.11 - Chromatogram of humidified methanol ammonolysis at 450°C using 40- 60wt % FSO-Ni/CGO calcined to 1300°C

As the temperature increased, the content of carbon dioxide, nitrogen and water increased the HCN content decreased. The HCN and the oxidised product concentrations increased in the presence of steam. This can be seen by comparing Tables 5.12 and 5.15.

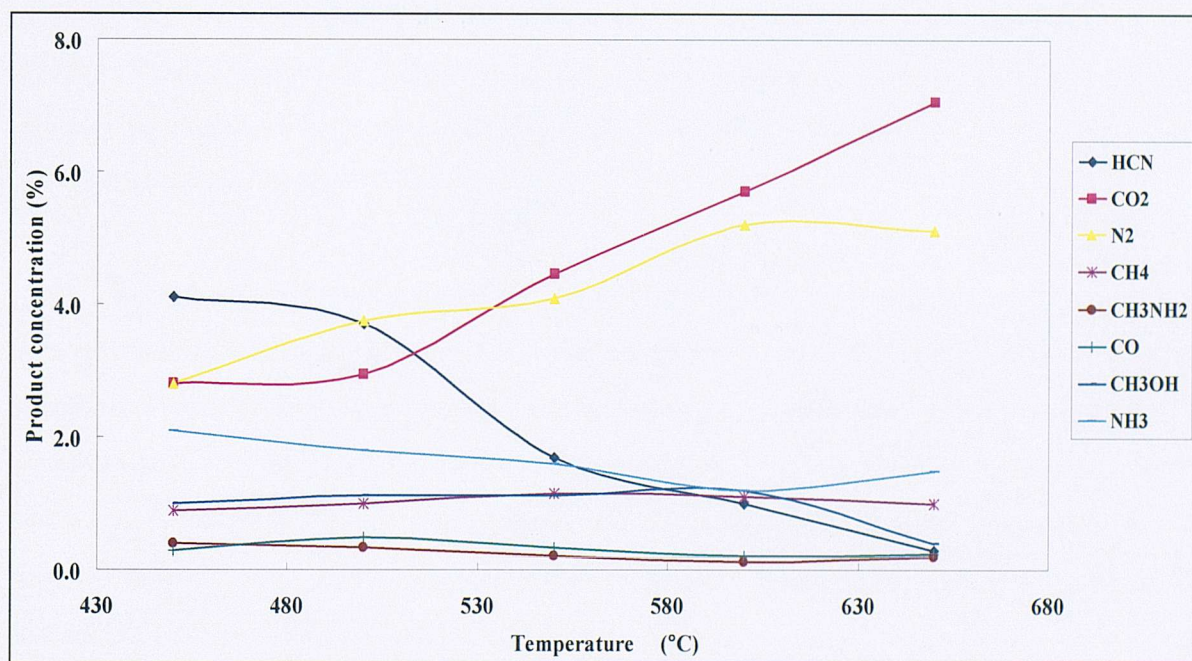


Figure 5.12 - Product concentration plot of humidified methanol ammonolysis using 40- 60wt % FSO-Ni/CGO sintered to 1300°C

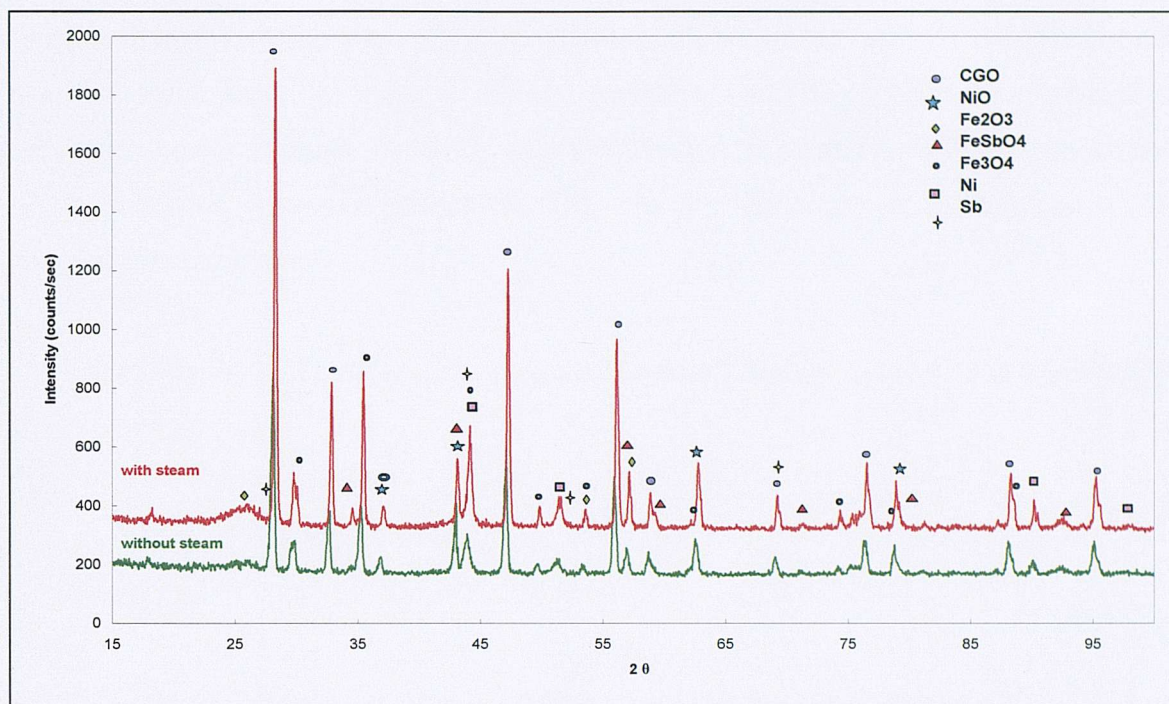


Figure 5.13 - Combined XRD pattern of 40- 60wt % FSO-Ni/CGO catalyst after ammonolysis with and without steam

In addition to the phases, Fe_2O_3 , FeSbO_4 , Fe_3O_4 and metallic Sb and Ni were found to exist due to the partial reduction of NiO by ammonia in the reaction mixture with or without steam. CGO and NiO were also seen in the catalyst after reaction confirming that the CGO remains stable throughout. The XRD pattern of the catalyst after reaction with steam also appears to show an increase in crystallinity compared with the catalyst reacted in the absence of steam (Figure 5.13).

5.6 Selectivity and product yield

The product yield was calculated quantitatively using the GC response factors. The response factor is the concentration divided by the GC peak area corresponding to the component [33]. The response factor of each component was calculated as explained in detail in Chapter 4. In all calculations, the terms such as $(\text{HCN})_{\text{product}}$ refer to the concentration of the product gas expressed in mol. In the case of HCN this is given by (using the response factor in Table 4.2).

$$(\text{HCN})_{\text{product}} = \text{HCN peak area} \times 1.12 \quad - (\text{eqn 5.20})$$

Since both methanol and ammonia are feed stocks in this system, selectivity to HCN can be based on either feed. The molar C and N selectivities and HCN yield were calculated and are reported on both bases. The HCN selectivity is defined as moles HCN formed per mole of methanol or ammonia consumed. The product selectivity is a function of feed composition and temperature.

The selectivity for HCN, S_{HCN} with respect to methanol input is calculated as follows [34]:

$$S_{HCN} = \frac{(HCN)_{product}}{(CH_3OH)_{in} - (CH_3OH)_{out}} \quad - \text{(eqn 5.21)}$$

The methanol conversion, X_{CH_3OH} , in the reaction is calculated as:

$$X_{CH_3OH} = \frac{(CH_3OH)_{in} - (CH_3OH)_{out}}{(CH_3OH)_{in}} \quad - \text{(eqn 5.22)}$$

Therefore, the HCN yield can be obtained from the above equations as:

$$\text{HCN yield} = S_{HCN} \times X_{CH_3OH} \quad - \text{(eqn 5.23)}$$

or

$$\text{HCN yield} = \frac{(HCN)_{product}}{(CH_3OH)_{in}} \quad - \text{(eqn 5.24)}$$

or

$$\text{HCN yield} = \frac{(HCN)_{product}}{(HCN + CO_2 + CH_4 + CH_3OH)_{product}} \quad - \text{(eqn 5.25)}$$

For example, using FSO precalcined to 1300°C at 450°C, the selectivity to HCN was calculated as:

$$S_{HCN} \% = \frac{5.4}{9.8 - 0.3} \times 100 = 57\%$$

Methanol Conversion,

$$X_{CH_3OH} \% = \frac{9.8 - 0.3}{9.8} \times 100 = 97\%$$

Ammonia Conversion,

$$X_{NH_3} \% = \frac{12.7 - 2.1}{2.1} \times 100 = 83\%$$

HCN yield based on methanol

$$= 0.57 \times 0.97 \times 100 = 55\%$$

HCN yield based on ammonia

$$= 0.51 \times 0.83 \times 100 = 43\%$$

Tables 5.16 and 5.17 show the selectivity and the yield of HCN in all the experiments from methanol and ammonia, respectively. A comparison of HCN yield with FSO precalcined to 1300°C with respect to methanol and ammonia input is presented in Figure 5.14. Tables 5.16 and 5.17 show the selectivity to HCN, its yield and conversions of methanol and ammonia. The conversion of both ammonia and methanol increased with reaction temperatures in all experiments indicating that they had been consumed to a greater extent forming carbon and nitrogen by-products. Low concentrations of unreacted ammonia and methanol were seen in the product stream.

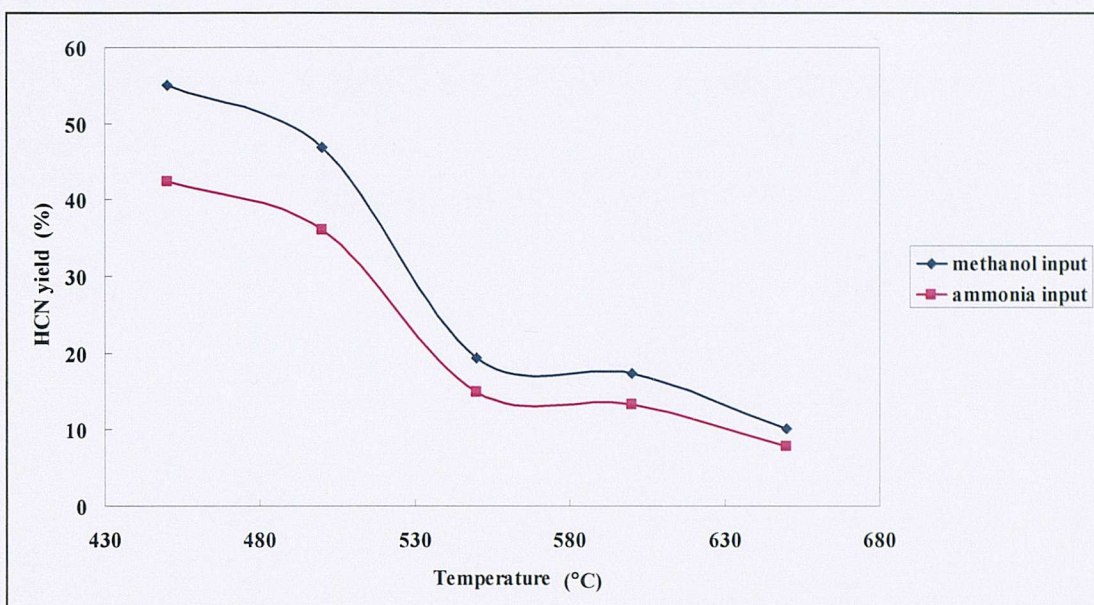


Figure 5.14 - Comparison of HCN carbon yield and HCN nitrogen yield with precalcined FSO to 1300°C

The reaction temperature for maximum HCN yield was 450°C in all experiments. Methanol and ammonia conversion remained above 75% over the entire range of conditions. The reaction between the reactants in all experiments was believed to be stoichiometrically complete and selectivity to HCN was higher at initial temperature which further decreased with temperature to below 2%. The overall ammonia conversion to the products was found similar to methanol. The ammoxidation reaction gives higher HCN selectivity and yield as expected since the FSO catalyst is intended for this reaction. Nevertheless, the FSO catalyst and FSO-Ni/CGO composite are only slightly less effective for the ammonolysis reaction.

Table 5.16 – Selectivity and yield of HCN based on methanol input

Ammoxidation of methanol with FSO			
Temp (°C)	S _{HCN} (%)	Methanol Conversion (%)	(Yield) _{HCN} (%)
450	59	90	53
500	48	92	44
550	20	87	17
600	14	88	12
650	9	92	8
Ammonolysis of methanol with FSO			
450	35	95	34
500	29	97	29
550	17	88	15
600	7	91	6
650	1	96	1
Ammoxidation of methanol with FSO calcined to 1300°C			
450	57	97	55
500	50	94	47
550	22	88	19
600	19	90	17
650	11	92	10
Ammonolysis of methanol with FSO-Ni/CGO calcined to 1300°C without steam			
450	40	98	39
500	40	92	37
550	18	96	17
600	10	98	10
650	3	97	3
Ammonolysis of methanol with FSO-Ni/CGO calcined to 1300°C with steam			
450	47	90	42
500	43	89	38
550	20	88	17
600	12	88	10
650	3	96	3

Table 5.17 - Selectivity and yield of HCN based on ammonia input

Ammoxidation of methanol with FSO			
Temp (°C)	S _{HCN} (%)	Ammonia Conversion (%)	(Yield) _{HCN} (%)
450	46	90	41
500	38	90	34
550	16	83	13
600	11	88	10
650	7	90	6
Ammonolysis of methanol with FSO			
450	33	81	26
500	28	83	23
550	15	83	13
600	5	88	5
650	1	90	1
Ammoxidation of methanol with FSO calcined to 1300°C			
450	51	83	43
500	43	84	36
550	17	89	15
600	15	90	13
650	9	91	8
Ammonolysis of methanol with FSO-Ni/CGO calcined to 1300°C without steam			
450	35	84	30
500	33	86	28
550	15	86	13
600	9	88	8
650	3	85	2
Ammonolysis of methanol with FSO-Ni/CGO calcined to 1300°C with steam			
450	39	83	33
500	34	86	29
550	15	87	13
600	9	90	8
650	3	88	2

5.8 Conclusions

HCN synthesis was performed at temperature range of 450-650°C with various mixed oxide catalysts at different conditions. There was no evidence for the HCN formation below 430°C. It was maximum at 450°C and decreased at higher temperatures. By-products were CO₂, N₂, CH₃NH₂, H₂O, CH₄ and CO. In ammoxidation, the total oxidation products were found to increase with reaction temperature. In the absence of oxygen (ammonolysis) methylamine was found to be the major product followed by HCN. HCN synthesis by ammonolysis over the anode composite gave encouraging HCN selectivity and yield. An approximate molar ratio of water vapour to methanol of 2:1 was employed to avoid carbon deposition. The anode catalyst after the experiment was found to contain Fe₃O₄, Ni and Sb, as a result of partial reduction.

5.9 Chapter 5 – References

- 1 W. Sedriks, PEP Reviews 76-3 (1977)
- 2 Y. Sasaki and M. Fukatsu, Catal. Surv. Jpn. 2 (1998) 199
- 3 G B Patent 913, 836 (Dec. 28 1962), F.J Bellinger and F.C. Newman (to the Distillers Co. Ltd)
- 4 Y. Sasaki, H. Yamamoto, K. Mori and K. Miyaki, Science and Technology in Catalysis 121 (1998) 335
- 5 L.M. Gomez-Sainero, R.T. Baker, I.S. Metcalfe, M. Sahibzada, P. Concepcion and J.M. Lopez-Nieto, Appl. Catal. A: Gen 294 (2005) 177
- 6 M. Sahibzada, B.C.H. Steele, K. Hellgardt, D. Barth, A. Effendi, D. Mantzavinos and I.S. Metcalfe, Chem. Eng. Sci. 55 (2000) 3077
- 7 J.P. Breen and J.R.H. Ross, Catal. Today 51 (1999) 521
- 8 A.K. Shukla and R.K. Raman, Annu. Rev. Mater. Res. 33 (2003) 155
- 9 A.Y. Rozovskii and G.I. Lin, Top. Catal. 22 (2003) 137
- 10 M. Sahibzada, B.C.H. Steele, K. Zheng, R.A. Rudkin and I.S. Metcalfe, Catal. Today 38 (1997) 459
- 11 M. Sahibzada, B.C.H Steele, K. Hellgardt, D. Bart, A. Effendi, D. Mantzavinos and I. S. Metcalfe, Chem. Eng. Sci. 55 (2000) 3077
- 12 N. Dekkar and B. Rietveld, European Symposium (2004) 1524
- 13 A. Wojcik, H. Middleton, I. Damopoulos and J Van herle, J. Power Sources 118 (2003) 342
- 14 J. R. Rostrup-Nielson and L.J. Christiansen, J. Catal. Today 23 (1995) 126
- 15 R. Metkemeijer and P. Achard, J. Power Sources 49 (1994) 271
- 16 C.A. McAuliffe, Hydrogen and Energy, MacMillan London (1980)
- 17 N. Maffei, L. Pelletier, J.P. Charland and A. McFarlan, J. Power Sources 140 (2005) 264
- 18 J.R. Ebner, J.T. Gleaves, T.C. Kuechez and T.P. Li AC Symposium series 328 (1987) 189
- 19 C.H. Bartholomew, Catal. Rev. Sci. Eng. 24 (1982) 67
- 20 M.B.I. Choudhury, S. Ahmed, M.A. Shalabi and T. Inui, Appl. Catal. A: Gen 314 (2006) 47
- 21 S. Takenaka, T. Shimizu and K. Otsuka, Int. J. Hydrogen Energy 29 (2004) 1065
- 22 R. T. Baker, I.S. Metcalfe, P.H. Middleton and B.C.H. Steele, Solid State Ionics 72 (1994) 328
- 23 R.M. Ormerod, Chem. Soc. Rev. 32 (2003) 17
- 24 S. McIntosh, H.P. He, S.I. Lee, O. Costa-Nunes, V.V. Krishnan, J.M. Vohs and R.J. Gorte, J. Electrochem. Soc. 151 (2004) A604
- 25 W.Z. Zhu and S.C. Deevi, Mater. Sci. Eng. 362 (2003) 228
- 26 J. Liu, Prog. Chem. 18 (2006) 1026
- 27 G. Fwah and A. Sacco, Carbon 30 (1992) 415
- 28 C.G. Lee, K.S. Ahn, H.C. Lim and J.M. Oh, J. Power Sources 125 (2004) 166
- 29 K. Sasaki, K. Watanabe, K. Shiosaki, K. Susuki and Y. Teraoka, J. Electroceram. 13 (2004) 669
- 30 K. Sasaki and Y. Teraoka, J. Electrochem. Soc. 150 (2003) 878
- 31 D.J.L. Brett, A. Atkinson, D. Cumming, E. Ramirez-Cabrera, R. Rudkin and N.P. Brandon, Chem. Eng. Sci. 60 (2005) 5649
- 32 R.H. Perry and D.W. Green, Perry's Chemical Engineers' Handbook, 7th ed. McGraw-Hill (1997)
- 33 A. Braithwaite, Chromatographic Methods, 4th ed. Chapman and Hall London (1985)
- 34 M.A. Goula, S.K. Kontou and P.E. Tsiakaras, Appl. Catal. B: Environmental 49 (2004) 135

Chapter 6

Electrocatalytic synthesis of HCN in electrochemical reactor (SOFC)

6.1 Introduction

The main aim of the research project is to synthesise hydrogen cyanide in an electrochemical reactor using a suitable anode material. 40-60 wt% FSO-Ni/CGO was found satisfactory to catalyse HCN production by both ammonolysis and ammoxidation of methanol in micro reactor experiments. In this chapter, the feasibility of cogeneration of electrical power and hydrogen cyanide in a SOFC has been investigated. This chapter describes the characterisation of the electrodes, fabrication of the complete fuel cell and HCN synthesis in the fuel cell. The first section describes the experimental procedures used for the preparation of the fuel cell components. The electrolyte, the anode and the cathode are the main components of a fuel cell. Almost full densification of ceramic electrolytes must be achieved to ensure acceptable optimised performance of the cell. On the other hand, anode and cathode materials must be porous and electronically conducting and should also be catalytically active towards the reacting species. The selection and preparation of the electrolyte and electrode materials are discussed. As required, characterisation techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and nitrogen gas adsorption were used to investigate the electrode structures. In addition, oxygen transported through the SOFC electrolyte arrives at the electrocatalyst of the anode in ionised form and might participate in the MVK redox mechanism in a different way from gaseous oxygen which has to chemisorb and desorbate.

6.1.1 Anode and Cathode Materials

Electrodes may be purely metallic or a composite of metal and ceramic oxide (referred to as a cermet) or a mixed electronic/ ionic conducting ceramic oxide. Electrode materials selected for investigation in the fuel cell are listed in Table 6.1.

They were chosen to operate at relatively low temperatures for a SOFC, since the synthesis of HCN is usually carried out at temperatures in the range of 400- 500°C.

Table 6.1 - Electrode materials used in this study

Material	Representation	Function
Platinum	Pt	Anode - Cathode current collector
Ni-Ce _{0.9} Gd _{0.1} O _{1.95}	Ni-CGO	Anode cermet
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ}	LSCF	Cathode
Iron Antimony Oxide	FSO	Anode HCN catalyst

6.1.2 CGO electrolyte pellet preparation

To make the best use of the properties of ceramics, powders with high purity, high homogeneity and fine particle size are necessary. Other important powder characteristics include particle size distribution and particle shape, state of agglomeration, chemical composition and phase composition [1]. The ceramic powder for the electrolyte Ce_{0.9}Gd_{0.1}O_{1.95} (CGO-10) was purchased from Rhodia and was selected because of its fine particle size and high homogeneity. The parameter often used to compare different powders is the median particle size denoted by the d₅₀ value [2]. Typical d₅₀ and surface area data are shown in Table 6.2, as provided by the manufacturer. Very fine particles with high specific area tend to agglomerate and can form microstructural defects in sintered specimens. An optimum surface area for sintering to high relative density has been estimated to be roughly 10 square meters per gram [3].

Table 6.2 - Ceramic powders d₅₀ and surface area data

Material	d ₅₀ (μm)	Surface area (m ² /g)
Ce _{0.9} Gd _{0.1} O _{1.95}	4.96	70 -100
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ}	6.01	4 - 8

A cylindrical dense electrolyte pellet was prepared by dry pressing the electrolyte powder followed by sintering. About 2g of fine CGO-10 powder was placed in a 25mm diameter stainless steel die and pressed uniaxially under 1 tonne load. The pressed pellet was sintered in an Elite Thermal Systems box furnace under static air

with a heating rate of 120°C /h up to 1450°C for a dwell time of 2h. During sintering, the weakly bonded ceramic green compact transforms into a rigid component. This process gave a sintered pellet approximately 20% smaller in diameter than the green body, the pellet diameter after sintering being 18.6mm. Both faces of the ceramic electrolyte were ground and polished on 1200 SiC grit paper to ensure uniformity of surface followed by cleaning in acetone in an ultrasonic bath. The electrolyte pellet thickness was 0.69mm and the calculated density was approximately 95% of the theoretical density. A Mitutoyo digital micrometer was used for dimension measurements.

6.1.3 Anode preparation and deposition

Preparation of Ni-CGO and FSO-Ni/CGO anode slurries were discussed in Chapter 4 earlier. The major steps involved in fabricating a workable SOFC are the synthesis of the dense electrolyte material and the deposition of the anode and cathode materials on either side of the electrolyte. Once the dense electrolyte disc has been prepared, it is necessary to carefully deposit the electrodes and sinter them to the electrolyte in order to carry out fuel cell studies.

Electrodes can be deposited by using various techniques, including magnetron sputtering, screen printing, spraying, tape casting, and chemical vapour deposition (CVD) or by simple paint brushing. Sputtering is a non-thermal vaporisation process where the surface atoms are physically ejected from target by a momentum transfer from an atomic-sized energetic bombarding particle (i.e. a gaseous ion) and then transferred to the substrate (electrolyte) [4]. Screen-printing involves the preparation of a homogeneous and stable paste containing the powdered electrode material and a solvent with other organic additives. The paste is then forced through a screen on to the surface of the electrolyte. Spraying and paint-brushing are less complex relative to the above two techniques, but more difficult to control reproducibly. For spraying, a solution of low viscosity is prepared containing the electrode powder in a solvent. A dispersant or a binder may also be added. The solution is then sprayed on the surface of the electrolyte. For paint brushing, an ink is prepared and brushed carefully on to the electrolyte surface. In all powder- based processes, the electrode deposit is dried and baked at elevated temperature to burn out organics and ensure good adherence to the electrolyte. During the deposition

process it should be ensured that the surface of the electrolyte is covered uniformly and that adequate surface area is provided for the desired electrode reactions to take place. Good contact at the electrode/electrolyte interface is essential to minimise interfacial polarisation losses in high temperature fuel cells. Changes in the porous electrode morphology may produce changes of over three orders of magnitude in the length of the triple phase boundary at which the electrochemical reaction takes place [5, 6].

6.1.3.1 Doctor blade casting

The anode in the present study was deposited by *doctor blade casting*, which falls between screen printing and tape casting. The equipment used is illustrated in Figure 6.1.

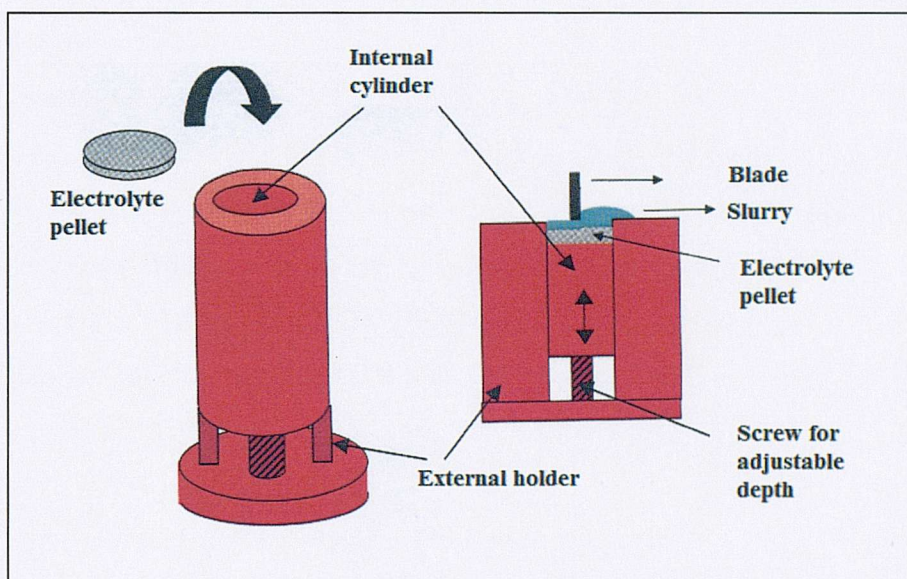


Figure 6.1 - Schematic of doctor blade casting set up [7]

The apparatus comprises two cylinders; an outer hollow cylinder and an inner closed cylinder, on which the electrolyte pellet can be mounted for electrode deposition. A screw at the bottom of the inner cylinder is used to adjust its height with respect to the outer one. The pellet was placed on the inner cylinder such that its top surface was lower than the outer cylinder. A depth micrometer was used to set the height difference of the pellet surface and the outer cylinder to be equal to the required anode thickness. The slurry was then poured on the pellet, and a doctor blade was wiped over the outer cylinder in order to remove the excess slurry. Care was taken to get a uniform thin coating on the electrolyte surface.

Table 6.3 - Sintering profile for the anode FSO-Ni/CGO

Starting Temp	~ 20°C
Heating Rate	0.5/min
Sintering Temp	500°C
Dwell Time	4h
Heating Rate	5°C/min
Sintering Temp	1300°C
Dwell Time	2h
Cooling Rate	5°C/min

After deposition, the pellet with the anode slurry on was removed from the holder and placed on a clean surface, covered to avoid skin formation, and then left to dry slowly overnight. The anode was then fired at 1300°C following the profile shown in Table 6.3. After drying and firing, the anode reduced in thickness. Typically, the anode produced by applying the slurry on the pellet was initially 100µm thick which after drying and firing was reduced to approximately 13µm. The anode precursor was pre-reduced in a stream of 10% H₂/N₂ for electrical characterisation. A separate pre-reduction was not necessary for the anode in the fuel cell experiment as the anode is reduced in-situ by the fuel.

6.1.4 LSCF-CGO cathode preparation and deposition

At lower temperatures, CGO-10 has higher oxygen diffusion than LSCF and therefore it is important to use composite cathodes to improve their effective oxygen diffusion [8]. The LSCF-CGO cathode composite was used in this study to increase the effective oxygen diffusion coefficient of the cathode. The composite cathode was made by mixing 10g of 70-30 wt% LSCF/ CGO-10 composite powder together with 0.5g of KD1 dispersant and 25g of acetone. The mixture was then ball milled for 24h. 2.3g of terpeneol binder and another 25g of acetone were then added to the mixture and further ball milling was carried out for 10 minutes. This composite cathode ink was sprayed on to the electrolyte using a pressurised air brush sprayer. The spraying procedure was repeated 5 times uniformly over the whole surface of one face of the electrolyte pellet to acquire a final thickness of 15µm after firing at

850°C for 0.5h in air. The cathode was applied after the anode firing step (which was at the higher temperature of 1300°C).

6.1.5 Platinum current collectors

Platinum is a commonly used current collector material for fuel cells and here was used on top of each electrode. Platinum mesh (99.99%, 0.06mm wire diameter, 0.25mm aperture) was used on the anode and cathode sides of the cell as current collector with electrical connection made with platinum wire (99.99%, 0.25mm diameter; Goodfellow, UK).

6.1.6 Fabrication of fuel cell

The cell consisted of a dense CGO-10 electrolyte, a FSO-Ni/CGO anode and LSCF-CGO cathode as shown in Figure 6.2. The thickness of CGO-10, FSO-Ni/CGO and LSCF-CGO layers as measured from SEM were 696µm, 15µm and 15µm respectively. Only a central area of the electrolyte of approximately 15mm diameter was coated with the anode slurry using the doctor blade, leaving the outer space for the final sealing with the fuel cell rig. The anode active cell area was measured to be 1.76cm². Once the anode was coated to the desired thickness, it was fired at 1300°C for 2h in air.

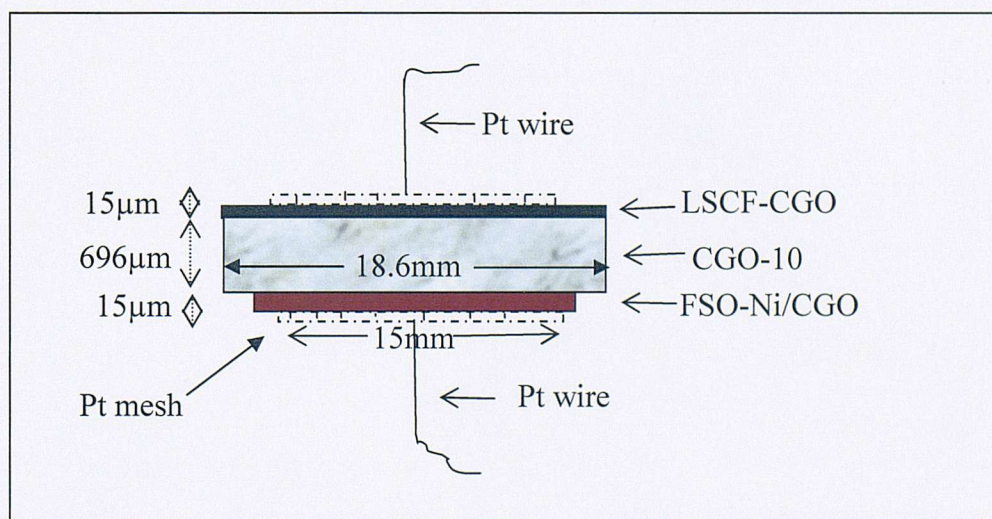


Figure 6.2 - Schematic diagram of fuel cell for HCN synthesis

The heat treatment profile is as given in Table 6.3. A platinum mesh, used as current collector, was spot welded to the Pt lead wire and sealed with the anode by applying

some FSO-Ni/CGO slurry over the surface of the mesh making sure that the mesh was well adhered to the anode surface. This was followed by a second identical heat treatment as before. The LSCF-CGO cathode was deposited on the other face of the CGO-10 electrolyte by slurry spraying and then fired at 850°C for 2h. The cathode platinum current collector was fixed in a similar way to that of the anode side and a second heat treatment following the same thermal profile. The active cathode area (2.71cm^2) was slightly greater than that of the anode.

6.1.7 Electrical Connectivity and Sealing

Once the cell was fabricated, it was placed as a cap on top of the outer stabilised zirconia tube, as shown in Figure 6.3 using a glass-based dielectric paste (Dielectric IP 041, Heraeus, UK) as sealant, with the cathode facing outwards in order to be exposed to air and the anode facing inwards to be exposed to the fuel.

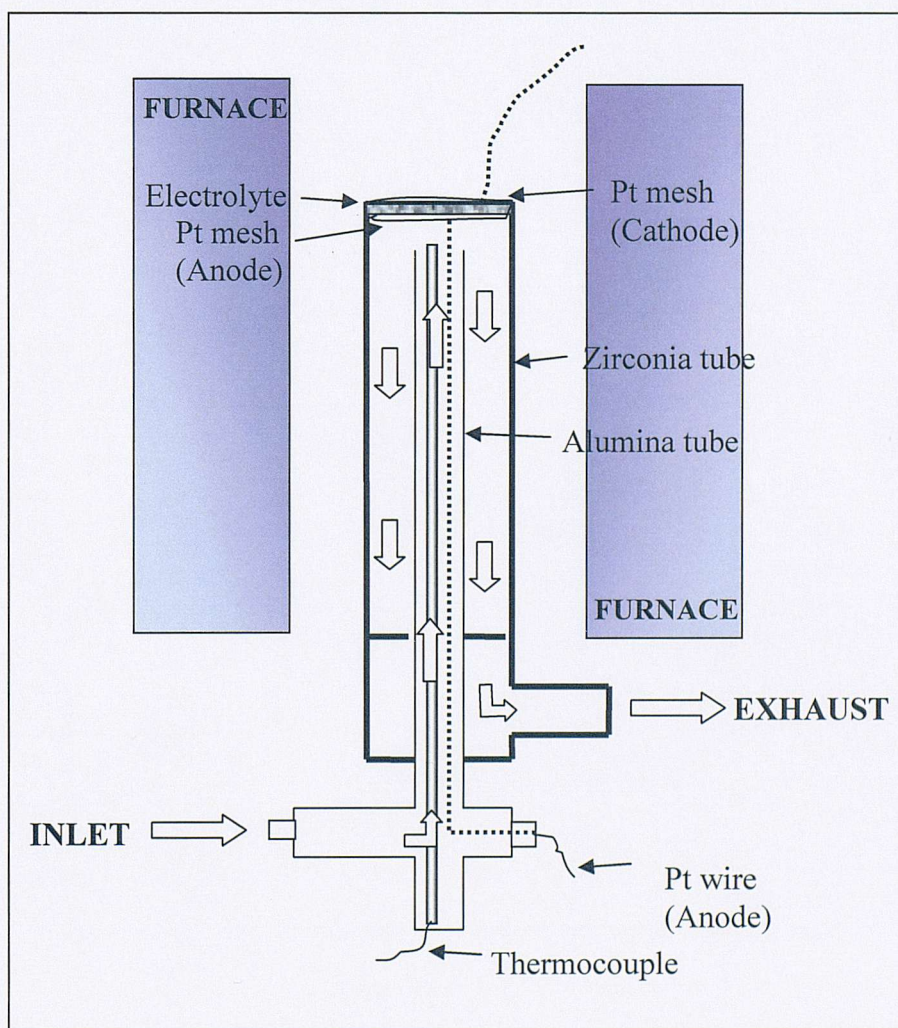


Figure 6.3 - Schematic diagram of the fuel cell rig

The glass sealant was applied between the cell edge and the rim of the zirconia tube and then heated to the flow temperature of the glass for a few minutes to form a gas-tight seal. Stabilized zirconia was selected for the outer tube because of the thermal expansion similarity between this material and the ceramic electrolyte. The cell was placed in the middle of a vertical split-tube furnace with the cathode exposed to air in the furnace. A thermocouple was located as close as possible to the electrolyte via a narrow tube on the fuel side to record the actual operation temperature of the cell.

6.1.8 Fuel Cell Gas Supply and Analysis

The rig designed for gas supply and analysis under various conditions is shown in Figure 6.4. Calibrated mass flow controllers (Brooks, UK) were used to provide a mixed gas feed to the anode compartment of the fuel cell. Methanol (AnalaR, 99.8%, BDH), steam and ammonia were introduced to the anode of the fuel cell through the inner tube in the required composition. A heated line (70°C) ensured that there was no condensation of any components before entering the fuel cell, situated within the vertical furnace (Lenton, UK).

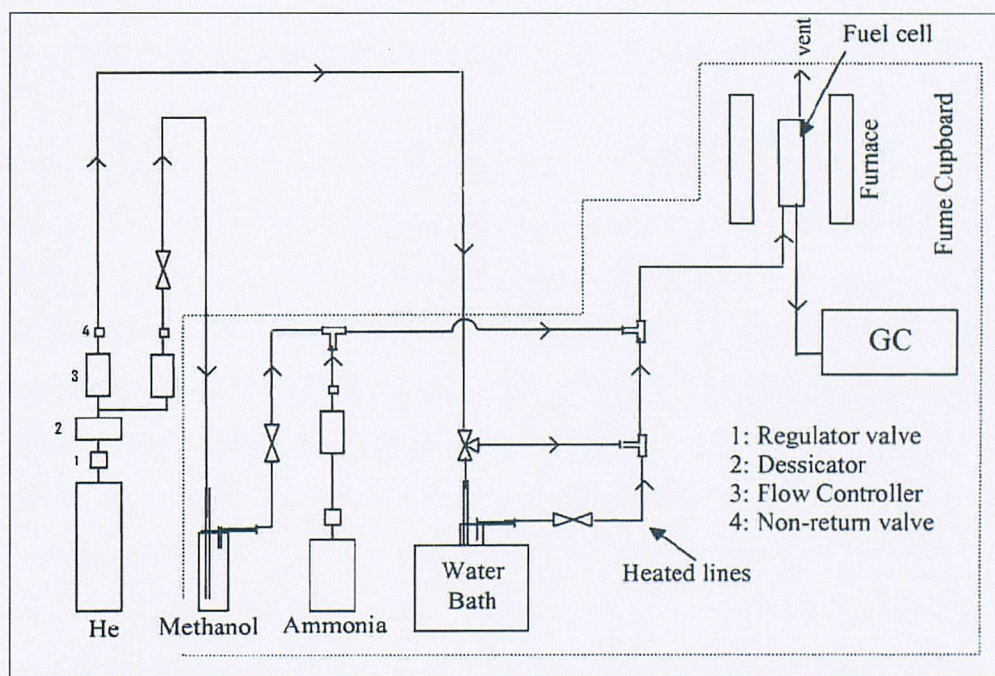


Figure 6.4 - Schematic diagram of the experimental set up for HCN synthesis in fuel cell

The concentrations of the methanol and steam were set using bubble columns situated inside the thermostatic water baths. The experiments were carried out with set molar ratios of $\text{CH}_3\text{OH}/\text{He}$ and $\text{H}_2\text{O}/\text{He}$ maintaining a constant total pressure with a balance of helium. All experiments were performed in a fume hood, with manual gas flow shut off valves located outside the fume hood. After reaction at the anode, the unconsumed fuel and the product flowed back in the opposite direction between the outside of the alumina feed tube and the inside of the zirconia tube and finally routed through stainless steel lines maintained at 70°C to the gas chromatograph (GC) for product analysis. Chemical analysis of the outlet stream from the fuel cell was carried out by a Shimadzu GC with a thermal conductivity detector and a column combination of molecular sieve 5A and HayeSepC. Since nitrogen was one of the products in this experiment, it could not be used as a carrier gas. Before doing experiments, the GC was calibrated as described previously (carrier helium) for hydrogen, oxygen, water, ammonia, hydrogen cyanide, carbon dioxide, carbon monoxide, methylamine, dimethyl ether, nitric oxide, formaldehyde and methanol using calibration gas cylinders supplied by Cryoservice UK Ltd. and AirLiquide, Germany.

6.1.9 Fuel cell testing methodology - Investigation of electrical power generation

Electrical power generation by the fuel cell was investigated in the temperature range of $500 - 650^\circ\text{C}$ with HCN synthesis. Platinum wires that connected to the current collectors at the anode and cathode were in turn connected to an electrochemical workstation (Sycopel) to control the current output being drawn in the external circuit and measure the voltage across the cell. Any change in the operating temperature was induced at a slow rate of $60^\circ\text{C}/\text{h}$ and the cell was left under steady state temperature conditions for at least 30 minutes before taking measurements.

The open-circuit voltage (OCV), i.e. the voltage at zero current, was measured initially. After introducing the fuel to the anode at the set temperature, the OCV reached a steady value within a few minutes. This was associated with the reduction of NiO to the metal Ni. Subsequently, the current-voltage characteristic was obtained by drawing current at incremental steps and measuring the cell voltage at

each step at steady state. All the measurements were repeated at least twice to ensure reproducibility.

6.1.10 Synthesis of HCN in fuel cell

HCN synthesis was carried out in the fuel cell at elevated temperatures in the range of 500°C to 650°C. The pressure at which the reaction was conducted was atmospheric. The reaction was carried out on a continuous basis using helium as diluent and also as a carrier gas. The reactant gases methanol, ammonia and water vapour with approximate molar ratio 1:1.3:2 and total flow rate of approximately 66 ml/min (STP) were fed into the reactor. Ammonia was supplied in a compressed form from a high purity pressurised liquid ammonia cylinder. For methanol, a flow of helium was allowed through a Dreschel bottle containing methanol at room temperature. Similarly, water was added to the reaction mixture by heating the water bubblers to 60°C in the constant temperature water bath. A base-line experiment was conducted before the catalytic fuel cell using an electrolyte pellet and platinum current collectors in place of the fuel cell. Methanol, ammonia and steam were passed through the blank reactor at temperatures and gaseous compositions similar to those employed in the fuel cell experiments. In the blank experiment preceding the fuel cell experiment, the initial flow rates were slightly adjusted to obtain the appropriate target reactant concentrations according to the response factors from the GC calibration. The anode was exposed to the methanol, ammonia and water fuel mixture and the cathode was exposed to air. Oxygen from air is transported in the form of O^{2-} through the solid electrolyte disc and reaches the anode where it reacts with the fuel. The bulk gas composition at the anode was assessed by analysing the off-gas stream from the fuel cell using the GC.

6.1.11 Electrode Characterisation

For electrode characterisation studies, CGO-10 electrolyte discs of 13mm diameter (green disc) were prepared by uniaxial pressing. In all cases, uniaxial load did not exceed 1 tonne. The green discs were sintered at 1450°C for 2h and the electrodes (anode and cathode) were coated on the electrolyte and fired as described previously. The porosity and microstructure of the sintered electrodes were analysed by scanning electron microscopy (SEM) as explained in Chapter 3. The anode and

cathode composite powders were characterised by X-ray diffraction (XRD) and nitrogen gas adsorption. The characterisation of the anode powders has been discussed in Chapter 4 and this chapter deals only with the LSCF/ CGO cathode composite and SEM of the anode coated on CGO electrolyte.

6.2 Results and Discussion

6.2.1 X-ray Diffraction

The X-ray characterisation of the anode FSO-Ni/CGO has been discussed in Chapter 4 previously and the cathode LSCF-CGO characterisation is explained here in this section.

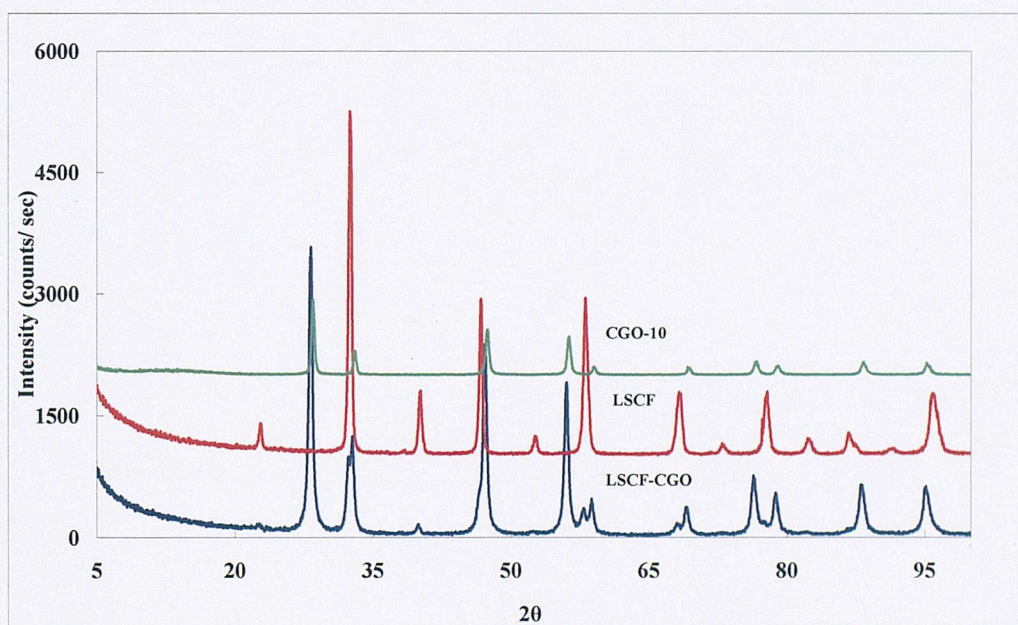


Figure 6.5 - Combined XRD patterns of as received $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO-10), $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and 70-30 wt% LSCF-CGO composite

X-ray diffraction was performed on $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO-10) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) obtained from the commercial supplier (Rhodia) with the aim to ascertain phase purity. Figure 6.5 shows the combined X-ray diffraction patterns of as received CGO-10, LSCF and 70-30 wt% LSCF-CGO powders. The patterns obtained were compared to those available in the online Chemical Database Services provided by the Daresbury Laboratories, UK. After matching, the patterns for the purchased powders to those in the database, unit cell

parameters and crystallographic structure types could be identified. The XRD pattern of CGO-10 was determined to be single phase and no impurity peaks can be seen. All the peaks are very sharp showing the good crystalline nature of the powder. The pattern obtained at room temperature was fitted to a cubic fluorite structure [9]. Due to the dopant Gd, there is a slight shift in the lattice parameter and diffraction peak angle (2θ) compared to the undoped fluorite structure (CeO_2).

The XRD pattern of LSCF shows a single-phase perovskite structure with sharp peaks. The LSCF was found to be in the rhombohedral structure. Compositions with $\text{Sr} \geq 0.3$ have been shown to exist in a stable rhombohedral phase at room temperature, while for $\text{Sr} \leq 0.2$ the orthorhombic phase predominates [10,11].

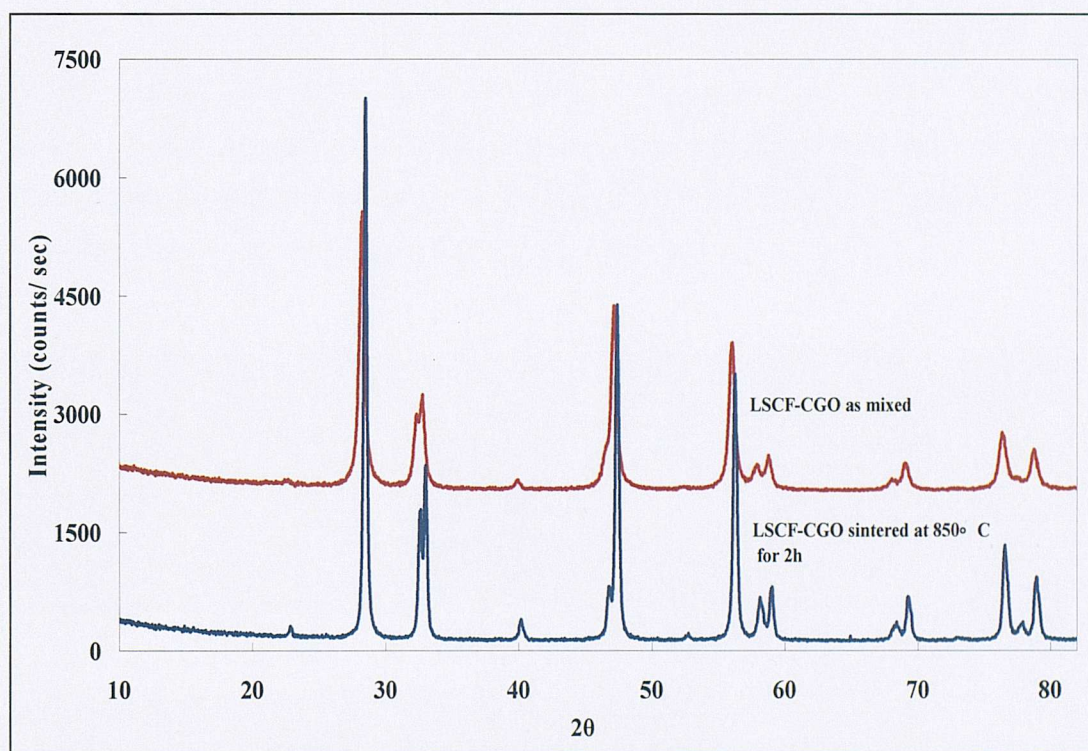


Figure 6.6 - Combined XRD patterns of 70 – 30 wt% LSCF-CGO composite as mixed and calcined to 850°C

Tai *et al.* [10] reported that $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ is orthorhombic and their investigations showed that this composition lies at the point where the structure changes from the orthorhombic to the rhombohedral symmetry. For iron content up to 0.7 (at $\text{Sr} = 0.2$) the perovskite is rhombohedral, while for $\text{Fe} > 0.7$ it is orthorhombic. The X-ray diffraction pattern of the 70-30 wt% LSCF-CGO mixture (Figure 6.6) shows no evidence of the formation of new phases after sintering at

850°C. The XRD for the anode constituents and iron antimony oxide were discussed in Chapter 4 individually in detail.

6.2.2 Nitrogen gas adsorption

The gas adsorption technique was used to measure the specific area of the powdered material. Nitrogen adsorption was performed at 77.4K with 0.9g of 70-30 wt% LSCF-CGO composite powder (Quanta Chrome Autosorb AS6). The specific surface area for the LSCF-CGO measured by the BET method was 6.71m²/g.

6.2.3 Micro structural studies by SEM

The microstructures of FSO-Ni/CGO anode, LSCF-CGO cathode and the current collectors were examined using a scanning electron microscope (SEM). For the FSO-Ni/CGO anode, the anode was pre-reduced in a tube furnace at 700°C for 0.5h in 10% H₂/N₂. The anode turned grey possibly due to the reduction of NiO to Ni, and this reduction process also increased the porosity due to the removal of oxygen. The anode/electrolyte bilayer was cut using a diamond saw set in resin, polished, and either carbon coated or gold coated prior to examination.

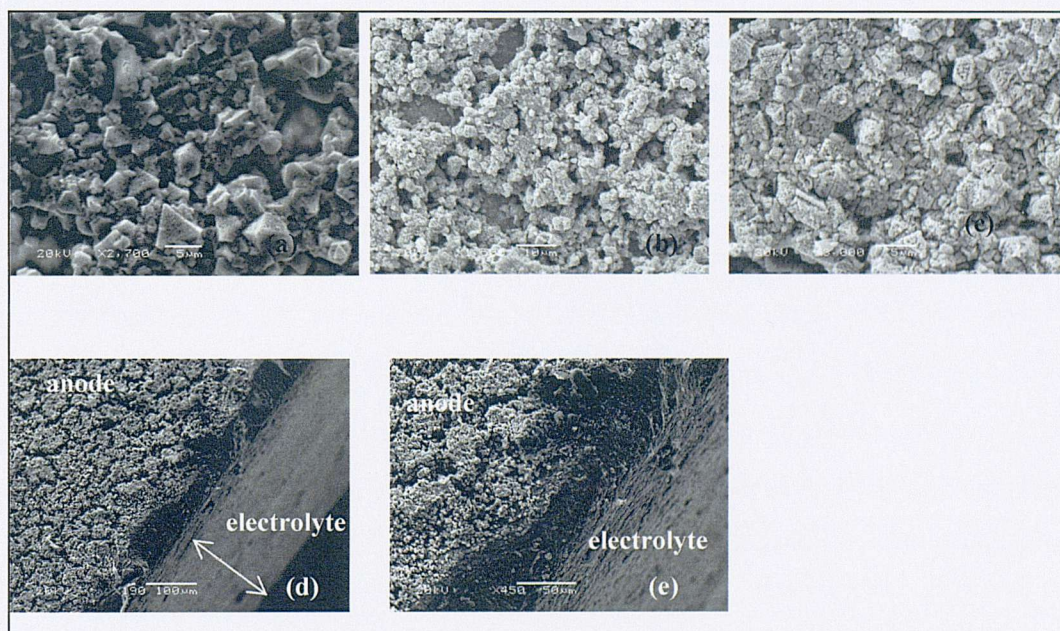


Figure 6.7 - SEM of 40-60 wt% FSO-Ni/CGO anode on CGO-10, sintered to 1300°C/ 2h and reduced. (a) no coating, no polishing. (b)- (c) gold coated, no polishing, (d) and (e) cross-section

Figures 6.7, 6.8 and 6.9 show the SEM micrographs of the anode and cathode materials. Figure 6.7 shows the topographic and cross-sectional image of 40-60 wt% FSO-Ni/CGO coated on uniaxially pressed CGO-10 sintered at 1300°C for 2h and reduced under 10% hydrogen at 700°C for 0.5h without polishing. Unlike the electrolyte, the anode should possess a porous structure which must be maintained even during processing and at operating temperatures. The required porosity was achieved by nickel dispersion with the solid electrolyte material CGO-10 to form a cermet. This inhibits sintering of nickel particles during operation and maintains porosity and also gives the anode a thermal expansion coefficient closer to that of the solid electrolyte CGO-10 [12, 13]. The pores are interconnected and it is seen that the anode has some finer structure similar in scale to the d_{50} values 0.7 and 0.58 μm of the NiO and CGO-10 starting powders, respectively. The sintering temperature of 1300°C of the anode precursor material has led to well dispersed, round and fine particles with a good interconnected porosity of linked channels (Figure 6.7a – 6.7c). Figure 6.7d and 6.7e show the cross section of the CGO-10 electrolyte with anode coated on it. A dense CGO-10 electrolyte with a porous electrode can be seen. A polished cross section is shown in Figure 6.8 from which it can be seen that the anode is approximately 6 μm in thickness. The apparent porosity in the electrolyte is artefact caused by grain pluck-out during specimen preparation.

For LSCF-CGO cathode characterisation, the cathode composite was coated on a 13mm dense CGO-10 electrolyte by the spray technique to a final thickness of approximately 15 μm . It was then sintered at 850°C for 2h. Figure 6.9 shows the SEM micrographs of the LSCF-CGO cathode sintered on CGO-10. It was fractured and examined by SEM both with and without polishing and coating. After sintering at 850°C, evenly dispersed particles in the cathode layer touching neighbouring grains can be identified. Furthermore the grains remained small in size which should produce an active cathode. Interconnected porosity in the cathode material on a dense electrolyte is also evident.

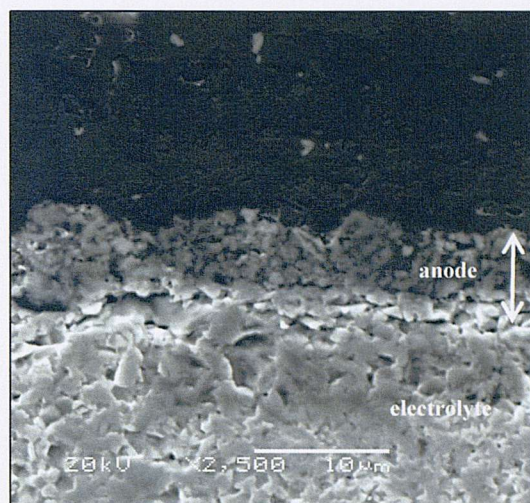


Figure 6.8 – SEM image of polished and gold coated 40-60 wt% FSO-Ni/CGO anode on CGO-10 sintered to 1300°C for 2h and reduced at 700°C for 0.5h

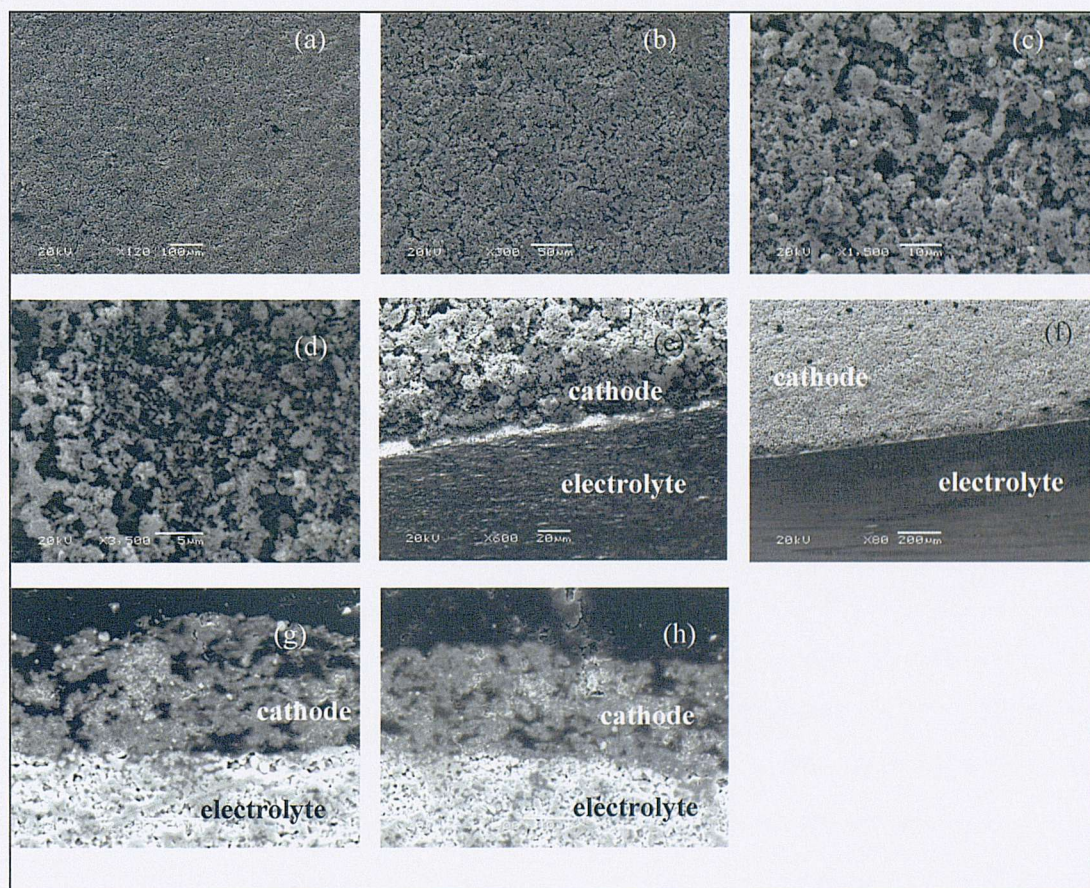


Figure 6.9 - SEM of 70-30 wt% LSCF-CGO cathode on CGO-10, sintered for 2h at 850°C (a)- (f) unpolished, no coating (a) - (d) surface view, (e) and (f) cross sectional view, (g) and (h) polished and gold coated cross sections

The micrographs illustrate the fine microstructure of the sprayed and sintered cathode layers next to the dense CGO-10 electrolyte. The thickness of the electrode layer was found to be approximately 15 μ m, with good interconnected porosity. The electrode microstructure also appears uniform throughout with a very good bonding and contact at the interface between the electrode and the dense electrolyte. The electrode showed good adherence to the electrolyte.

6.2.4 Product analysis

In order to assess the bulk gas composition at the anode, the off-gas from the fuel cell was analysed using gas chromatography (Table 6.4). The flow rates of the reactants were maintained at the values used in the micro reactor experiments (ammonolysis of methanol with steam using calcined FSO-Ni/CGO at 1300°C for 2h) for comparison. Other experimental conditions were the same throughout the experiment. The flow rate of ammonia was set approximately at 4ml/min and the helium carrier gas was set at 26ml/min for the methanol and 36ml/min for the water vapour lines. The total flow rate was 66ml/min of reactants. Estimation of input fuel gas compositions followed the same approach as explained in Chapter 5.

With the current (I) at 20 mA, the corresponding oxygen (O_2) flow rate through the electrolyte was calculated using the formula

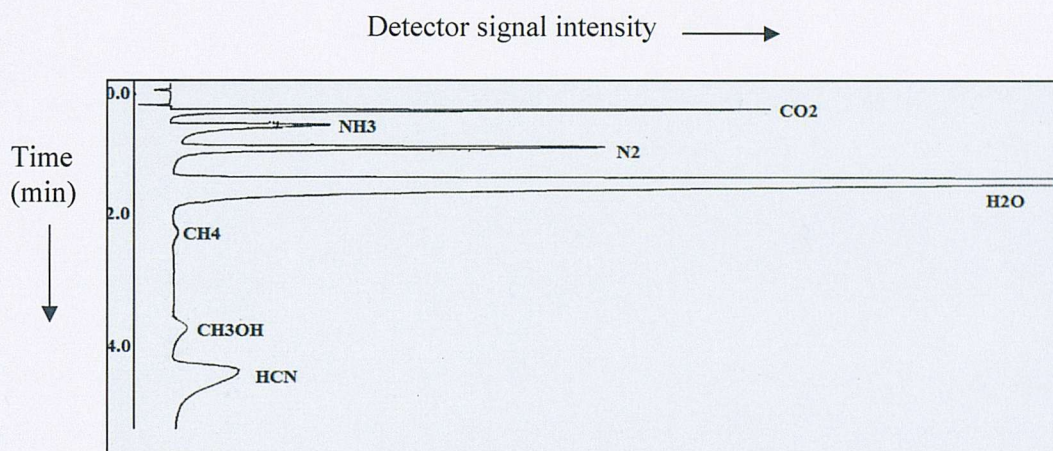
$$\text{Number of moles of } O_2 / \text{sec} = \frac{I}{4 \times F} \quad - \text{ (eqn 6.1)}$$

where I is the current and F is the Faraday's constant (95484.56 C/mol). The oxygen flow rate was calculated to be 3.11 μ mol/min or approximately 0.07ml/min. Since the oxygen ion permeation flux was much smaller than the input of other reagents, this resulted in negligible contribution to the total flow. Table 6.4 presents the overall product distribution at temperatures between 500-650°C from the fuel cell. In addition to unreacted CH_3OH and NH_3 , the components identified in the effluent stream were the main product HCN and other by-products such as CO_2 , N_2 , CH_4 , and H_2O . Since the SOFC current made a negligible difference to the product concentrations (see next section) the values for different currents are averaged in Table 6.4.

Table 6.4- Product concentrations of HCN synthesis in fuel cell

Temp (°C)	HCN (mol %)	CO ₂ (mol %)	N ₂ (mol %)	H ₂ O (mol %)	CH ₄ (mol %)	CH ₃ OH (mol %)	NH ₃ (mol %)	C _{TOTAL} (mol %)	N _{TOTAL} (mol %)
500	3.8	3.2	3.4	20.2	0.60	1.6	1.8	9.2	12.4
550	3.4	3.6	3.7	20.7	0.60	1.7	1.1	9.3	11.9
600	1.7	6.0	4.2	20.1	0.50	1.0	1.2	9.2	11.3
650	1.4	7.3	5.0	22.0	0.30	0.4	1.0	9.4	12.3

Unfortunately, it was not possible to quantify the amount of hydrogen formed in the system as hydrogen could not be detected. The thermal conductivity of helium (0.152 W/mK) and hydrogen (0.182 W/mK) are very similar [14, 15]. This renders poor response to hydrogen when using helium as a carrier gas and a thermal conductivity detector.

**Figure 6.10** - Chromatogram of HCN synthesis in fuel cell at 500°C

Hydrogen can be detected using nitrogen as carrier gas but in our experiments, nitrogen cannot be used as carrier gas as it is also one of the by-products in the reaction. Figure 6.10 shows the chromatogram plot of HCN synthesis at 500°C and Figure 6.11 shows the product concentration over the temperature range 500-650°C. The experimental error in the measured concentration was typically less than 5% relative. The N: C and O: C atomic ratio across all the products varied slightly as that in the feed. The use of platinum is the only difference between the micro reactor and the SOFC experiment with the same anode catalyst (Table 5.15). Except for methane, the concentrations of HCN, CO₂, N₂ and H₂O were found to be higher in the fuel cell experiment than the micro reactor. Neither methylamine nor carbon monoxide was detected here in the fuel cell experiment.

Table 6.5 - Product concentrations of HCN synthesis in fuel cell as a function of cell current and temperature

Temp (°C)	500		550		600			650		
Current (mA)	0	20	0	20	0	20	40	0	20	50
Components										
HCN	3.7	3.8	3.4	3.4	1.6	1.7	1.7	1.3	1.4	1.3
CO ₂	3.1	3.2	3.5	3.6	5.8	6.0	6.0	7.2	7.2	7.3
N ₂	3.4	3.3	3.6	3.7	4.2	4.2	4.1	4.9	5.0	4.9
CH ₄	0.5	0.6	0.60	0.60	0.50	0.49	0.50	0.28	0.30	0.29
H ₂ O	20.2	20.2	20.6	20.7	20.1	19.9	20.1	21.9	21.7	22.1
CH ₃ OH	1.5	1.6	1.6	1.8	0.9	1.0	1.0	0.3	0.4	0.4
NH ₃	1.9	1.7	1.1	1.0	1.2	1.1	1.2	1.1	1.0	0.9

Table 6.5 shows the composition of products as a function of cell current and temperature. Most of the ammonia had been used for the HCN and N₂ production in the experiment. The ammonia conversion to HCN production was greatest at the lowest temperature. Within the scatter of results there is no consistent discernible effect of the fuel cell current on product composition. This is because the oxygen input through the fuel cell was much lower than the input of gaseous reactants.

The GC analysis showed a high HCN concentration in the cell at 500°C and decreased with increasing temperature whereas the concentrations of CO₂, N₂ and H₂O increased. CO₂ and H₂O were the primary oxidation products. At 500°C, the reactants CH₃OH and NH₃ were consumed mainly for HCN production but at higher temperatures, for CO₂ and N₂ formation respectively.

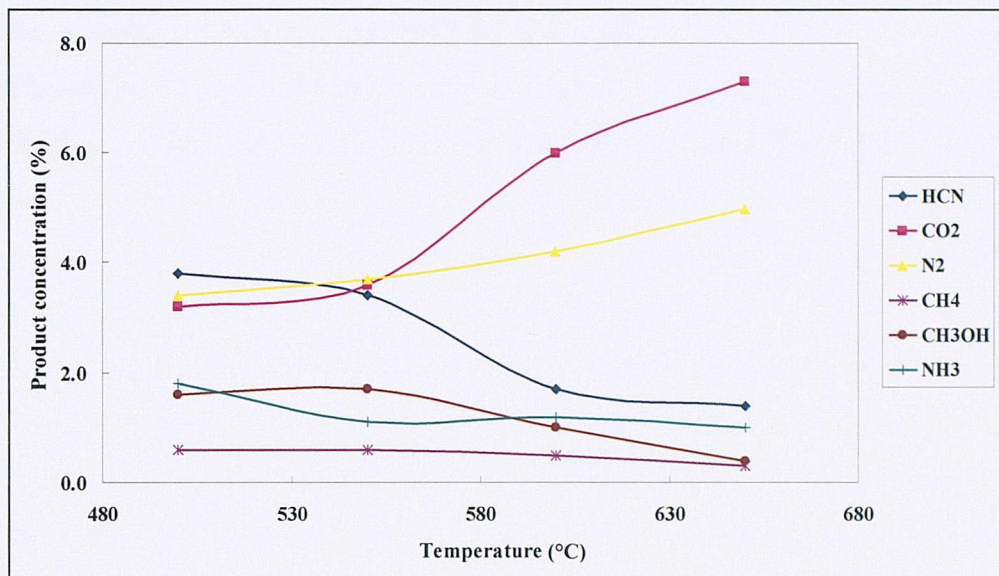


Figure 6.11 - Product concentration plot of methanol ammonolysis at 500-650°C in fuel cell

The anode catalyst promoted the non-oxidative ammonolysis of methanol according to equation 6.3 and this made non-oxidative HCN production possible at the anode in the SOFC. It was evident that the small flux of oxygen passing through the electrolyte was not involved in HCN synthesis as HCN was produced even at $I = 0$. Thus the ammoxidation reaction (eqn 6.2) was not taking place in the SOFC.



The increase in CO_2 concentration at higher temperatures may be due to methanol steam reforming (eqn.6.4) and water gas shift reaction (eqn. 6.5) [16-18]



The above reactions and reaction 6.3 also produce H_2 and hence power output from the SOFC.

Ammonia is a well known feedstock for the production of hydrogen and therefore can be used as a fuel in SOFC. Catalytic cracking of ammonia (eqn. 6.6) produces hydrogen and nitrogen and the H_2 is partially converted into electricity in a fuel cell [19- 22].



The cracking readily takes place on a catalyst, such as Fe, Fe_2O_3 , or a nickel-based compound, at temperature above $450^\circ C$ [20, 21]. It has been shown that SOFCs can convert pure NH_3 into electricity by using Fe, Ag or platinum electrodes [21, 22]. There was neither CO nor CH_3NH_2 detected at any temperature. Unlike the flow reactor, CO was not detected in the fuel cell experiment.

6.2.5 Selectivity and product yield

In the fuel cell, the methanol conversion to the products was above 80% but the selectivity to HCN product was low (15% at $650^\circ C$) compared to the selectivity to carbon dioxide (54% at $650^\circ C$). Table 6.6 and 6.7 show the selectivity and the yield of HCN from methanol and ammonia respectively.

Table 6.6 - Selectivity and yield of HCN based on methanol input

Temp ($^\circ C$)	S_{HCN} (%)	Methanol Conversion (%)	HCN yield (%)
500	48	83	40
550	44	82	36
600	20	89	18
650	15	96	15

Table 6.7 - Selectivity and yield of HCN based on ammonia input

Temp ($^\circ C$)	S_{HCN} (%)	Ammonia Conversion (%)	HCN yield (%)
500	35	86	30
550	30	91	27
600	15	90	13
650	12	92	11

The selectivity (based on ammonia) to the main product, HCN was low (12% at 650°C) in comparison with nitrogen formation (80% at 650°C). The selectivity for HCN and its yield in the fuel cell experiment were found to be higher than the micro reactor experiment with the same anode catalyst. At 500°C, the yield of HCN in the fuel cell experiment was 40% whereas the yield was 38% in the micro reactor based on reactant methanol input. Similarly, the selectivity to HCN at 500°C was 48% whereas it was 43% with the micro reactor confirming the enhanced catalytic activity by platinum.

6.2.6 Influence of Platinum

Difference in the observed products in both the micro and electrochemical reactors using 40-60 wt% FSO-Ni/CGO with steam are summarised for comparison in Table 6.8. The main difference between the two experiments was the involvement of platinum in the fuel cell. The same temperature, flow rates and the reactant concentrations were maintained in both the experiments.

Table 6.8 - Comparison of products formed in micro and electrochemical reactors using 40-60 wt% FSO-Ni/CGO anode catalyst

HCN synthesis in micro reactor	HCN synthesis in electrochemical reactor
• Less HCN • CO and CH₃NH₂ formed • Less H₂O product • Less CO₂ • More CH₄ • Less N₂	• More HCN • Neither CO nor CH₃NH₂ were seen • More H₂O • More CO₂ • Less CH₄ • More N₂

Platinum is known to be a better catalyst for H₂O formation and also for the conversion of NH₃ to N₂. The platinum anode current collector increased activity for the decomposition and reforming of methanol [23, 24]. The water- gas shift reaction was also more effective in the presence of platinum converting carbon monoxide to carbon dioxide. It is evident that the yield of HCN in the electrochemical reactor is higher than in the micro flow reactor at a given temperature (Table 6.16), which suggests that the platinum had contributed to the HCN yield. The surface area of the

FSO-Ni/CGO anode composite was found to be $2.4 \times 10^3 \text{ cm}^2$ and the surface area of platinum mesh was 2.1 cm^2 . Therefore platinum is much more active for HCN formation and other oxidation reactions than anode composite by up to 1000 times.

6.2.7 Current-Voltage measurements during HCN synthesis

The cell comprised an FSO-Ni/CGO anode, a CGO-10 electrolyte and a LSCF-CGO cathode as described previously. The anode compartment was first purged with helium for 0.5h to check for any leakage in the cell. The absence of any peaks for nitrogen and oxygen in the chromatograph assures that the system was leak tight. Ammonia was adjusted first for a few minutes, followed by the other reactants at 500°C for 0.5h to reach a steady state, while the open circuit voltage of the cell was monitored. After experiments were completed at one temperature, the operating temperature was increased at a slow rate of 60°C/h and the cell was then left under steady state temperature conditions for at least 0.5h before taking measurements. A set of experiments (different temperatures and currents) was completed in one day and afterwards, the cell was maintained overnight under wet ammonia at 550°C and the experiments were repeated the next day. All measurements were repeated at least twice to ensure reproducibility.

The current - voltage and power density values obtained for the cell,



at constant feed composition for HCN synthesis in the temperature range of $500\text{-}650^\circ\text{C}$ are summarised in Tables 6.9 -6.12.

In spite of the thick electrolyte pellet cell geometry (thickness - $696\mu\text{m}$), dilute reactants at the anode and stagnant air at the cathode, the current-voltage results were quite encouraging. The theoretical reversible cell potential can be calculated by the Nernst equation and is in the region of $1.0\text{-}1.1\text{V}$ for the fuel reactants (methanol and water) used in this experiment [25]. It can be seen that the temperature increase had an adverse effect on the OCV, which were $0.920, 0.889, 0.847$ and 0.846V at $500, 550, 600$ and 650°C . The decrease in OCV may be due to the fact that the CGO electrolyte has a finite electronic conductivity in addition to

high ionic conductivity [26, 27] i.e. it is not a perfect ionic conductor. Hence, under open circuit conditions there may be some short circuiting, i.e. flux of electrons across the electrolyte from the anode to the cathode.

Table 6.9 - Fuel cell results at 500°C

500°C			
I (mA)	I (mA/cm²)	Cell Voltage (V)	P(mW cm⁻²)
0	0.0	0.92	0.0
2.5	1.6	0.86	1.4
7.5	4.9	0.71	3.5
10.0	6.5	0.62	4.0
12.5	8.1	0.52	4.3
15.0	9.7	0.41	4.0
17.5	11.4	0.27	3.1
20.0	13.0	0.10	1.3

Table 6.10 - Fuel cell results at 550°C

550°C			
I (mA)	I (mA/cm²)	Cell Voltage (V)	P(mW cm⁻²)
0	0.0	0.89	0.0
2.2	1.4	0.86	1.2
6.0	3.9	0.81	3.1
10.3	6.7	0.74	5.0
13.7	8.9	0.68	6.1
15.4	10.0	0.65	6.5
17.4	11.3	0.61	6.9
19.4	12.6	0.56	7.1
20.6	13.4	0.53	7.0

Table 6.11 - Fuel cell results at 600°C

600°C			
I (mA)	I (mA/cm ²)	Cell Voltage (V)	P(mW cm ⁻²)
0	0.0	0.85	0.0
2.2	1.4	0.83	1.2
6.0	3.9	0.78	3.1
10.3	6.7	0.74	4.9
13.7	8.9	0.70	6.2
15.7	10.2	0.67	6.9
17.4	11.3	0.65	7.4
19.4	12.6	0.62	7.8
22.0	13.0	0.62	8.0
20.8	13.5	0.60	8.1
27.0	17.5	0.51	9.0
40.1	26.0	0.11	2.8

Table 6.12 - Fuel cell results at 650°C

650°C			
I (mA)	I (mA/cm ²)	Cell Voltage (V)	P(mW cm ⁻²)
0	0.0	0.85	0.0
2.2	1.4	0.83	1.2
6.0	3.9	0.80	3.1
7.5	4.9	0.79	3.9
10.2	6.6	0.77	5.1
12.5	8.1	0.75	6.1
13.7	8.9	0.74	6.6
15.4	10.0	0.73	7.3
17.4	11.3	0.71	8.0
19.4	12.6	0.69	8.7
20.0	13.0	0.68	8.9
27.4	17.8	0.61	10.8
35.2	22.9	0.53	12.1
40.3	26.2	0.46	12.0
50.1	32.5	0.34	11.0
52.5	34.1	0.30	10.3
60.1	39.0	0.19	7.6
63.8	41.4	0.13	5.3

The typical current- voltage and power density plots at constant feed composition for HCN synthesis in the temperature range of 500- 650°C are given in Figures 6.12 and 6.13, respectively.

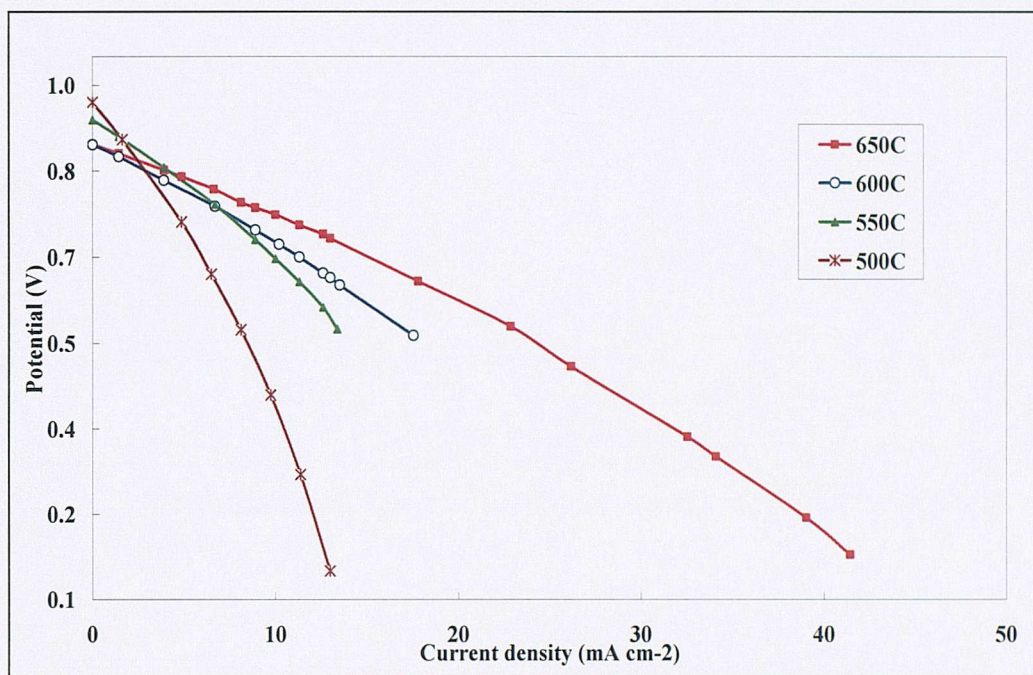


Figure 6.12 - I-V curves of fuel cell HCN synthesis

6.2.8 Power density

High power densities can be achieved with thin-film electrolytes at lower operating temperatures [28]. Nevertheless, a reasonable power density was seen in the temperature range of 500- 650°C with the CGO-10 electrolyte, considering its rather large thickness (696µm thick).

The maximum cell power outputs delivered at the test temperatures are shown in Tables 6.9 - 6.12. A power density of 4mW cm⁻² was obtained at 500°C compared to 12mWcm⁻² at 650°C. Sahibzada *et al.* [25] reported power densities of approximately 10mWcm⁻² at 550°C and 120mWcm⁻² at 650°C using CH₃OH/H₂O mixtures in pellet cells with CGO electrolyte.

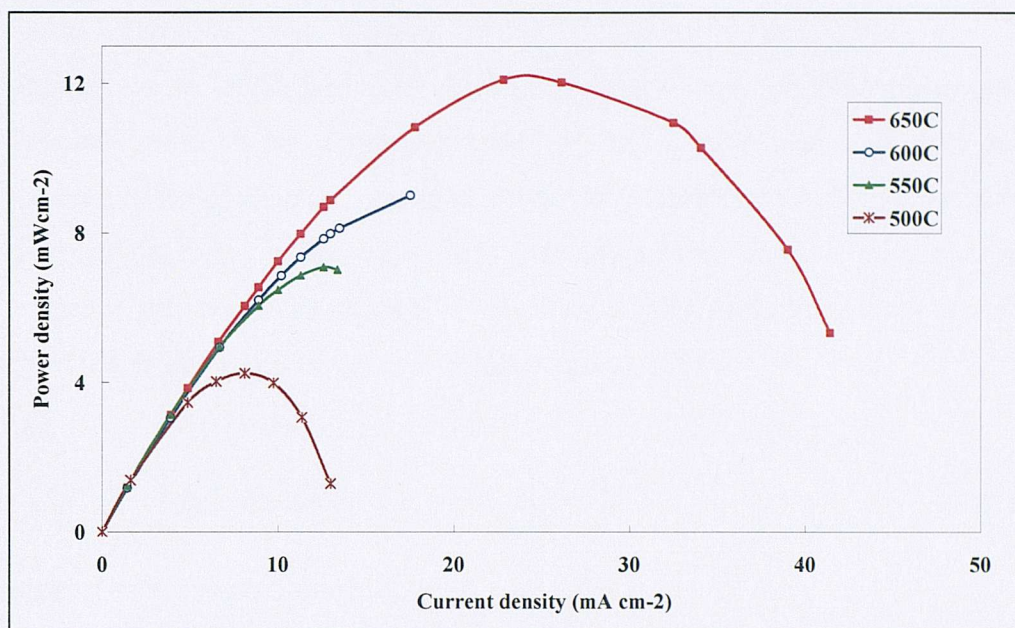


Figure 6.13 - Power density curves of fuel cell HCN synthesis

Table 6.13 - Maximum power densities in the HCN synthesis

Temp (°C)	Max power density (mW cm ⁻²)
500	4.3
550	7.1
600	9.0
650	12.1

6.2.9 Area-Specific Resistance (ASR)

The fuel cell performance can be described by two parameters, namely area specific resistance (ASR) and its overall activation energy, E_a . The area specific resistance of the cell is defined as:

$$\text{ASR} = \text{Emf} - V / I \quad \text{- (eqn 6.9)}$$

where, Emf is the electromotive force with the inlet fuel and air, and V is the cell voltage at the current density, I . By determining the ASR at different temperatures, apparent activation energy, E_a , may be derived [29]. The area specific resistance

(ASR) of the cell at various temperatures was calculated using the slopes of the I-V curves. The ASR was $61\Omega\text{cm}^2$ at 500°C compared to $17\Omega\text{cm}^2$ at 650°C as summarised in Table 6.14. The ASR gives an indication of the overall resistance associated with all the transport/reaction processes occurring in the fuel cell. The greater resistance (steeper slope) at lower temperatures was due to the decreased ionic conductivity in the electrolyte and the slower kinetics of electrode [30]. Apparent cell resistivity can be obtained from ASR and the inverse of resistivity gives the conductivity of the cell which is shown below.

$$\text{Apparent resistivity, } \rho \text{ } (\Omega \text{ cm}) = \frac{ASR(\Omega\text{cm}^2)}{L(\text{cm})} \quad - \text{ (eqn 6.10)}$$

where L is the electrolyte thickness.

The apparent cell conductivity is given by,

$$\text{Apparent conductivity, } \sigma \text{ (S/cm)} = \frac{1}{\rho(\Omega\text{cm})} \quad - \text{ (eqn 6.11)}$$

Table 6.14 - Fuel cell performance data of HCN synthesis

Temp ($^\circ\text{C}$)	OCV (V)	ASR (Ωcm^2)	Apparent resistivity ρ ($\Omega \text{ cm}$)	Apparent conductivity σ (S/cm)
500	0.92	61	842	0.0012
550	0.889	35	487	0.0021
600	0.847	26	357	0.0028
650	0.846	17	236	0.0042

Table 6.15 - Typical data of expected ASR of the CGO-10 electrolyte

Temp ($^\circ\text{C}$)	Resistivity ρ ($\Omega \text{ cm}$)	Conductivity σ (S/cm)	ASR (Ωcm^2)
500	2.63E+02	3.8E-03	18.3
700	2.78E+01	3.6E-02	1.9

From the known conductivity of CGO-10 electrolyte [29, 31] and its thickness (0.0696cm), the expected contribution of the electrolyte to the ASR was calculated which is listed in Table 6.15. The ASR of the electrolyte in this experiment was found to be much less than the measured cell ASR, confirming that the ASR mainly originated due to the electrodes.

6.2.10 Activation Energy (E_a)

The apparent activation energy of the electrochemical cell corresponding to an assumed ionic conduction and the conduction mechanism can be calculated by plotting the data in the form of an Arrhenius plot (Figure 6.14). The required parameters may then be found from the linearised Arrhenius equation below. The temperature, pre-exponential factor, apparent activation energy and the Boltzmann constant are denoted by T , A , E_a , and k_b , respectively.

$$\ln \sigma T = \ln A - \frac{E_a}{k_b T} \quad - \text{(eqn 6.12)}$$

The value of Boltzmann's constant, $k_b = 1.38 \times 10^{-23}$ J/K. By plotting $\ln \sigma T$ vs. $1/T$, slope = E_a/k_b , from which the activation energy was calculated.

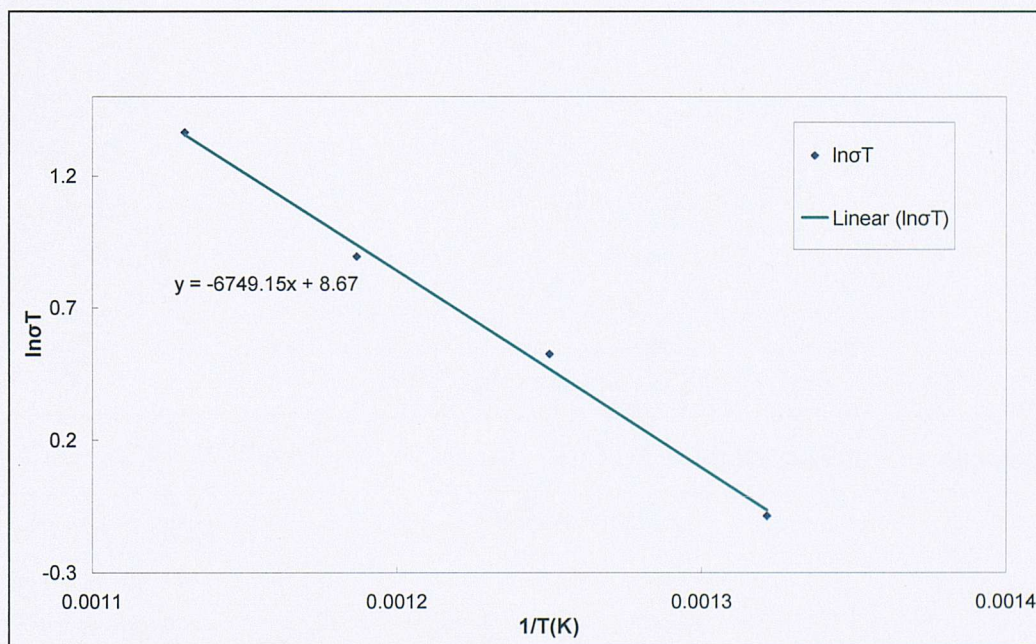


Figure 6.14 - Arrhenius plot of the fuel cell conductivity

The calculated activation energy of the cell from ASR values was found to be 56 kJ/mol or 0.6eV. This is similar to the activation energy for oxygen diffusion in CGO-10 (70 kJ/mol [31]) indicating that the SOFC performance was probably limited by oxygen ion transport in one of the electrodes.

6.2.11 Ageing of Cell

After completing a set of experiments (different temperatures and currents) in one day, the cell was maintained overnight under wet ammonia at 550°C and the experiments were repeated the next day. The power output was stable initially for several hours in the temperature range 500- 650°C but later the cell performance slowly decreased with time. Visual inspection of the cell after the experiment showed that the anode itself remained free of obvious carbon deposition although the OCV and power densities deteriorated drastically over a period of 120h as seen in the I-V (Figure 6.15) and power density (Figure 6.16) plots.

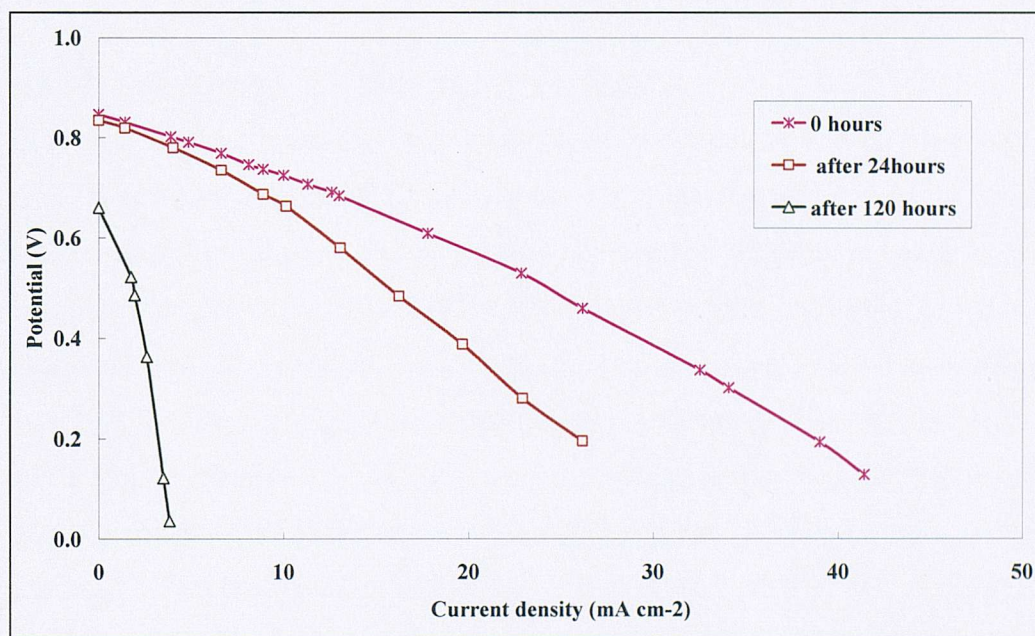


Figure 6.15 - I-V curves at 650°C of the fuel cell after increasing exposure time to the reactants

This degradation is probably caused by the reduction of the anode electrocatalyst described earlier in the micro reactor experiments. This might be avoided with a faster supply of oxygen through the SOFC electrolyte.

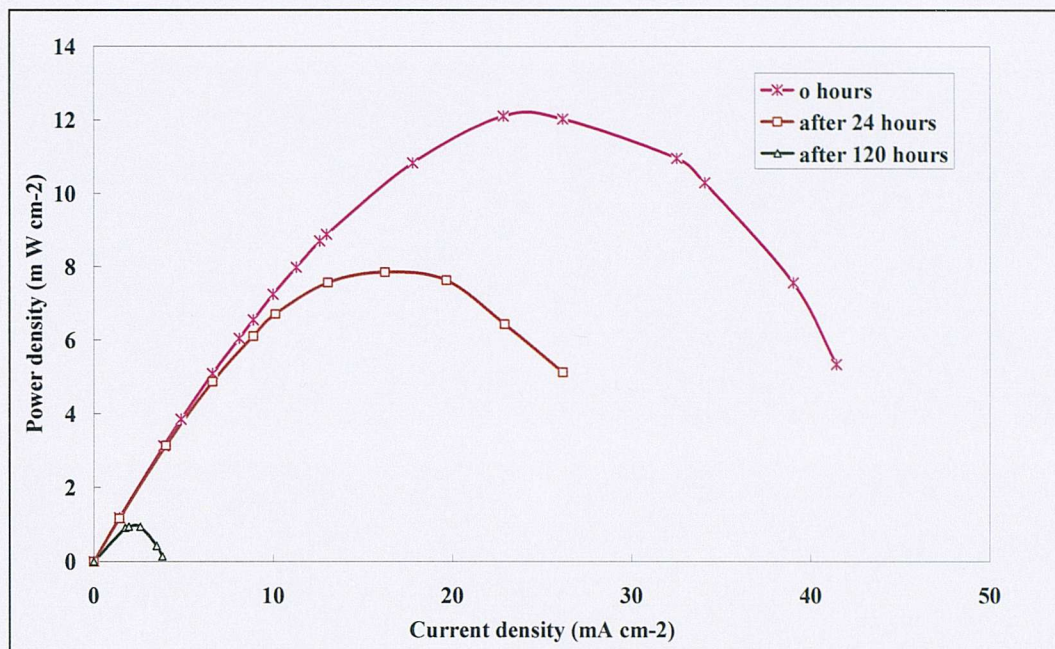


Figure 6.16 - Power density curves at 650°C of the fuel cell after increasing exposure time to the reactants

6.2.12 Post-mortem cell SEM image analysis

Scanning electron micrographs prepared with the backscattered electron signal can give direct information on compositional heterogeneity but without any specific information about the elements present. In the method of X-ray mapping or element mapping, the detection of an X-ray photon registers as a dot at the position of the scanned beam. The emitted X-rays are analysed according to the X-ray energy and matched for the corresponding element, thus presenting visual information about elemental distributions. SEM/EDX analyses were performed on the tested cell after the experiment. Care was taken to try and recover the whole cell, but unfortunately the anode layer fractured in several places and peeled off from the electrolyte with the platinum wire. Hence, only the cross-sectional image of the electrolyte/cathode interface could be obtained as shown in Figure 6.17. The sample was mounted in epoxy resin; vacuum impregnated and allowed to harden at room temperature for approximately 12h. The hardened resin was ground using SiC paper and polished using diamond paste down to 1 μm finish. The polished specimen was coated with approximately 50nm of gold using a sputter coater. The examination showed no obvious evidence of damage to the cathode/ electrolyte interface.

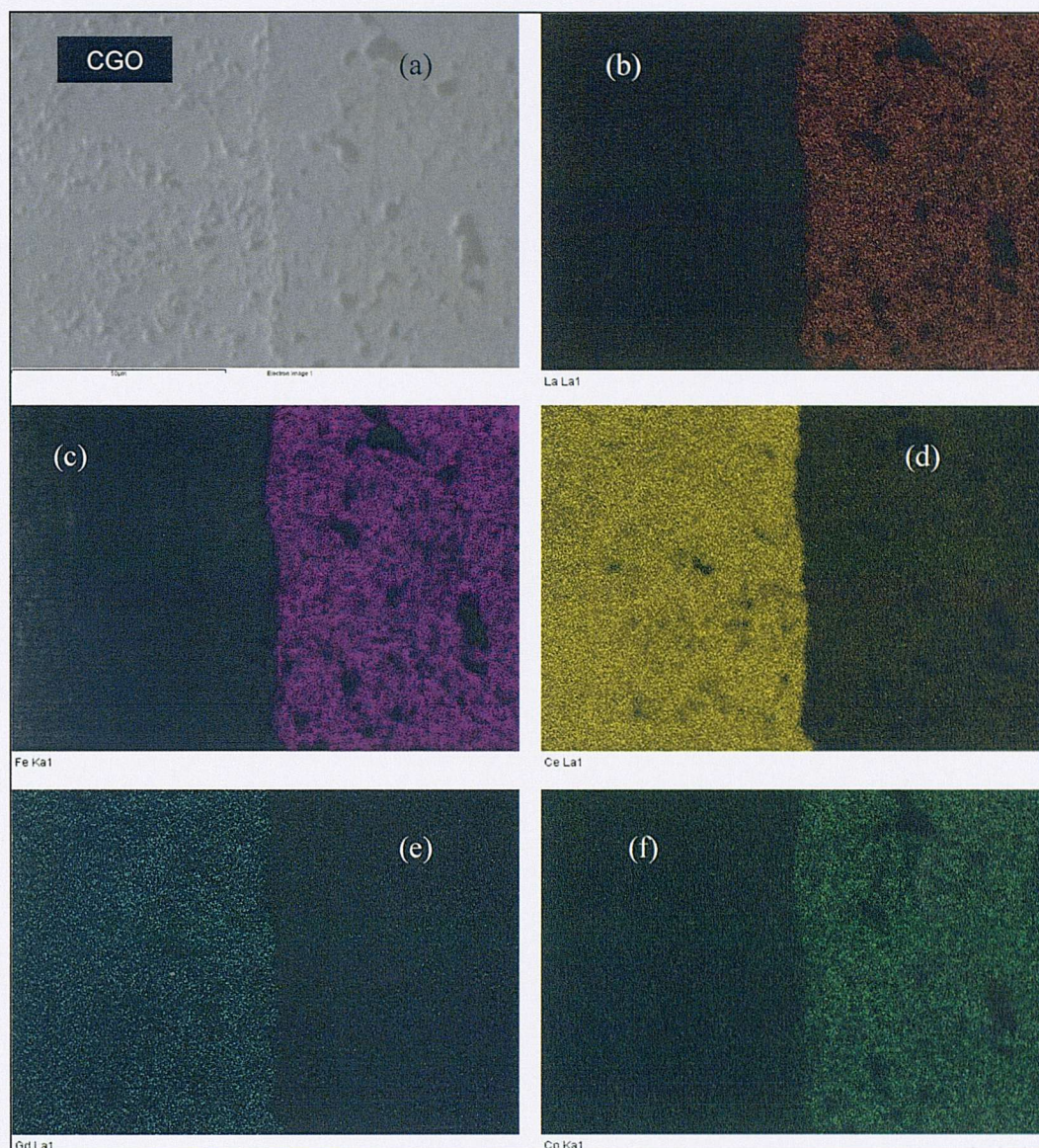


Figure 6.17 - Post-mortem EDX element mapping of the electrolyte/cathode interface secondary electron image (b)-(f) element maps of La $L\alpha 1$, Fe $K\alpha 1$, Ce $L\alpha 1$, Gd $L\alpha 1$ and Co $K\alpha 1$, respectively

A good interface was retained after the fuel cell test, indicating good compatibility of the electrolyte and cathode as expected. EDX mapping of the elements indicates that La, Sr, Co, and Fe were homogeneously distributed in the cathode. No significant diffusion or local reaction was observed at the CGO- LSCF interface after the fuel cell test.

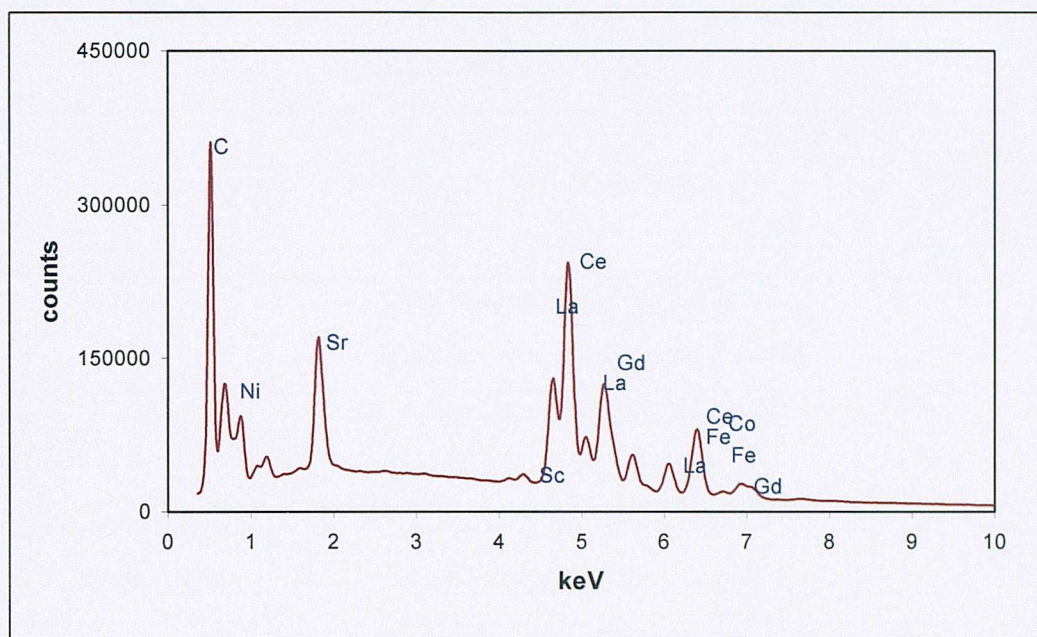


Figure 6.18 - EDX spectrum of the element mapping of the CGO/LSCF-CGO electrolyte/ cathode interface

Figure 6.18 shows the EDX spectrum of the mapping in the range of 1-10 keV. The EDX spectrum, along with the compositional elements, shows the presence of small amounts of scandium. This is expected to be an impurity present in the electrolyte powder.

6.3 Conclusions

Preparation of 70-30 wt% LSCF-CGO cathode composite and its deposition procedure were described and its physical properties were characterised by XRD, nitrogen adsorption and SEM techniques. The fabrication of the complete fuel cell comprising FSO/Ni-CGO anode, CGO-10 electrolyte LSCF-CGO cathode and Pt current collector was outlined in this chapter. Hydrogen cyanide was produced with a maximum yield of 40% in the SOFC reactor with simultaneous generation of electrical energy. The yield of HCN throughout all the experiments is given in the descending order for comparison (Table 6.16).

Table 6.16 - List of the main experiments for HCN synthesis at 500 °C with yield in this study (based on methanol input)

Catalyst	Condition	HCN yield (%)
FSO	precalcined to 1300°C/2h/ ammoxidation in micro reactor	47
FSO	as received/ ammoxidation in micro reactor	44
40-60 wt% FSO- Ni/CGO anode	anode fired at 1300°C/ 2h/ ammonolysis with steam in fuel cell	40
40-60 wt% FSO- Ni/CGO	precalcined to 1300°C/ 2h/ ammonolysis with steam at in micro reactor	38
40-60 wt% FSO- Ni/CGO	precalcined to 1300°C/ 2h/ ammonolysis in micro reactor	37
FSO	as received / ammonolysis in micro reactor	29
60-40 wt% Ni-CGO	as prepared / ammoxidation in micro reactor	-
CGO -10	as received / ammoxidation in micro reactor	-

The anode material used in this study has been shown to be suitable for cogeneration of HCN and electricity in a SOFC. Due to the thick electrolyte (696µm), the contribution of electrochemical oxygen (3.11×10^{-6} moles/min) was too low for any ammoxidation reaction to be detected in the SOFC. There is no evidence for direct electrochemical ammoxidation of methanol; rather the fuel cell consumes by-product hydrogen from side reactions. The electrical power was necessarily low because of the low temperatures and the relatively large thickness of the electrolyte.

6.4 Chapter 6 – References

- 1 D. Segal, Chemical Synthesis of Advanced Ceramic Materials: University Press Cambridge (1989)
- 2 J. Will, R. Stadler, M.K.M. Hrusehka and L.J. Gauckler, Oxygen Ion and Mixed Conductors and their Technological Applications, H.L. Tuller, J. Schoonman and I. Riess, Editors. Kluwer Academic Publishers (2000)
- 3 J. Shanefield., Organic Additives and Ceramic Processing, Kluwer Academic Publishers Boston (1995)
- 4 Kirk-Othmer, Concise Encyclopedia of Chemical Technology, New York: Wiley (1999)
- 5 N.P. Brandon, S. Skinner and B.C.H Steele, Annu. Rev. Mater. Res. 33 (2003) 183
- 6 B.C.H Steele, Solid State Ionics 86-8 (1996) 1223
- 7 S. A. Baron, Anodes for Solid Oxide Fuel Cells with Ceria Electrolytes, Ph.D. Thesis Imperial College London (2004)
- 8 B C H Steele, Solid State Ionics 129 (2000) 95
- 9 CELREF V3, LMGP suite for Windows by J. Laugier and B. Bochu
- 10 L.W. Tai, M.M. Nasarallah, H.U. Anderson, D.M. Sparlin and S.R. Sehlin, Solid State Ionics 76 (1995) 259
- 11 L.W. Tai, M.M. Nasarallah, H.U. Anderson, D.M. Sparlin and S.R. Sehlin, Solid State Ionics 76 (1995) 273
- 12 R.M. Ormerod, Chem. Soc. Rev. 32 (2003) 17
- 13 J.M. Ralph, A.C. Schoeler and M. Krumpelt, J. Mater. Sci. 36 (2001) 1161
- 14 H.M. McNair and J.M. Miller, Basic Chromatography, John Wiley New York (1998)
- 15 C. Scott, manuscript, A Thermal Conductivity Approach for Measuring Hydrogen in Engine Exhaust (2004)
- 16 D.J.L. Brett, A. Atkinson, D. Cumming, E. Ramirez-Cabrera, R. Rudkin and N.P. Brandon, Chem. Eng. Sci. 60 (2005) 5649
- 17 A.Y. Rozovskii and G.I. Lin, Topics in Catalysis 22(3-4): (2003) 137
- 18 J. R. Rostrup-Nielsen and L.J. Christiansen, J. Catal. Today 23 (1995) 126
- 19 A. Wojcik, H. Middleton, I. Damopoulos and J Van herle, J. Power Sources 118 (2003) 342

- 20 N. Dekkar and B. Rietveld, European Symposium (2004) 1524
- 21 R.W. McCabe, J. Catal. 79 (1983) 445
- 22 A.S. Chellappa, C.M. Fischer and W.J. Thomson, Appl. Catal. A: Gen 227 (2002) 231
- 23 L.M. Gomez-Sinero, R.T. Baker, I.S. Metcalfe, M. Sahibzada, P. Concepcion and J.M. Lopez- Nieto, Appl. Cat A: Gen 294 (2005) 177
- 24 S. McIntosh and R.J. Gorte, Chem. Rev. 104 (2004) 4845
- 25 M. Sahibzada, B.C.H. Steele, K. Hellgardt, D. Bart, A. Effendi, D. Mantzavinos and I. S. Metcalfe, Chem. Eng. Sci. 55 (2000) 3077
- 26 N.M. Gamanovivh and G.I. Novikov, Russ. J. Appl. Chem. 70 (1997) 1136
- 27 N.M. Gamanovivh, V.A. Gorbunova and G.I. Novikov, Russ. J. Appl. Chem. 74 (2001) 746
- 28 S. Park, J.M. Vohs and R.J. Gorte, Nature 404 (2000) 265
- 29 S.C. Singhal and K. Kendall, High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications, Elsevier Ltd. (2003)
- 30 M. Sahibzada, B.C.H. Steele, K. Zheng, R.A. Rudkin and I.S. Metcalfe, Catal. Today 38 (1997) 459
- 31 M. Mogensen, N.M. Sammes and G.A. Tompsett, Solid State Ionics 129 (2000) 63

Chapter 7

Summary, Conclusions and Future Work

7.1 Summary and Conclusions

The feasibility of cogeneration of HCN and electricity from methanol and ammonia in a SOFC was studied together with the catalytic properties of the anode constituents towards HCN synthesis.

An introduction to the hydrogen cyanide (HCN) synthesis by various methods was given in Chapter 2 and some of their unique features were discussed. The fundamentals of methanol ammoxidation were considered including the performance of typical catalysts. Iron antimony oxide (FSO) with a weight composition of 76% Fe_2O_3 , 15% FeSbO_4 , 8% Sb_2O_3 and 1% Cr_2O_3 was selected for incorporation into a SOFC anode in this study due to its good catalytic activity and stability. Since FSO is not an electrocatalyst, it was combined with a conventional Ni-CGO anode for use in a SOFC with CGO electrolyte and LSCF-CGO cathode to work in the temperature range 500 – 650°C. Initial experiments with a proton-conducting electrolyte cell showed poor adherence of the anode catalyst to Y: BaCeO_3 electrolyte and therefore proton-conducting SOFCs were not explored further. In the later section of Chapter 2, each SOFC component was discussed in detail. A conventional 60-40 wt% Ni-CGO anode cermet was combined with FSO as a composite in ratios 40:60, 50:50 and 60:40. The 40-60 wt % FSO-Ni/CGO composite was found to exhibit electrical conductivity and therefore was selected for the anode of the electrochemical reactor.

The physical structure of the electrocatalyst and its constituent materials were studied using XRD, nitrogen gas adsorption and SEM/EDX. As the anode cermet has to undergo firing to high temperature (1300°C) during the electrode fabrication on the CGO-10 electrolyte, the FSO was calcined at that temperature to check the stability of the FeSbO_4 phase (squawcreekite) which is the catalyst for the HCN product formation. Firing increased the FeSbO_4 content and additional pseudorutile structure $\text{Fe}_2(\text{TiO}_3)_3$

appeared. Nevertheless, this catalyst showed the highest HCN yield (55%) in the methanol ammoxidation reaction at 450°C in the micro reactor. The XRD pattern of 40-60 wt% FSO-Ni/CGO composite confirmed the presence of all the phases Fe_2O_3 , FeSbO_4 , NiO and CGO required for the electrocatalysis of HCN in the SOFC. A high surface area and fine porosity (mesoporous) were seen on all the powder catalysts (FSO, FSO-Ni/CGO and LSCF/CGO) by nitrogen gas adsorption. The microstructure of the SOFC electrodes was examined using scanning electron microscopy (SEM) equipped with EDX for compositional analysis. The FSO-Ni/CGO anode composite after firing on CGO-10 electrolyte at 1300°C and then reducing at 700°C for 0.5h in 10% H_2/N_2 resulted in a well interconnected porous anode with adequate mechanical strength and electrical conductivity. A suitable cathode was produced using 70-30wt% LSCF/CGO composite after firing to 850°C for 2h.

Chapter 3 describes the experimental set up for the synthesis of HCN and product analysis by gas chromatography (GC). The experimental procedure involved development specific analytical methods that allowed the accurate quantitative determination of gaseous product species. HCN synthesis was studied initially in a fixed bed catalytic reactor system, comprising a liquid methanol saturator and mass flow controllers for supplying helium, ammonia and oxygen to silica glass tubular reactor containing the catalyst. HCN synthesis was carried out by ammoxidation and ammonolysis in the micro reactor with as received FSO, FSO calcined to 1300°C, 60-40wt% Ni-CGO, CGO-10 and 40-60 wt% FSO- Ni/CGO composite calcined to 1300°C. The yield and selectivity for HCN were determined at temperature in the range of 450 – 650°C. In addition to unreacted CH_3OH and NH_3 , the components identified in the effluent stream were the main product HCN and the by-products were CO_2 , N_2 , CH_4 , CH_3NH_2 , H_2O and CO. There was no HCN produced with Ni-CGO and CGO-10 catalysts. In presence of FSO-Ni/CGO composite, water vapour: methanol stoichiometric ratio greater than 2 was needed since nickel is well known to be susceptible to carbon poisoning. The maximum yield (42%) and selectivity (47 %) for HCN using the FSO-Ni/CGO anode as catalyst were obtained at 450°C.

Using this anode in the SOFC gave a reasonably good HCN yield (40%) at 500 °C and an electrical power density of 12.1 mW/cm⁻² at 650 °C could be achieved. The presence of water vapour at the anode of the fuel cell though found to prevent carbon deposition, suppressed the electrical performance to a certain extent. However, there was evidence in the results of this study that supplying water vapour does not hinder HCN formation and its yield. The HCN concentration produced in the cell was high at 500°C and started to decrease with increasing temperature whereas the concentrations of CO₂, H₂O and N₂ increased.

HCN production in the SOFC was studied as a function of current density drawn from the cell. However, the current density was found to be too low to have a detectable effect on the off-gas composition. Temperature increase had an adverse effect on the OCV, which decreased from 0.92V at 500°C to 0.85V at 650°C. The current densities were low, but this was to be expected because of the low operating temperatures and the relatively thick electrolyte (0.69 mm). Nevertheless, it was found that in the fuel cell mode most of the measured ASR originates from the electrodes. The oxygen ion permeation flux was much smaller than the input flux of other reagents which accounts for the negligible effect the fuel cell current had on the anode off-gas composition. The power output of the cell was stable initially for a few hours, but afterwards the cell performance slowly degraded with time.

It may be concluded from the present study that HCN synthesis can be operated stably in the temperatures of approximately 500°C using methanol and ammonia in SOFC. To our knowledge, this is the first attempt to synthesis HCN in a fuel cell using methanol. Also it can be stated that the FSO-Ni/CGO anode cermet used in this study is effective for HCN formation and is also an effective good electrocatalyst for hydrogen oxidation. However, there is no evidence for direct electrochemical ammoxidation of methanol; rather the fuel cell consumes by-product hydrogen from side reactions.

7.2 Suggestions for Future Work

Recommendations for the future work are outlined below:

- Analysis of hydrogen using Mass Spectroscopy - in order to provide a more comprehensive mass balance analysis, the output of hydrogen is required.
- Fabrication of thinner CGO-10 electrolyte to increase the oxygen supply during HCN synthesis in SOFC - the oxygen flow through the electrolyte of the SOFC was too low to have a measurable effect on the reaction and probably resulted in deactivation of the anode.
- Proton conductors in principle allow better product separation since there should be formation of water on the cathode side and no oxidation to CO and CO₂ on the anode side. However this will require further work to fabricate suitable electrodes adherent to proton conductors such as BCY.
- SOFC studies with the FSO-Ni/CGO anode materials using hydrogen - to characterise the standard performance characteristics on hydrogen
- Performance of AC impedance on the anode materials to identify electrode resistances and mechanisms.
- Since the catalytic activity for HCN production was best at 450°C, experiments should be conducted to reduce the SOFC operating temperature.