

HIGH TEMPERATURE MATERIALS CHEMISTRY OF DOPED CERIUM OXIDE CERAMICS

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ABSTRACT

Solid oxide fuel cells are promising to be an efficient source of energy for the future. Development of an anode that can be used for direct oxidation of methane will increase the efficiency and reduce the expense of cells operating on natural gas. Cerium IV Oxide was believed to be a good candidate material.

In this project Cerium IV Oxide has been doped with both lower (In^{3+} , Y^{3+}) and higher (Nb^{5+}) valent cations in order to modify its properties for use as an anode; to eliminate expansion problems during reduction and to increase electrical conductivity. The properties of the material have been examined by electrical conductivity measurements, thermogravimetry, electron microscopy, x-ray diffraction and catalytic activity measurements. Comparison has been made between materials containing different levels of dopant, and materials have been examined both on their own, and sintered onto an yttria stabilised zirconia or ceria gadolinia electrolyte.

It was found that doping reduced the maximum conductivity of the material within oxygen pressure-temperature space when compared to the singly doped material. The solubility of dopant fell within the predicted range for the doubly doped material. The results are considered from a theoretical standpoint, and with respect to the defect structure of the material, and the implications for lattice expansion. Double doping reduced the lattice parameter of the material, whereas in the singly doped material this had been reported to increase. It did not prove possible to limit the lattice expansion at low oxygen pressures. The material proved to be a good catalyst for the complete oxidation of methane above 450°C, but not for dimerisation reactions.

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1. INTRODUCTION

This thesis examines doped cerium oxide for use in a solid oxide fuel cell anode. The literature survey is divided into two chapters, the first dealing with fuel cells, the materials used, and the use of cerium oxides in these cells to date. The second chapter of the literature survey deals with the known physical and chemical properties, including transport data and defect chemistry, of cerium oxides.

Fuel cells are a promising means of producing energy in the future on both the small and large scale. Research is being carried out worldwide, particularly in Japan and the US. This project was carried out primarily in the Department of Materials at Imperial College, and also at the Research Laboratory for Nuclear Reactors at the Tokyo Institute of Technology. The help of individuals both in London and Tokyo is acknowledged at the relevant points throughout the thesis, and in particular in chapter 4.

Solid Oxide Fuel Cells now seem to be nearing commercialisation, but there is still scope for improvement in both the materials and the design. Current cells are expensive because they require a large proportion of gas reforming to be carried out outside the cell (15); the present nickel-zirconia anode operates poorly on dry methane. Development of a cell in which all reforming can be carried out in situ or of an anode that can operate using dry methane, eliminating the need for reforming altogether, would greatly reduce costs. It has been suggested that cerium oxide would be suitable for such an anode (4). If ceria is to be used as an anode, there are a number of problems that need to be overcome. Ceria undergoes a severe lattice expansion on reduction. Under anodic conditions the conductivity (1S/cm) is lower than would be ideal. However ceria is an excellent catalyst.

All experimental techniques and apparatus are described in chapter 4; weight loss with temperature and oxygen pressure, conductivity, oxygen diffusion, coefficient of thermal expansion and catalytic activity. In addition, early experimental data influencing the direction of research are discussed in chapter 4. All other results are presented and discussed in chapter 5.

2. FUEL CELLS AND CERIUM OXIDE

2.1 INTRODUCTION TO FUEL CELLS

2.1.1 BACKGROUND

As fossil fuel resources are being exhausted, alternative sources of energy, and more efficient use of fossil fuels are being examined. A fuel cell provides a means of producing dc electricity by electrochemical reaction, as does a battery; converting the enthalpy of the fuel and oxidant directly into electrical energy and heat. Unlike batteries, the design of a fuel cell is such that the electrodes of a fuel cell are not consumed in the reaction taking place, but act as catalysts for the reaction. Additionally, the reactants are stored outside the cell. Ideally, the cell will continue to operate as long as reactants are supplied and products removed

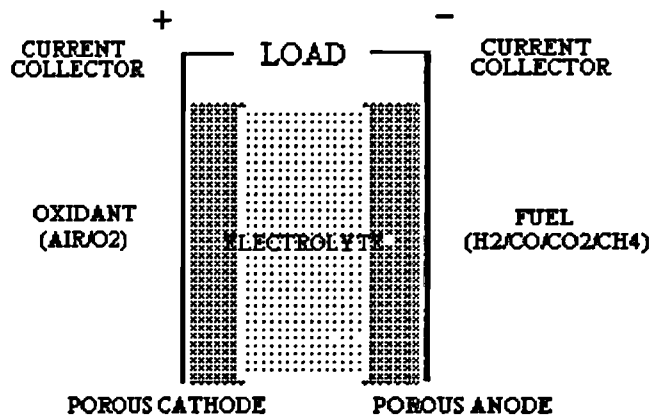


FIG. 2.1.1 SCHEMATIC DIAGRAM OF A FUEL CELL (1)

The electrode reactions are generally described as taking place at the 3 phase boundary, where the electrode, chemical reactant, and electrolyte meet. This is believed by some (2) to be rather an oversimplification (section 2.3 3).

For most fuel cells the oxidant is oxygen supplied as air. Cells are expected to operate with this and readily available, cheap and easy to handle, fossil fuels such as natural gas or other hydrocarbons. These can be converted to impure hydrogen by steam reforming. The steam reforming equipment is the most expensive part of the fuel cell (3). Recently however, some researchers (4) have been looking at the possibility of using nonreformed methane, which would greatly reduce the cost of the cell. This will be covered in more detail in section 2.4. This thesis examines a possible anode material for the purpose.

2.1.2 COMPARISON WITH CONVENTIONAL POWER STATIONS

Fuel cells offer a more efficient, and less environmentally polluting means of providing electrical energy than that offered by conventional fossil fuel based power stations. In particular, the levels of SO_x and NO_x gases released into the environment are very much lower for fuel cells, than for the conventional power stations. This is shown in the table below, taken from Appleby and Foulkes (3).

TABLE 2 1 2 POWER SYSTEM EXHAUST EMISSION COMPARISON (3)			
TYPE OF POWER STATION			
CONTAMINANT	GAS-FIRED	OIL-FIRED	FCG-1 FUEL CELL
SO _x	-	3.35	0.000046
NO _x	0.89	1.25	0.0031
PARTICULATES	0.45	0.42	0.0000046

UNITS kg/1000kWh

The basic principles behind the operation of a fuel cell (3,5-7) will be described here. The enthalpy change associated with the oxidation of the fuel can be written:

$$\Delta H = \Delta G + T \Delta S \quad [1]$$

where the electrical energy is ΔG and the heat $T \Delta S$. The maximum theoretical efficiency of the cell is given by:

$$\text{Eff}_{\text{max}} = \Delta G / \Delta H = 1 - T \Delta S / \Delta H \quad [2]$$

Assuming that these parameters are independent of temperature, it can be seen that the theoretical efficiency of the cell decreases as the temperature increases. The theoretical open circuit potential of the cell, E_0 , is related to ΔG as shown.

$$E_0 = - \Delta G / nF \quad [3]$$

For a reversible cell reaction given by:



there is an associated chemical potential for each species represented by μ , and the free energy is given by:

$$\Delta G = c\mu_C + d\mu_D - (a\mu_A + b\mu_B) \quad [5]$$

In each case:

$$\mu_i = \mu_i^0 + RT \ln a_i \quad [6]$$

where μ_i^0 represents the chemical potential at an activity under standard conditions with a_i of unity, or in the case of gases, a pressure of 1 atmosphere. Thus:

$$\Delta G = c\mu_C^0 + d\mu_D^0 - (a\mu_A^0 + b\mu_B^0) + RT \ln (a_C a_D / a_A a_B) [7]$$

and potential can therefore be represented by:

$$E_0 = E_0^0 + (RT/nF) \ln (a_C a_D / a_A a_B) \quad [8]$$

where E_0^0 is the potential under standard conditions, as defined by an activity of unity above. This is known as the Nernst equation.

Whilst operating at lower temperatures increases the fraction of chemical energy converted directly to electrical energy, increasing E_0 , the operating potential of the cell, E , can fall below E_0 as a result of ohmic and electrode polarisation losses.

$$E = E_0 - IR_i - V_p \quad [9]$$

I is the current delivered by the cell, and R_i the internal resistance. V_p represents the electrode polarisation losses. Often a higher operating temperature is required to reduce these losses. Higher operating temperatures also offer the advantage that fuels other than hydrogen can be used.

The efficiency of conventional power stations is limited by the Carnot cycle, where the maximum efficiency is given by:

$$\text{Eff}_{\max} = (T_1 - T_2) / T_1 \quad [10]$$

This in itself is not a problem (3). Burning fuel undergoes a spontaneous reaction, and all the energy is released as heat. Were it possible to control the combustion so that the reaction was completely reversible, taking T_1 as the combustion temperature of the fuel and T_2 as the sink temperature, the theoretical efficiency of a perfect Carnot heat engine would be the same as that for a perfect isothermal fuel cell operating at temperature T_2 . In practice however, T_1 is required to be very much lower than the

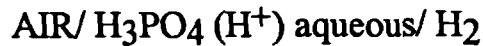
combustion temperature of the fuel, because of materials limitations. While a fuel cell is by no means free from materials problems, these are not nearly so severe when comparing like efficiencies.

2.1.3 HISTORY

The idea of using a fuel cell as a means of energy production has been around for at least 150 years. The first reported attempt to produce electricity from a fuel in this way is believed to be that of Sir Humphrey Davy in 1802, using a cell with a carbon anode and an aqueous nitric acid cathode reactant. However Sir William Grove is generally regarded as the creator. He developed a hydrogen oxygen fuel cell using a sulphuric acid electrolyte, and demonstrated this at the London Institute 150 years ago. 50 years later, Mond and Langer developed a fuel cell operating on industrial gas extracted from coal, and air. In order to try and prevent degradation of the electrodes they soaked asbestos or plaster of Paris with H_2SO_4 . However, the platinum that they were using was rapidly poisoned by CO in the gas and this led to severe polarisation of the cell. Dr.W.W.Jaques is believed to be the first person to perceive that a fuel cell could provide energy for domestic use; he published data on a cell he had developed for this purpose in 1896. The first major project leading to a successful device was that of Francis Bacon in 1932, switching from an acid to an alkaline electrolyte, and replacing platinum electrodes with nickel, later developing porous electrodes. By 1959 he and his co-workers were demonstrating a 5kW system. Following this, the development of fuel cells for use in space travel was rapid; fuel cells operating on pure oxygen and pure hydrogen also having the advantage that the product, water, can be used during a space mission. Such cells were used in both the US Gemini and Apollo missions. Since then research has been carried out on a number of different categories of cell.

Fuel Cells can be divided into two general categories of low and high temperature, and within this, are classified by electrolyte type. Low temperature systems require a hydrogen fuel, whereas the high temperature cells should be capable of in-situ reforming of hydrocarbons, and therefore be more efficient. Three low temperature, and two high temperature systems (3,11) will be outlined here.

2.1.4 PHOSPHORIC ACID FUEL CELL

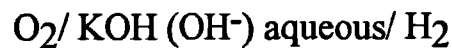


In the PAFC hydrogen is produced by external steam reforming of hydrocarbons, which involves reacting the hydrocarbon with steam at high temperature (around 750°C). The temperature is generally maintained by using the heat provided by the exhaust gases of the cell. The efficiency of the cell is around 40%.

The electrodes of the cell are fabricated from carbon black, finely divided, and held together by a PTFE binder, which is supported on a porous carbon paper substrate. The electrocatalyst is deposited as crystallites onto the carbon black. The electrodes operate satisfactorily for about 40000 hours. The separator material is a PTFE bonded SiC composite, incorporating the electrolyte.

PAFC stacks have been extensively tested in both Japan and the US and are close to commercialisation. They are available in 40kW, 200kW, and 11MW sizes, and are fabricated as planar cells.

2.1.5 ALKALINE FUEL CELL



This is the fuel cell that was used for the Apollo space craft, and the space shuttle. It is very expensive to operate as it requires pure hydrogen and oxygen. The electrode materials are also expensive; composed of finely divided platinum on carbon. In spite of this it is being considered for some transport applications. However, in this role, it is expected to be displaced by new SOFC's with a lower operating temperature.

2.1.6 SOLID POLYMER ELECTROLYTE FUEL CELL



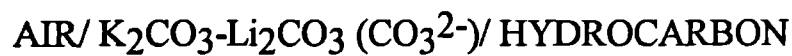
This fuel cell was originally developed for the US space program, but it was found that the AFC performed better. However a new polymer membrane has since been developed which enables higher power densities to be achieved.



It is the SO_3 group that enables the cation exchange.

This system is also expensive, requiring relatively pure gases and large amounts of noble metal in the electrodes. It is now undergoing evaluation for defence and space applications. High power SPFC systems have been found to operate successfully with air, and have shown a tolerance of CO_2 , so if hydrocarbon reformers can be incorporated the cell may yet be used in transport applications, though as for the AFC there is now the competition of the lower temperature SOFC.

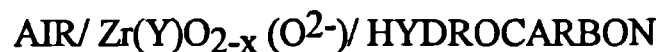
2.1.7 MOLTEN CARBONATE FUEL CELL



This is the first of the high temperature fuel cells, and has been under development for the last 20 years in both Japan and the US. There are still some material problems with this cell, namely the corrosion of the components by the electrolyte. In theory the electrolyte is immobilised in a ceramic matrix of $\gamma\text{-LiAlO}_2$, designed to prevent leakage into the electrodes. The problem arises with the NiO cathode material which dissolves in the electrolyte. Precipitation of the nickel in the more reducing atmosphere of the anode leads to short-circuiting. The anode has been found to sinter and deform under compressive load operating conditions. The bipolar plate, usually fabricated from thin alloy sheets, must also be protected from corrosion whilst maintaining good conduction paths. Alternative materials are being evaluated.

The main studies of MCFC's so far, have involved external rather than in-situ reforming of the hydrocarbon. There have been problems with traces of sulphur in the fuel used, which can deactivate the reforming catalysts at the MCFC operating temperature (650°C). Satisfactory in-situ reforming will be necessary if MCFC's are to compete with alternative methods of producing energy.

2.1.8 SOLID OXIDE FUEL CELL



This cell operates at higher temperature ($900\text{-}1000^\circ\text{C}$) than the MCFC, and therefore doesn't suffer the same problems of internal reforming of the fuel. Because the electrolyte is a solid, corrosion problems are greatly reduced, and management/containment problems are eliminated. As with MCFC's, SOFC's can

utilise CO gas as a fuel, but are also more tolerant of sulphur-containing impurities. The high operating temperature of SOFC's makes them unsuitable for some applications, but they are eminently suited to large scale power units. Having said that, SOFC's operating at a lower temperature, incorporating a CeO₂- rather than ZrO₂-based electrolyte (12) for possible transport applications are now under development. The efficiency of an SOFC can be increased by making use of the excess heat generated within the cell for on-site heat requirements, or as a heat supply for steam turbines. Solid oxide fuel cells will be discussed in more detail in section 2.2.

2.2 SOLID OXIDE FUEL CELLS

2.2.1 BACKGROUND

A solid oxide electrolyte was first used in 1900 by Nernst; a 15%Y doped ZrO_2 . The first SOFC was built by Baur and Preis in 1937, with a Mg or Y stabilised ZrO_2 (3). This operated at temperatures greater than 1000°C, but current densities of only $1\text{mA}/\text{cm}^2$. Pioneering work was carried out in the 1960's at Westinghouse Research and Development Centre, and Brown-Boveri in Germany (3). These were the first cells to achieve current densities of greater than $100\text{mA}/\text{cm}^2$. The cells used hydrogen and oxygen. The basic components of the SOFC were developed by Westinghouse. An extensive survey of solid oxide fuel cells has recently been carried out by Minh (13).

2.2.2 PRINCIPLES OF OPERATION

At the cathode, the oxygen reacts with incoming electrons from the external circuit to form oxygen ions.



The oxygen ions migrate to the anode through the electrolyte. Hydrogen reacts with the oxide ions to form water vapour, and freeing electrons to the external circuit.



This is the simplest scenario, though solid oxide fuel cells can also operate on carbon monoxide fuel or mixtures of both hydrogen and carbon monoxide.



The following reaction can also occur where there is a mixture of fuel:



More recently, work is being done on operating the cell on non reformed methane (4).

The voltage of the cell is given by the Nernst equation, for reaction nos. 11 and 12:

$$E = E_0 + \frac{RT}{2F} \ln \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{O}_2}^{1/2}} \right) \quad [15]$$

However, since the oxygen ion is the only conducting species in the electrolyte, and the oxygen pressure is so low on the anode side, the cell can be viewed as an oxygen concentration cell (3).

$$E = (RT/4F) \ln (pO_2^i / pO_2^{ii}) \quad [16]$$

where pO_2^i and pO_2^{ii} are the partial oxygen pressures at the cathode and anode respectively. This equation holds for a reversible oxygen concentration cell with an oxygen ion transport number equal to 1. It is seen that the driving force for reaction in an SOFC is the difference in oxygen partial pressure across the electrolyte.

2.2.3 LOSSES

There are a number of ways that energy can be lost within the cell, the most important of which are electrode polarisation and ohmic losses. These have the effect of reducing the cell voltage by an amount that increases with the output of the cell. There are two types of polarisation: activation and concentration.

Activation polarisation occurs when the charge transfer across the electrode/electrolyte interface is slow. Potential is lost in driving the transfer rate to that which is required by the current demand. The extent of this depends very much on the electrode material; the ion-ion interactions and double layer characteristics at the interface with the electrolyte.

Concentration polarisation is caused by mass transport limitations; the availability of the required species at the interface. A constant supply of the species is required to sustain current flow. Diffusion rate limitations can reduce the availability, creating concentration gradients which effectively reduce the activity of the electrode, causing a drop in the output voltage. The same can occur if the reaction products are allowed to accumulate at the interface, as this reduces the driving force of the reaction taking place. For these reasons, the electrodes in an SOFC are generally porous, although some interest has been taken in non porous electrodes (14, 2).

Ohmic losses are due to the internal resistances of the cell. These are to be found in (a) the electrolyte, where there is an ionic resistance; the resistance is lower, the higher the operating temperature, or the thinner the electrolyte. The electrodes (b) have both electronic and ionic resistances, and the terminal connections (c) of the cell have an electronic resistance.

Polarisation can lead to a limiting current, which is the result of a complete lack of reacting species at the reaction site. The extent of polarisation is related to the current density of the cell. The greater the current density required from the cell, the lower the power, since the voltage drops. The fuel cell becomes less efficient; generating more heat in the cell.

2.2.4 CONFIGURATION

One of the most important factors to be taken into account in the design of an SOFC unit, known as a stack, is the area to volume ratio, which should be high for efficient reaction. Westinghouse use a development of a tubular configuration that was used in many early projects. The different layers are deposited by chemical vapour deposition, onto a ceramic support tube of CaO stabilised ZrO_2 . The tubular cells are brought together as a bundle, and connected in parallel by nickel felts. This design has the advantage that the stack will continue to operate in the event of failure of a cell. The support tube is porous, to enable the flow of air to the cathode, and the nickel felt pads inhibit destructive stresses from developing in the cell. More recent developments have been seen in the elimination of the support tube (15), the cathode now supporting the cell.

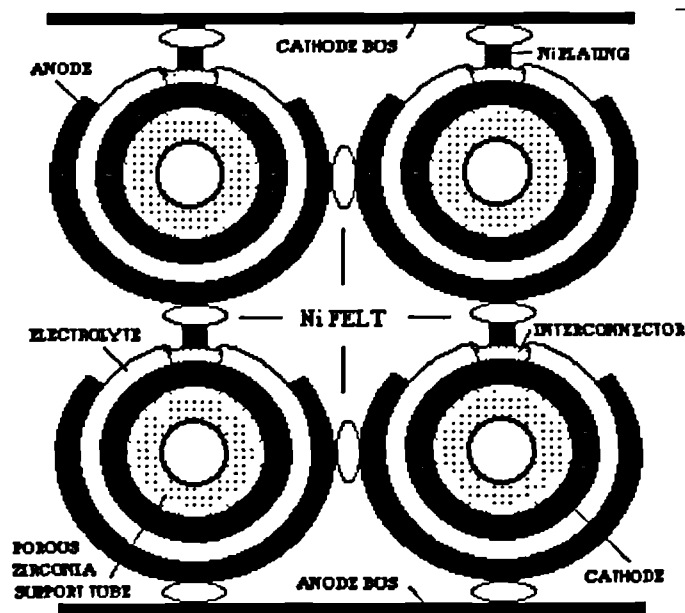


FIG.2.2.4a WESTINGHOUSE TUBULAR SOFC STACK (11)

A tubular design is also being examined in Japan, at the Electrotechnical Laboratory (3,16-17), based on thin films. Their design is more traditional in that it is the anode that is inside the tube, rather than the cathode.

simplest and most versatile. However, the present high operating temperature of the SOFC creates problems here, when it comes to the materials required to seal in the cells.

ICI have developed a new electrolyte-interconnect composite (19), made by coextruding the two materials, onto which the electrodes can later be deposited. They have made both flat sheets and tubes by this method. A single sheet can contain many cells. This method of production is expected to reduce the assembly costs of the cell.

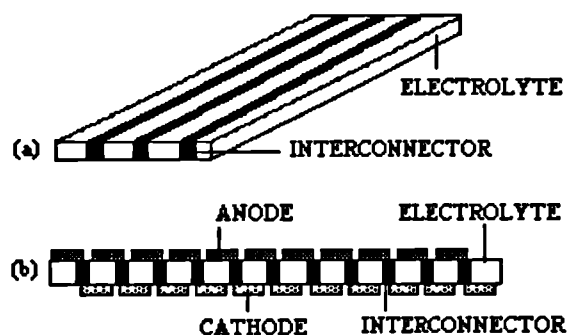


FIG.2.2.4d ICI CO-EXTRUDED ELECTROLYTE AND INTERCONNECTOR (A), (B) SHOWS A CROSS-SECTION, AFTER DEPOSITION OF ANODE AND CATHODE (19).

2.2.5 MATERIALS USED IN PRESENT SOFCS

The materials used in present SOFCs are listed in the table below:

TABLE 2 2 5. SOFC COMPONENTS (3,18)			
ELECTROLYTE	INTERCONNECTOR	CATHODE	ANODE
Zr(Y)O ₂	La(Sr,Ca)CrO ₃ LaCr(Mg)O ₃	La(Sr,Ca)MnO ₃	Ni Ni/ZrO ₂ CERMET

The maximum oxygen ion conductivity for the zirconia electrolyte has been found at 16.9% of yttria by weight (10 mol%) (3). The cathode is porous, the strontium or calcium doping of LaMnO₃ giving a p-type conductivity. The porosity is required to aid mass transfer of oxygen to the cathode electrolyte interface. The anode is most commonly a nickel-zirconia cermet. The zirconia is required to prevent the nickel from sintering. It also improves the compatibility of the thermal expansion with that of the electrolyte. The final cermet is expected to contain 20-40% of interconnected porosity. The anode will be discussed in more depth in section 2.3. The interconnector is reported as having the most stringent requirements (3); good electronic conductivity, and a material impervious to both the fuel and oxidant.

2.2.6 STATUS SO FAR

While the US is the most advanced in SOFC development, the vast majority of research is now going on in Japan. The US Westinghouse Science and Technology Centre is working with Japanese companies in testing their cells.

Westinghouse has tested 0.4-20kW tubular stacks at US department of energy, Tokyo Gas and Osaka Gas between 1984 and 1991 (15). In 1992, tests were begun on two 25kW stacks, one DC and one converting to AC at Osaka Gas, cooperating with Kansai Electric Power Company, and at Tokyo Gas. At the last report, these had been tested successfully for more than 1400 hours (20), though previous single and multicell tests have been carried out for over 32000 hours. There are plans to test a 100kW cell by 1994. At the moment cells are such that a high proportion of gas reforming must be carried out outside the cell, rather than in situ, making them expensive. At Argonne National Laboratory the monolithic fuel cell has reached the bench scale stage. Research on intermediate temperature cells is now underway in the US.

In Japan much of the research is government funded under the "Moonlight Project"; energy resources are a very serious issue in Japan. Research covers every area from basic materials technology, characterisation, processing and construction. They are also examining a wide range of configurations. The following is a summary of the work being carried out by companies and laboratories (16-17).

Tokyo Electric Power Company (TEPCO), the Electric Power Development Corporation (EPDCO), and Mitsubishi Heavy Industry (MHI) are developing a tubular SOFC and are aiming at a 10kW generator by 1994. TEPCO and MHI are also developing a planar SOFC. MHI is collaborating with Chubu Electric Power Company in the development of sealing materials for the planar cell, and have produced a 1kW plate monolith. MHI are looking at plasma spraying for both tubular and planar cells. Mitsui Engineering and Shipbuilding Company are looking at SOFC's for powering ships, are developing planar cells, using tapecasting and screen printing techniques, and are studying the stability of the interconnect. Nippon Oil Company is developing electrocatalysts for the internal steam reforming of naphtha. Ishikawajima Harima Heavy Industries (IHI) are looking at cofiring and the effect of morphology on electrode polarisation. NGK Insulator Ltd. is seeking to reduce electrical contact resistances, and is examining planar component materials. In addition, several companies have built multicell stacks based on both planar and

tubular configurations ranging from 103W-1.3kW: Tokyo Gas, Tonen Corporation, NKK, Fujikura, Fuji Electric Corporation.

In Europe (21), research is being carried out in a number of countries, and there is a fair amount of cooperation between these countries. Siemens in Germany, ECN in the Netherlands, and GEC in Britain are looking at the planar SOFC with metallic bipolar plates. 100W stacks have been tested successfully. Dornier in Germany, and Cookson in Britain are looking at ceramic bipolar plates. Riso in Denmark, and INPG in France, are aiming to reduce the operating temperature of the cell from 1050°C to 850°C; materials costs for piping etc. will then be reduced. The Danish programme is looking to develop fabrication technology. In Switzerland, Sulzer, in cooperation with Ceramtec Inc. of the US, research is being carried out on heat exchanger integrated stacks. Considerable research is being carried out by a number of organisations in Norway.

Ceramic Fuel Cells Ltd. was set up in Australia in 1992 to coordinate research activity in that country. Australia's fuel cell program is still in the early stages, but the aims have been given as follows (22): Optimisation of current materials; direct conversion of natural gas at the lowest possible steam:carbon ratios; examination of electrocatalytic activity of materials; mathematical model to predict performance, fluid dynamics and thermal stresses. The hardware and software for testing and evaluation have already been produced, and evaluation of current materials and fabrication methods is already underway.

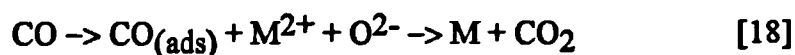
2.3 THE ANODE

2.3.1 INTRODUCTION

The anode acts as an electrocatalyst for the anodic reaction. In electrocatalysis, the reaction rate is a function of the catalytic activity of the catalyst (3). This depends on the how effectively the catalyst can adsorb the reacting gas at the anode, and the rate of electrical charge transfer. The anode is required to be stable in a fuel environment, and have a sufficiently high electronic conductivity to act as a current collector.

Adsorption is usually an exothermic process, occurring spontaneously. There are two types of adsorption, physical adsorption and chemical adsorption. For physical adsorption the enthalpies are generally less than 20kJmol^{-1} , and for chemical adsorption, between 40 and 200kJmol^{-1} (23). Physical adsorption is due to van der Waals forces between the molecules. Van der Waals forces include electrostatic forces between molecules with permanent dipoles, or that are readily polarisable. There are two types of chemical adsorption, associative and dissociative. In dissociative adsorption the adsorbing molecule splits, and the fragments adsorb separately. The forces of adsorption must be neither too low, or the catalyst will not be used to full capacity, nor too high as this will make it difficult for the reactants to escape; they will block active sites. Active electrocatalysts include transition metals and their compounds. The vacant d orbitals of these materials encourage chemical adsorption, by introducing an electronic factor. There is also a geometric factor to be taken into account in adsorption. The different crystal faces of a catalyst material tend to have different activities, additionally, the macrostructure, or morphology, of the material is important (23). In summary the anode must enable the following to occur (24): diffusion of gaseous reactants to the surface of the catalyst; diffusion of gaseous reactants from the external to internal surface of a porous grain; adsorption of reactants onto active sites; desorption of products from active sites; diffusion of products from the internal to external surface; diffusion of products away from the external surface.

The adsorbing gases also have different properties. The adsorption of nitrogen, or inert gases is generally weak. However, reducing gases, particularly when being adsorbed on semiconducting oxides can undergo an irreversible chemical adsorption (23). Two examples (21) are given below:



where M represents a metal ion.

2.3.2 THE NICKEL-ZIRCONIA ANODE

As has already been mentioned, it is the nickel-zirconia cermet that is currently being used in solid oxide fuel cells, and numerous papers have been published about its characteristics. A summary of the findings follows.

Some of the first studies examined, looked at the ratios of Ni:ZrO₂ in the cell. Kawada et al (25) found that the nickel content should be greater than 30 volume%. Below this, the cermet behaved like ZrO₂. At volumes greater than 30% the anode displayed an electronic conductivity close to that of nickel metal. Murakami et al (26) found that the anode tended to degrade during the long term, if the zirconia content was less than 50 weight%. In order to operate effectively as an electron sink, the nickel particles in the anode must be interconnected. The cermet is made by mixing the required quantities of nickel (in the form of nickel oxide) and zirconia together. This is then reduced to the cermet. Kawada et al (25) found that the anode should be baked onto the electrolyte at temperatures greater than 1600°C and that precalcination helped to prevent the nickel from sintering together. In another paper Kawada and coworkers (27) examined the nickel-zirconia interface. They found that the sintered material consisted of porous networks of zirconia containing nickel particles. The nickel particles had a tendency to segregate during reduction.

The porosity of a cermet anode and its electrical properties have been examined by Chou et al (28). They used a slurry coating technique, followed by pressure infiltration. They found that the process was reproducible. A porosity of 30-37% was achieved, and a sheet resistance of between 0.0064-0.019Ω/square was measured.

The kinetics of the reaction at the anode has been studied. Norby et al (29) have examined the effect of the three-phase-boundary length on the reaction rate, at a variety of hydrogen partial pressures, obtained by mixing hydrogen, water vapour and argon. At moderate partial pressures of hydrogen, it was found that the charge transfer resistance varied linearly with the inverse of the boundary length. However, at high boundary length, there was an additional resistance, believed to be due to the small surface area available per length of boundary; the kinetics are dominated by the reaction resistance. At high partial pressures of hydrogen it was not possible to come to any conclusion, as the reaction appeared to be limited by the kinetics at the cathode. Mizusaki and Tagawa et al (30) found that the electronic conductivity of the cell increased linearly with the three-phase-boundary length. Mogensen and

Lindegard (31) also varied the partial pressure of hydrogen, using water vapour and hydrogen. They found that the polarisation resistance of the anode was strongly dependent on the ratio water vapour/hydrogen. They suggest a mechanism in which a part of the resistance is independent of p_{H_2} due to proton transfer across the interface, and the other part being strongly dependent on p_{H_2O} . They suggest a reaction:



Temperature Programmed Reduction (TPR) has been carried out by two groups. Perego et al (32) carried out experiments at a variety of heating rates, p_{H_2} , gas flow rates and amounts of reducible sample (NiO). The nickel content was found to have a significant effect on the reduction kinetics, giving rise to higher activation energies of reaction. Shirakawa et al (33) characterised the material at two different sintering temperatures. They found that the oxide sintered at 1400°C was more reducible than that sintered at 1000°C. The former was found to have a lower conductivity, believed to be due to nickel aggregation, causing breaks in the intended interconnection. They suggest that interaction between the nickel and zirconia should be increased.

Guindet et al (34) have investigated the oxidation of nickel that can occur in the cell at high overpotentials. The electronic conductivity of nickel oxide (10^{-3} Scm^{-1}) is very much lower than that of nickel metal (10^4 Scm^{-1}) and can have a serious effect on cell operation. Thus it is doubly important to keep the polarisation from all sources as low as possible. Seiersten and Middleton (35) studied the oxidation kinetics of nickel in the cermet. It was found that the kinetics were dominated by the diffusion of nickel ions, and that only that nickel in contact with the oxide was oxidised. They also found (36) that, as would be expected, the performance of the anodes depends on the degree of surface oxidation of the nickel. Apart from this problem however, the cermet works well as an anode for reformed gases (H_2 and water vapour) at 1000°C.

Westinghouse, who are the most advanced in their development of the SOFC incorporating the cermet anode, have not yet been able to achieve complete internal reforming of the fuel used. A high proportion, though not all, of the fuel must be reformed before being introduced into the cell; the reforming reaction is endothermic and causes too much cooling at the end of the cell into which the gases are introduced. This reduces the efficiency of the cell, and greatly increases cell production costs. Mogensen (4) tested the anode for use in a dry (3% H_2O) methane

atmosphere. They found that, at any given potential, the current density was a factor of 10 lower than that obtained when using hydrogen, and that the polarisation was higher. Because methane is thermodynamically unstable at the cell operating temperature, there is also a problem with carbon deposition within the anode. This causes the anode to spall off the electrolyte, reducing the contact area.

2.3.3 MODIFIED NICKEL-ZIRCONIA ANODES

Okumura et al (37) used a drip pyrolysis method with a yttria stabilised zirconia sol for preparing the anode powder. They found that this gave the ceramic a high dispersibility in the anode, which reduced the overvoltage characteristics. Furthermore, the addition of small amounts of magnesium metal to the nickel was found to produce a much smaller polarisation than the nickel-zirconia anode. This was attributed to the difference in microstructure; the anode with the magnesium contained fine and porous nickel particles. McEvoy et al (2) have been examining nonporous cathodes. In this case, the reaction does not take place at the three-phase-boundary. The cathode is a mixed conductor with both electronic and oxygen ion conductivity. In addition, they incorporated small quantities of cerium or manganese at the cathode-electrolyte interface. They have begun initial experiments on improving the anode in the same way; by adding very small quantities of manganese, cerium or cobalt to the anode-electrolyte interface. One other method of improving anode performance would be to improve proton conduction (31) which is now believed to play an important role.

Several authors (38-41) have examined how modifying the surface of the cell electrolyte adjacent to the anode improves cell performance. Miyamoto et al (38) introduced a mixed conducting layer between the anode and electrolyte by impregnating the surface of the electrolyte with ceria, doped ceria (La and Sm) and praeosodymia. They found that all the ceria based dopants reduced the IR drop across the electrolyte and activation polarisation of the anode, but did not significantly affect the concentration polarisation characteristics. Doping the surface with praeosodymia increased the IR drop across the electrolyte. They suggest that an improvement caused by ceria is seen because of the increase in electron path; the layer links the nickel particles at the three-phase-boundary. Wang and Barnett (39) have tried modifying both sides of a thin film zirconia electrolyte, using an yttria stabilised bismuth oxide at the cathode side, and yttria doped ceria at the anode side. In this case rather than impregnating the electrolyte, the layers were sputtered onto the surface. The maximum power density increased by more than two times that when only the cathode side was modified (from 50 to 110mW/cm²). Eguchi, Setoguchi and

coworkers (40-41) have examined the effect of the oxide on anode performance, using nickel-zirconia, nickel-ceria, nickel-samaria doped ceria, and nickel-praesodymia anodes on a zirconia electrolyte. A high current density was found for the nickel-ceria anode, and they have suggested that the presence of the nickel works to promote the catalytic activity of the ceria. The electronic conductivity of the reduced ceria was believed to be high enough to operate as a current collector in the anode. Their results contradict those of Miyamoto in that the praesodymia was found to promote the anodic reaction and of all the oxides exhibited the slowest decrease in voltage with increasing current density as reported in the first paper (40). However, in their later paper, the results are more in line with those of Miyamoto, praesodymia exhibiting the worst polarisation characteristics. No explanation has been given for this contradiction, though the oxygen partial pressure has not been quoted in the second paper, and may be different. The same gases (H_2 , H_2O) were used in both cases. The properties of both doped and undoped cerias will be discussed in chapter 3.

2.3.4 ALTERNATIVE ANODE MATERIALS

Metallic anodes have been studied by some authors(30,41-42); platinum and nickel being the most common, but sometimes cobalt. Eguchi et al (42) compared a variety of metal anodes (Mn, Fe, Co, Ni, Ru, Rh, Pd, Pt, and Au) with nickel zirconia, on two different electrolyte materials: yttria stabilised zirconia and samaria doped ceria. Of the metals, the nickel exhibited the lowest overvoltage, and that of platinum was only better than the overvoltages exhibited by manganese, gold and palladium. The overvoltages were very much lower on the ceria electrolyte than on the zirconia. They also found (41) that the platinum anode, unlike the nickel-zirconia anode, was very sensitive to the kinds of gases reacting at the anode. Polarisation was lowest for H_2/H_2O mixtures and highest through CO/CO_2 to CH_4/H_2 . The nickel-zirconia anode behaved better than the platinum anode in each case.

Steele et al (43), have shown that a cell can be operated on 100% methane without carbon deposition, when ceramic oxide anodes are used. In a more recent study (44), it has been found that carbon deposition can occur on prereduced samples, which suggests that under long term use, this may always be a problem unless sufficient steam is present. One group of ceramics that could be used as an anode are perovskites (45). Perovskites have the basic formula ABO_3 , where the total charge of AB is 6+, and A and B are metals. Usually A and B have a charge of 3+ each. The most commonly studied perovskites for use in SOFC's have, until recently, had $A=La^{3+}$ and $B=\text{transition metal cation}$. These materials are p-type conductors and

may be doped to modify their properties. Such materials are already in use in SOFC interconnectors and cathodes (3,18). However, many of these materials are not stable under anode operating conditions (45). Furthermore, being p-type materials, conductivity decreases with both a decrease in oxygen pressure, and an increase in temperature, so that LaCrO_3 for instance, which is stable does not have a high enough conductivity (46). These materials may operate better as anodes for the lower temperature SOFC which is now being developed as reduction will not be so severe, and at lower temperature the electronic conductivity is expected to be higher. Brown-Millerite materials are a related system with the formula $\text{ABO}_{2.5}$. They are basically perovskites but with 1/6 of the oxygen positions vacant. The vacancies can enhance conductivity provided that they are not ordered. At lower temperature these vacancies generally are ordered, but can become disordered as the temperature increases (45).

There is a danger that some perovskites, most notably those containing calcium react with the zirconia electrolyte to form CaZrO_3 , an interfacial phase with very much poorer ionic and electronic conductivities. Tagawa et al (47) observed that this was the case for $\text{La}(\text{Ca})\text{CoO}_3$ but not $\text{La}(\text{Ca})\text{MnO}_3$. Yokokawa et al (48) examined $\text{La}(\text{Ca})\text{CrO}_3$ and LaMnO_3 , diffusion of calcium from the former into the zirconia electrolyte was observed. Sujita, Norby et al (49) have been examining iron-doped calcium titanate ($\text{CaFe}_x\text{Ti}_{1-x}\text{O}_{3-\delta}$). For higher levels of iron doping (>20%) a p to n type transition was found at oxygen partial pressures between atmospheric and 10^{-4} . The conductivity at low partial pressure for these materials was high enough for use as an anode (>10S/cm at 1000°C and a $p\text{O}_2$ of 10^{-15}). This was explained by the variable valency of the iron ion (4+, 3+). Below 20% iron doping, the conductivity was independent of oxygen pressure, and too low for use as an anode. Holt et al (50) have been studying titanium doped neodymium chromate ($\text{NdCr}_{1-x}\text{Ti}_x\text{O}_3$). The solubility of titanium was found to be about 20%. The p to n type transition occurred at a $p\text{O}_2$ of 10^{-6} , but the conductivity at fuel cell operating conditions was considered to be too low for use as an anode (~0.1S/cm at 1000°C and a $p\text{O}_2$ of 10^{-15}).

Another class of materials that could be used are fluorites (45). Yttria stabilised zirconia has the fluorite structure, as does ceria. Fluorites have a face centred cubic cell, but are more easily visualised as a simple cubic structure of oxygen ions with the cation in the centre of every other cube. Pyrochlores are related to fluorites in the same way that brown-millerites are related to perovskites. They have the basic fluorite structure, but with 1/8 of the oxygen positions vacant. Of all the materials

studied (51) the conductivity is quite low, and it has not proved possible to improve conduction by manipulating order-disorder in the lattice vacancies.

Marques et al (52-53) have examined zirconia doped with ceria or titania for use as an anode. The ceria doped materials exhibited negligible electronic conductivity when subjected to anodic conditions, whereas the titania was more successful in promoting the electronic conductivity, even though the titania doped material ($\text{Ti} > 5\%$) was less reduced. The electrons in the titania doped material were a lot more mobile, and it has been suggested that large rather than small polarons are present (52). Liou and Worrel (54) also examined titania-zirconia solid solutions. All their measurements were carried out in air. Work on zirconia-ceria mixed oxides has previously been carried out by others (55-58). The best result obtained for the conductivity was for the material containing the highest amount of ceria (70%), but was still $< 1 \text{ S/cm}$ under anodic conditions. Ishihara et al (59) studied an yttria-niobia fluorite type mixed oxide with a variety of dopants (Ce, Ti, Zr and Zn). Again, the conductivities were very much lower than those required for an anode ($< 0.01 \text{ S/cm}$ at 970°C and at a $p\text{O}_2$ of 10^{-20}). In this case the highest values were obtained for the ceria doped material, followed by the titania doped material. Little difference was seen in the activation energies of the two materials. Ceria based anodes will be discussed section 2.4.3.

2.4 USE OF CERIUM OXIDES IN FUEL CELLS

2.4.1 INTRODUCTION

Cerium oxide has been examined for use as an electrolyte, cathode and anode in a fuel cell by a number of people. As discussed in the previous section, McEvoy et al (2) have been employing small quantities of cerium at the cathode-electrolyte interface. Shingler (60) examined the suitability of niobia doped ceria for use as an MCFC cathode material. No more will be said about this here, but his work will be considered in chapter 3. The remainder of this section will be concerned with the use of cerium oxides in electrolytes and anodes of SOFC's.

2.4.2 THE ELECTROLYTE

When doped with lower valent cations, as is stabilised zirconia, ceria exhibits good ionic conductivity. The mechanism whereby this occurs will be explained in section 3.2. The ionic conductivity of doped ceria is better than that of zirconia, but the material was not initially used as an electrolyte, because it is reduced at the lower oxygen pressure present on the anode side of the cell, and at the high operating temperatures of the cell. Swarr et al (12) suggest that ceria could be used as the electrolyte of an SOFC at lower temperature, where it would not be reduced, and where its ionic conductivity would be comparable to that of zirconia operating at the higher temperature. This is recently being reconsidered here at Imperial College, though has been studied previously (61). In an effort to increase the power densities of SOFC's, the thickness of the zirconia electrolyte can be decreased or a higher conductivity material must be employed. Work has been carried out on composite electrolytes (62,65-68). These consist of a doped ceria bulk electrolyte coated with a thin layer of zirconia. Yahiro et al (62) used yttria-doped ceria, though others have found that gadolinia doped ceria shows the highest ionic conductivity (63-64). A stabilised zirconia layer was deposited on the anode face of the electrolyte to protect it from reduction. They found that the cell could be operated at temperatures between 600-1000°C with open circuit voltages close to the theoretical. Arai et al compared ceria (samaria doped) and zirconia electrolytes (65). It was found that the ceria electrolyte resulted in higher maximum power densities, but lower open circuit voltages than the zirconia electrolyte. The open circuit voltage of the ceria electrolyte could be improved by coating with zirconia on the fuel side of the electrolyte, but was still lower than that of zirconia.

Virkar et al (66-68) have also studied coated electrolytes. In the most recent paper, Virkar et al (66) have suggested that the stabilised zirconia layer is most effective when applied to the cathode rather than the anode side of the electrolyte, even though

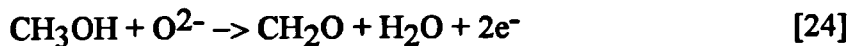
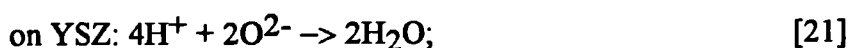
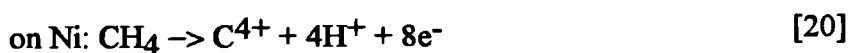
the ceria will be reduced at the anode side of the electrolyte. They argue that at the anode face the zirconia also exhibits some electronic conductivity, and that if a low pO_2 exists just inside the cathode electrolyte interface, depending on the rate of oxygen transfer, then the ceria at the cathode will also be slightly electrically conducting. This would lead to an internal leakage of electrons through the electrolyte, and can explain why the open circuit voltages found by Arai (65) were lower. With the zirconia coating at the cathode side, the oxygen pressure is not believed to be low enough to cause electronic conduction, so that even though the ceria is reduced, there is no electron path through the electrolyte. Their results show that, with the zirconia layer on the cathode side, the open circuit voltages were higher. In earlier work however (67) Virkar produced a model which indicated that the air side of the electrolyte should incorporate mixed conductivity whilst the anode side should have as low an electronic conductivity as possible. It is difficult to see how the two ideas can be reconciled. However, this model was not verified by experimental results. In another work Virkar et al (68) pointed out that where an electrochemical cell was being driven at an enforced voltage, there is a danger of internal precipitation of oxygen within the electrolyte leading to mechanical failure. However conditions are not believed to be as severe in reality (69). It is the opinion of the author, that provided there is no path for electronic conduction through the electrolyte from anode to cathode, it is reasonable to assume that the efficiency of the electrolyte cannot be affected by any electronic conductivity present at the anode side of the cell, and that the t_{ion} in this region is irrelevant, provided that the absolute value of ionic conductivity of the electrolyte material is not decreased. Thus the results of Virkar et al (66) would appear to be satisfactory.

The many workers (38-41) who have experimented with ceria either impregnated into or deposited as layers on the anode side of the electrolyte have been discussed in section 2.3. Their results suggest that some electronic conduction at the anode side of the electrolyte would be an advantage, rather than the detriment indicated by Virkar's second paper (67), as well as electronic conduction at the cathode side (39). The most recently published development in electrolyte materials is that of Iwahara et al (70). They have been examining a proton and oxide ion mixed conductor, $BaCe_{1-x}Sm_xO_{3-\alpha}$. Water vapour was obtained as a product at both electrodes of a trial cell, and results would appear to be encouraging.

2.4.3 THE ANODE

Ceria has been considered as a possible anode material by a number of authors (4,45,71-76), though there are some problems associated with the material in this

role. Mogensen (72) gives a brief resume of the history; a patent for ceria as an anode using CO, H₂ filed by Mobius and Rohland (75) over twenty years ago, and a report about yttria and lanthanum doped ceria electrodes for hydrogen oxidation by Takahashi et al (76). More recently Steele et al (45) suggested ceria may make a good anode based on its oxygen surface exchange flux and diffusion coefficients which they report as being 10⁻⁶ mols/scm (x 4F) and 10⁻⁸ cm²/s respectively for CeO_{1.9}. Problems were found with the changes in lattice parameter during oxidation and reduction however, which caused the electrode to crack and come away from the zirconia electrolyte. At the same time, research has been carried out in Denmark (4,71-74). Mogensen and Bentzen first examined ceria-zirconia mixtures for both methane and hydrogen oxidation. The solutions were inhomogeneous mixtures of the oxides. The reactions in methane showed much greater polarisation than in the hydrogen, but contrary to what may be expected, there was no carbon deposition. They report, that under standard conditions, at 1000°C, CH₄ and 3%H₂O almost all of the carbon will precipitate as free carbon. Even with the mixture of oxides, there was still a problem with the electrode spalling off the anode (71). In a later paper (4), a gadolinia doped ceria anode was compared with the nickel-zirconia cermet anode. In the mixture CH₄ and 3%H₂O the ceria anode behaved much better, having oxidation rates 100 times higher than was found for the nickel-zirconia cermet. They suggest that this is because on a mixed conductor the necessary reaction steps can all occur on the same site, whereas on the nickel-zirconia anode the reaction must occur at two separate sites.



etc.

Additionally, there was again no carbon deposition problem on the ceria anode, whilst it did occur on the nickel zirconia anode. The problem has been discussed in the section 2.3.2. Mogensen (72) reports that the expansion due to the increase in lattice parameter of the material is still the major problem of ceria electrodes. However work is still continuing on this material in Denmark (73), because of the promise it shows for direct oxidation of methane within the cell. The most recent study (74), has been

an examination of the stoichiometry of gadolinia doped ceria by Zachau-Christiansen et al.

Metcalf et al (77) have studied the oxidation of hydrogen, methane and propene gases over a niobia doped ceria anode. It was found that the reactivity decreased in the order hydrogen > propene > methane. Hysteresis was noted in cyclic voltammetry, and is believed to be caused by the compositional changes in the anode during reduction. Apart from the work by Metcalf et al (77) the majority of work on ceria based anodes has concentrated on ceria doped with lower valent cations. This has the advantage of reducing the extent of reduction in the material, as will be explained in section 3.2, but also reduces the electronic conductivity of the material under anodic conditions. This conductivity (<1S/cm) (79) is really rather too low for ceria to be used as an anode unless it forms part of a cermet as in the work by Eguchi et al (40-42) which has been discussed in section 2.3.3. Doping with higher valent cations such as niobium increases the electronic conductivity, but its effect on lattice expansion has not been studied. However because of the large difference in cation size (78), the solubility is too low to have any great affect on conductivity, though values of 5S/cm have been achieved (80) under anodic conditions. The aims of this project were to examine the possibility of increasing the solubility of niobium in ceria to sufficiently increase the improvement in electronic conductivity under anodic conditions, and to try to limit the lattice expansion that occurs during reduction of the material.

3. PHYSICAL AND CHEMICAL PROPERTIES OF CERIUM OXIDE

3.1 CRYSTAL STRUCTURE AND PHASE DIAGRAMS

Cerium oxide has a face centred cubic crystal structure of cations, with oxygen occupying tetrahedral interstitial positions, as shown.

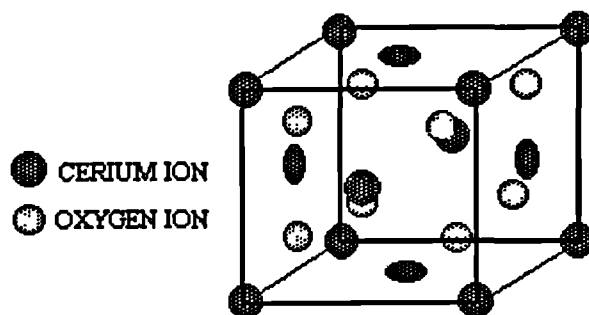


FIG.3.1a UNIT CELL FOR CERIUM (IV) OXIDE

The structure is known as the fluorite structure and is common to a number of materials; stabilised zirconia, thoria, hafnia, urania. The lattice parameter of pure cerium (IV) oxide has been reported as 5.4110 angstroms in JCPDS no. 4-593 (26°C).

The defect structure of cerium oxide has been much discussed. Cerium oxide is a nonstoichiometric oxide, which loses oxygen when subjected to a reducing atmosphere. This is possible because of the different charged states at which a cerium cation can exist: 4+ and 3+. The loss of oxygen is accommodated by a reduction in the charge from 4+ to 3+. A crystal lattice can accommodate such a loss by incorporating either oxygen vacancies or interstitial cations. There was some debate as to which of these defects reduced cerium oxide contained. Several early papers suggested that cerium interstitial ions were present (82-84). However, it has now been satisfactorily demonstrated that the predominant defects are oxygen vacancies (85-90). Steele and Floyd (85) had suggested that oxygen vacancies were the compensating defect, after measuring oxygen diffusion in the material. Faber et al (86-87) carried out xray and neutron diffraction studies, employing electron density mapping of a $\sim 1\mu$ powder at temperatures of 900 and 1000°C, and oxygen partial pressures varying between 1 and 10^{-21} atmospheres. Comparison of electron density maps for compositions CeO_2 and $\text{CeO}_{1.91}$ indicated that cerium interstitials were not predominant, and that the cation sublattice was not strongly affected by the defects. Neutron diffraction (87), which is more sensitive to anions than xray diffraction,

diagram shows phases at $n = 7, 9$ and 11 (δ , γ and β respectively). The results of Ray et al (93), indicated that an additional phase corresponding to $n = 10$ exists in samples annealed within the temperature range 400–450°C. There have been numerous problems with trying to pin down the crystal structure of these distinct phases, which are described as having a low symmetry (93). However, Ray et al (94) have successfully determined the structure for the δ phase. They found that it was isostructural with ternary oxides of the type UY_6O_{12} , and can be viewed as having either a hexagonal or rhombohedral unit cell. The phase can be more easily described (94) as a rhombohedral type of defective fluorite, in which pairs of oxygen vacancies are ordered along the $\langle 111 \rangle$ directions of the fluorite lattice. However, a similar relationship was not found for the other Ce_nO_{2n-2} phases (93).

Sorensen (92) examined the higher temperature region, given by α' on the phase diagram, looking for phases belonging to the same series. He reports on the work of Iwasaki and Katsura (95) who considered the phase to be a solid solution of CeO_2 and Ce_2O_3 . For small Ce_2O_3 above 1200°C this was consistent with an ideal model incorporating Raoult's and Henry's laws, but at lower temperatures and more reduced compositions, this was not observed. Sorensen's experiments consisted of thermogravimetric measurements and high temperature x-ray diffraction within the region of interest, resulting in a series of suggested subphases within the α' region, and corresponding to $n = 190, 100, 76, 68, 56, 40, 30, 28, 22, 20, 16, 14$ and 12 , though not all of the phases existing at the same temperature. However, this region has generally been viewed as having an extended homogeneous composition range (96-97). In a more recent work, Korner et al (98) carried out measurements which indicated that additional specific phases may be present at lower temperatures within this composition range, but no evidence was found for the phases suggested by Sorensen at higher temperature.

Cerium Oxide has been described by Tuller (81) as a mixed conductor exhibiting both oxygen ion and electronic conduction. These properties are considered in sections 3.2 and 3.3. Phase diagrams for mixed oxides of ceria: ceria-zirconia, ceria-niobia and ceria-tantala are available in Phase Diagrams for Ceramicists (American Ceramic Society). Apart from the first, they are far from complete.

3.2 OXYGEN ION DIFFUSION AND CONDUCTION

Fluorite materials have good oxygen ion conduction and diffusion properties (81, 99-103). As has been discussed in the previous section, cerium oxide is nonstoichiometric and loses oxygen when subject to a reducing atmosphere. Tuller (81) describes this reaction process in terms of mass transport i.e. diffusion from the bulk to the gas-solid interface. The kinetics of this depend upon the rate of oxygen diffusion in the material. The diffusion of ions is the movement of the ion from one site to the next throughout the material. For good ion mobility, loose open crystal structures and small ion size and charge are generally favoured. In most materials this is the case for cations. However, in fluorites the anion mobility is ten orders of magnitude greater than that of the cations. Fluorites have relatively open structures and can tolerate high levels of anionic disorder, whether this is caused by dopants, reduction or oxidation of the material (100).

Matzke (103) describes the diffusion process for fluorites containing excess oxygen, and those which are oxygen deficient. In the former case excess oxygen occupies an interstitial position in the lattice. Diffusion occurs as a migrating interstitial displaces a neighbouring lattice oxygen into an interstitial site, itself then occupying the lattice site. In an oxygen deficient material, diffusion occurs by direct jumps of lattice oxygen from its site into a vacancy. He states that for fluorite oxides, anion vacancy migration can be likened to small polaron hopping for electronic conduction. From here on the term diffusion will be used to refer to diffusion in oxygen deficient materials.

The good diffusion properties of fluorites mean that they are good oxygen ion conductors. Diffusion and conductivity are related by the following equation.

$$\sigma = N e^2 D / t_i k T \quad [1]$$

where N is the number of diffusing ions per cm^3 , e the total electronic charge per ion, D the diffusion coefficient and t_i the transference number (103). Strictly speaking, the diffusion coefficient calculated by tracer diffusion (D^*) in the material and that calculated from ionic conductivity measurements (D_σ) differ by a correlation factor of 0.653 for low defect concentrations (100).

$$D_\sigma = 0.653 D^* \quad [2]$$

All the above authors go into the more complex mathematics.

The transference number t_i gives the proportion of total conductivity measured that is attributable to ionic conduction.

$$\sigma_T = \sigma_i + \sigma_e \quad [3]$$

$$\text{and} \quad t_i = \sigma_i / \sigma_T \quad [4]$$

Where the ionic conductivity calculated from the diffusion coefficient is required, this may be omitted from the equation. Tuller (81) suggests that the transference number may be calculated by comparison of the self diffusion coefficient and the equivalent conductivity. For ceria under atmospheric conditions he gives $t_i = 0.999-0.5$.

Diffusion can occur both in the bulk material and along grain boundaries (103), though Kilner and Steele (101) report that the grain size dependence of conductivity is only noticeable for small grained samples, and that the effect of porosity is more severe.

Under constant oxygen pressure conditions the ionic conductivity can be related to temperature.

$$\sigma_T = A \exp\{-\Delta h_m/kT\} \quad [5]$$

where Δh_m is the activation energy for migration. The ionic conductivity depends upon the number of oxygen vacancies in the lattice, and this is included in the rather complex preexponential factor A.

$$A = B N e \exp\{\Delta S_m/k\} \quad [6]$$

$$\text{and} \quad N = N_O [V_O^\infty] \quad [7]$$

for small $[V_O^\infty]$ and N_O is the number of anion sites per unit volume (101).

Oxygen vacancies can be introduced either by reducing the material, or by doping with a lower valent ion. However, on reducing ceria, particularly at lower temperatures, Tuller and Nowick (104) suggest that the produced vacancies interact, forming vacancy-vacancy pairs and reducing ionic conductivity. Reduction also

introduces electronic conduction, so where a high t_i is required ionic conductivity is best improved by doping.

3.2.1 LOWER VALENT DOPING

Ceria has been doped with both di- and trivalent cations (74, 79, 105-114). Doping increases the range of electrolytic behaviour for cerium oxide, by increasing the number of oxygen vacancies.



It has been found that the dopant ions interact with the oxygen vacancies in the lattice (99-101), forming defect associates. For divalent doped materials these take the form $(D_{Ce}'' V_O^{\circ})^{\times}$ and for trivalent dopants $(D_{Ce}' V_O^{\circ})^{\circ}$ or $(D_{Ce}' V_O^{\circ} D_{Ce}')^{\times}$. In practice, the former has been found to be more common. In this case the conductivity is related to the temperature by

$$\sigma T = A \exp\{-E_a/kT\} \quad [9]$$

where E_a is the activation energy given by

$$E_a = \Delta h_m + \Delta h_a/n \quad [10]$$

Δh_a is the association enthalpy and n is the effective charge of the dopant in the lattice. For divalently doped materials isothermal conductivity

$$\sigma \propto x^{1/2} \quad [11]$$

where x is the proportion of dopant. It is only the preexponential factor that changes, whilst the activation energy remains constant. For trivalently doped materials, it was found that A remained constant whilst the activation energy decreased with increasing x (101).

Nowick (100) suggests that in yttria doped ceria each $(Y' V_O^{\circ})^{\circ}$ pair surrounds itself with Y' defects in a randomly arranged superlattice. The oxygen vacancy can migrate from one Y' to another. Thus the dependence of association enthalpy on dopant concentration for trivalently doped materials is believed to be a consequence of electrostatic interactions in which a free migrating V_O° spends more time in regions of favourable electrostatic interactions.

$$\Delta h_a = \Delta h_a^0 - \Delta h_{int}$$

[12]

where Δh_{int} is the electrostatic interaction energy contributed by surrounding ions, and Δh_a^0 is for the $(Y' V_O^{\infty})^{\circ}$ interaction at nearest neighbour separation.

The size of the dopant ion has also been found to have an effect on conductivity (81, 100, 106, 109, 112-118). It has been suggested that this is related to the binding energy or association enthalpy of the dopant ion-oxygen vacancy pair. Gerhardt-Anderson (114) found the following correlation.

TABLE.3 2 1a RELATION BETWEEN DOPANT ION AND ASSOCIATION ENTHALPY (114)

dopant	size ratio D3+/Ce4+	association enthalpy (eV)	
		1% D2O3	6% D2O3
La	1.21	0.14	0.18
Gd	1.03	0.12	0.16
Y	0.98	0.21	0.26
Sc	0.86	0.67	

Butler et al (115-116) suggest that the smaller ions bind more strongly in ZrO_2 , and have found a strong dependence of conductivity on dopant ion radii in ceria. They put forward a theoretical model for a number of associates and clusters, which was found to give the same form of relationship as the experimental data. There is now general agreement amongst authors that the minimum association enthalpy is found for the dopant ion having a radius closest to that of the host cation. Thus in ceria, gadolinia doped ceria gives the highest ionic conductivity. Ions smaller than the host cations show a much larger increase in association enthalpy with increase in size difference than is found for ions which are larger. Butler et al (116) suggest that for smaller ions the increase is caused by relaxation of the dopant towards the vacancy, whereas for larger dopants there is a reduction in strain in the crystal when a vacancy occupies a nearest neighbour site.

Sc ions have a particularly high association enthalpy, and have been found to scavenge vacancies. Gerhardt-Anderson and Nowick (114) found that Sc_2O_3 - Y_2O_3 doped ceria had an ionic conductivity thirty times smaller than that for ceria doped with Y_2O_3 only. Wang et al (111) in a recent study of In doped ceria, found $(In' V_O^{\infty})^{\circ}$ pairs even at trace concentrations of In, having an enthalpy of 0.35eV. Since the size ratio is 0.95 this would appear to correlate well with the results in the above table. They found that this complex was associated with a further oxygen vacancy at some distance.

Nowick (100) states that for certain compositions and cations, long-range ordered structures can be produced. For this to occur, an appreciable size difference between host and dopant is generally required. Pyrochlores are related to these structures. The basic feature is described as being one of oxygen vacancy pairs along the diagonal of the parent unit cell. The smaller cation becomes 6fold coordinated, a tetrahedron of cations surrounding each oxygen vacancy. Such structures may occur as microdomains within the parent. Wang et al (111) found a further defect in which vacancies were trapped either side of In along the <111> direction.

The type of dopant ion also affects the solubility of the dopant in the host lattice, and alters the lattice parameter of the fluorite structure (105, 108-109, 113-114).

TABLE 3 2 1b SOLUBILITY LIMIT DOPANT ION SIZE RELATIONSHIP

dopant	solubility limit DO, D2O3 mol%	size ratio
Ca	23	1.15
Sr	8	1.29
Ba	low	1.46
Mg	low	0.92
Sc	3	0.86
Gd	30-50	1.03

The saturation is commonly found by plotting change in lattice parameter against dopant concentration. This changes linearly until reaching a plateau. This start of the plateau is taken to indicate saturation. However Kudo and Obayashi (113) state that this is not necessarily accurate, and that the plateau may be caused by defect complexing at high concentrations, hence the wide range of values given for Gd. As can be seen, the closer the size of host and dopant the greater the solubility.

It has been stated by these authors that where $r_{\text{dopant}} > r_{\text{host}}$ the lattice parameter increases, and where $r_{\text{dopant}} < r_{\text{host}}$ the lattice parameter decreases. However according to JCPDS diffraction files, the lattice parameter of pure ceria is 5.4110Å (4-593) and of yttria doped ceria 5.41134(12) Å (34-394) both at 26°C. It is possible that the result for the pure ceria was influenced by impurities having a smaller radius. Garnier et al (105) give the lattice parameter of pure ceria as 5.4112Å (RT), but this is still smaller than the yttria doped value.

The type of dopant does not appear to affect the expansion coefficient given as $12.6 \times 10^{-6}/^{\circ}\text{C}$ by Kudo and Obayashi (113).

3.3 ELECTRONIC CONDUCTION

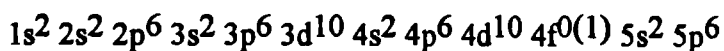
At high temperatures and under reducing conditions cerium oxide behaves as an n-type semiconductor. The electronic conductivity increases with both temperature and a reduction in oxygen pressure. The electronic conduction of ceria has not been studied to the same extent as oxygen ion conduction, but has been discussed by several authors (81, 119-120). The band gap for cerium oxide is given as 5.5eV (81). Electron transport in cerium oxide occurs via a small polaron hopping mechanism (119-120) that is thermally activated, and for constant oxygen pressure can be represented by the equation

$$\sigma T = A \exp\{-E_H/kT\} \quad [13]$$

where E_H is the activation energy for hopping.

Polarons are formed by interaction of the conduction electron with the surrounding lattice. Large polarons have relatively high mobilities as the interaction is only weak. They move as in a band with a slightly enhanced mass. Small polarons are formed when interactions are strong. The electron is self-trapped by the introduced lattice deformation at a particular lattice site. At high temperature the polaron can move by thermally activated hopping from site to site. Charge transport in this way also includes the lattice distortion, which creates additional drag. At low temperature small polarons tunnel slowly through the crystal as if in a band of large effective mass (81, 120-121).

Small polaron formation can occur in materials whose conduction electrons belong to incomplete d or f shells (119-120). Ce^{4+} has an empty 4f shell which contains one electron on reduction to Ce^{3+} .



The small polaron hopping mechanism in cerium oxide was examined at about the same time by two separate groups (119-120), using different experimental techniques. Tuller and Nowick used a nonequilibrium method whereby x in CeO_{2-x} was held constant, and the temperature varied for conductivity measurements, whilst Naik and Tien combined electronic conductivity and nonstoichiometry data. The results show some similarity at high x values, but differ for low x. Naik and Tien suggest that this is because the Tuller and Nowick data are dependent upon the history of the samples,

whilst Tuller and Nowick state that thermogravimetric data are unreliable at low x . Tuller and Nowick report on previous data by Blumenthal et al using the same methods as Naik and Tien, and giving results comparable to those of Naik and Tien ($E_H=0.16, 0.22$ at low x). The two sets of data are plotted below.

The Naik and Tien data show a marked increase in E_H with x , whilst the Tuller and Nowick data begin more or less constant, increasing gradually at higher x . Naik and Tien believe that an increase in E_H with x is to be expected. The higher the concentration of localised defects, the fewer the sites to which the electron can jump. Tuller and Nowick explain their increase as being due to increased ordering of oxygen vacancies in the reduced crystal immobilising some of the conduction electrons (104). Electronic conductivity is related to the concentration and mobility of electrons by

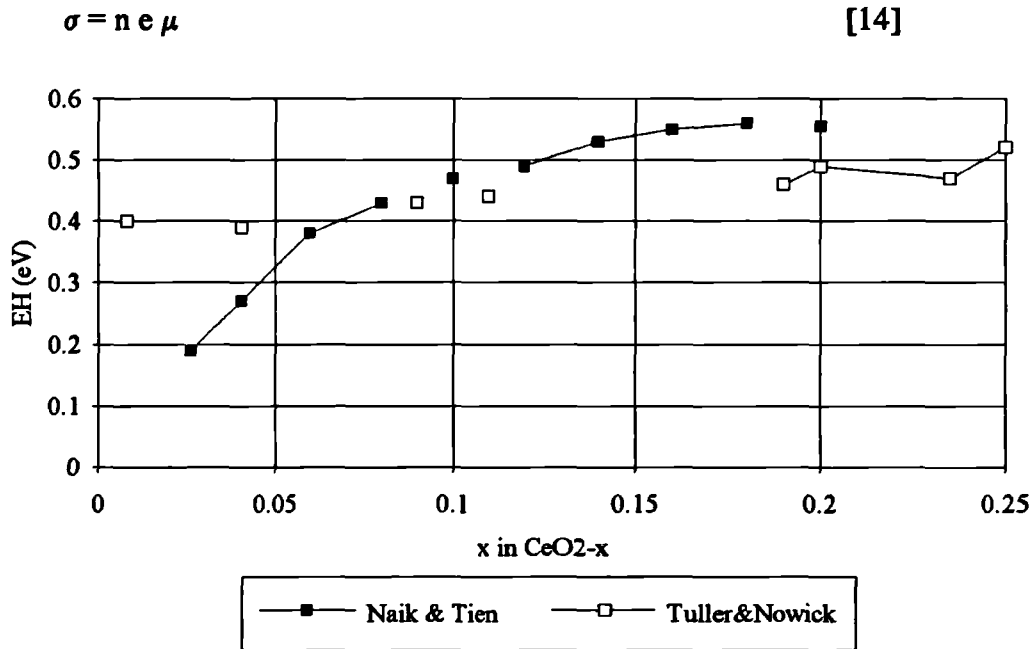


FIG.3.3 E_H V. x FOR PURE CERIA

In pure ceria under atmospheric oxygen pressure conduction is mixed ionic and electronic; $t_i = 0.999-0.5$ with increasing temperature. This is because in cerium oxide electron and oxygen vacancy mobilities differ only by a factor of 10 (81). Just as doping with lower valent cations increases the ionic/electrolytic range under these conditions, doping with higher valent cations can increase the electronic conduction.

3.3.1 HIGHER VALENT DOPING

There are relatively few studies of ceria doped with higher valent cations (60, 122-123) when compared to the numerous studies on doping with lower valent cations. All authors agree that doping with a higher valent cation increases the electronic conductivity at high temperature under high pO_2 . There are several possible charge compensation mechanisms. The first is a reduction of the Ce^{4+} ion to Ce^{3+} . In addition to this, Naik and Tien (123) suggested that oxygen interstitials were also responsible, whilst Shingler (60) would not rule out the possibility that cerium vacancies were present.

The ions used are Ta and Nb, both having a charge of 5+. The solubility of these ions is generally low because of the small ionic radii.

TABLE 3 3 1 SOLUBILITY LIMIT DOPANT ION SIZE RELATIONSHIPS (78)

dopant	solubility limit DO _{2.5}	size ratio
Nb	~1.2%	0.8 (VI/VI)
Ta		0.8(VI/VI)
		0.71(VIII/VIII)
(VIII coordination radius for Nb unavailable)		

Both Naik and Tien (123) and Shingler found a $CeNbO_4$ second phase above the solubility limit, Naik and Tien pinpointing the limit to between 1.2 and 1.6% and Shingler to between 0.82 and 1.28% of cations. Addition of Nb to cerium oxide was found to increase the lattice parameter to 5.41435Å for a dopant concentration of greater than 1% (60).

Examination of the σT v. $1/T$ graphs showed that the material exhibited two activation energies for conduction in what is described as a high and low temperature region. In the high temperature region this was found to be 0.18eV (123) comparable to that for pure ceria at low defect concentrations. Naik and Tien found that it in the low temperature region the value was lower. The data of Naik and Tien covers a far wider pO_2 range ($1-10^{-19}$) than that of Shingler ($1-10^{-4}$). Under 1atm pO_2 Shingler found that the data plotted as a curve rather than a straight line, as though E_H was constantly changing with temperature. At $pO_2 = 10^{-4}$, above 700°C an activation energy of 0.286eV was found Both groups found that the activation energy was independent of dopant concentration above this temperature, though the low solubility makes it difficult to be sure. Shingler found that below 700°C for a 1.28% doped sample, there was a sharp increase in activation energy which he attributes to

precipitation of CeNbO₄. He suggests that the formation of this precipitate is quite simple.



The hopping electron on Ce is electrostatically attracted to the Nb ion forming a microprecipitate or cluster by trapping the electron. Trapping probability increases with decrease in temperature and increase in dopant concentration and oxygen pressure. He calculated a precipitation energy of 0.57eV. With a decrease in oxygen pressure the electronic conductivity became less dependent on dopant concentration, and approached that of pure ceria; that is, was of the same order of magnitude, but remained higher by a factor of around 2 at low pressure.

3.4 DEFECT MODELS

Vest (124) considered the phase rule $F + P = C + 2$ where F is the number of degrees of freedom, P the number of phases and C the number of components. For a compound of the form M_aX_b in equilibrium with its vapour there are two phases, the vapour and the solid, and two components M and X . The system has only 2 degrees of freedom, thus temperature, pressure and composition cannot be varied independently (124). Vest indicated that it is usually only the more electronegative component (e.g. O_2) that is considered in this equilibrium, he then produces a series of equilibrium relationships for every possible point defect and interaction.

There are four kinds of point defects that can be found in a lattice: missing atoms, misplaced atoms in either lattice or interstitial sites, impurity atoms on those same sites and electronic defects, which are defined as those points containing a charge other than that normal for the lattice. In a pure material disorder on the lattice increases with temperature, and can take two forms.



by migration of M and X from inner lattice positions to positions on the crystal surface, and



where anions or cations leave a lattice position and occupy an interstitial position. Anionic frenkel disorder is reported to be the intrinsic disorder found in cerium oxide (81).

For small defect concentrations the activity of a component can be taken as proportional to its concentration, and simple models can be constructed to explain the ionic and electronic properties.

3.4.1 BASIC DEFECT CHEMISTRY

As has been discussed in section 3.1, the predominant defects in nonstoichiometric cerium oxide are oxygen vacancies. The relationship between oxygen partial pressure and the concentration of vacancies can be expressed in the following manner, using



notation proposed by Kroger and Vink (125). There are a number of possible equations that can be used to describe what is happening within the material.



Equations 19 and 20 represent two alternative predominant situations that can occur, which depend on the temperature. For near stoichiometric composition, at low temperature intrinsic frenkel disorder as given by equation 19 will predominate, whilst at high temperature intrinsic thermal electron-hole generation given by equation 20 will predominate. As the oxide is exposed to a reducing atmosphere equation 21 will come into operation, supplemented by 22 and 23. Each of the above equations have an equilibrium constant given below.

$$K_1 = [O_i''] [V_o^{\infty}] \quad [24]$$

$$K_2 = n p \quad [25]$$

$$K_3 = [V_o^{\infty}] n^2 pO_2^{1/2} \quad [26]$$

$$K_4 = [V_o^{\circ}] / [V_o^{\infty}] n \quad [27]$$

$$K_5 = [V_o^x] / [V_o^{\circ}] n \quad [28]$$

The general charge neutrality condition is given here.

$$n + 2[O_i''] = p + [V_o^{\circ}] + 2[V_o^{\infty}] \quad [29]$$

Brouwer (126) has suggested that the neutrality condition can be simplified for any particular region of oxygen pressure where there is one defect species that

predominates above the rest, thus simplifying the equations. The following is a demonstration of his theory.

At lower temperature and intermediate oxygen pressure

$$[O_i''] = [V_O^{\circ}] \neq f(pO_2) \quad [30]$$

Thus the variation of the defect species in this region with pO_2 can be approximated using equations 24-28.

$$n: \log K_3 = \log [V_O^{\circ}] + 2\log n + 1/2\log pO_2 \quad [31]$$

$$2\partial\log n = -1/2\partial\log pO_2 \quad [32]$$

$$\partial\log n/\partial\log pO_2 = -1/4 \quad [33]$$

$$p: \log (K_3/K_2) = \log [V_O^{\circ}] - 2\log p + 1/2\log pO_2 \quad [34]$$

$$2\partial\log p = 1/2\partial\log pO_2 \quad [35]$$

$$\partial\log p/\partial\log pO_2 = 1/4 \quad [36]$$

$$[V_O^{\circ}]: \log K_3K_4^2 = -\log [V_O^{\circ}] + 2\log [V_O^{\circ}] + 1/2\log pO_2 \quad [37]$$

$$2\partial\log [V_O^{\circ}] = -1/2\partial\log pO_2 \quad [38]$$

$$\partial\log [V_O^{\circ}]/\partial\log pO_2 = -1/4 \quad [39]$$

$$[V_O^{\times}]: \log K_3K_4K_5 = \log [V_O^{\times}] + 1/2\log pO_2 \quad [40]$$

$$\partial\log [V_O^{\times}]/\partial\log pO_2 = -1/2 \quad [41]$$

At high temperature the simplified neutrality condition is

$$p = n \neq f(pO_2) \quad [42]$$

and

$$[V_O^{\infty}]: \quad \partial \log [V_O^{\infty}] / \partial \log pO_2 = -1/2 \quad [43]$$

$$[O_i^{\bullet}]: \quad \partial \log [O_i^{\bullet}] / \partial \log pO_2 = 1/2 \quad [44]$$

$$[V_O^{\circ}]: \quad \partial \log [V_O^{\circ}] / \partial \log pO_2 = -1/2 \quad [45]$$

$$[V_O^x]: \quad \partial \log [V_O^x] / \partial \log pO_2 = -1/2 \quad [46]$$

This intermediate region is generally observed at standard oxygen pressure in pure cerium oxide, though the relationships shown are very often not seen because lower valent impurities alter the behaviour in this region. The behaviour in the higher and lower oxygen pressure regions can be characterised by the following simplifications to the neutrality condition

$$p = 2[O_i^{\bullet}] \quad [47]$$

$$n = 2[V_O^{\infty}] \quad [48]$$

$$n = [V_O^{\circ}] \quad [49]$$

These results can be shown in what is known as a Brouwer diagram, where $\log pO_2$ is plotted against $\log$ [concentration] of the defect species in each of the predominant defect regions. The two diagrams below are for the low temperature (intrinsic frenkel disorder) and high temperature (intrinsic thermal electron-hole generation). It can be seen that in the intermediate region there is a difference in the variation of n between the two diagrams. " n " contributes to the electronic conductivity with oxygen partial pressure. In all other regions the variation is the same.

The diagrams refer to defect concentration, and it is expected that the pattern can be observed in both thermogravimetric and electronic conductivity measurements. In thermogravimetry, measurements are made of change in weight of the sample with oxygen pressure and temperature. Generally measurements are made isothermally, at a series of constant temperatures by varying the oxygen pressure, allowing the sample to equilibrate at each pressure. This is the method that was used by Bevan and Kordis (91). The weight loss is due to the loss of oxygen from the sample, and can therefore be seen as a direct measure of the oxygen vacancy concentration. Where oxygen vacancies of a particular charge are predominant, they are expected to show the variation with oxygen partial pressure indicated. Similarly, electronic conduction is

due to the mobile electron concentration created as the departing oxygen ion becomes an oxygen atom. This is given by the equation:

$$\sigma = n e \mu \quad [14]$$

where e is the charge of an electron, and μ is the electron mobility. Assuming that the mobility is independent of oxygen pressure, then the conductivity is expected to show the same variation with pO_2 given by n on the diagram.

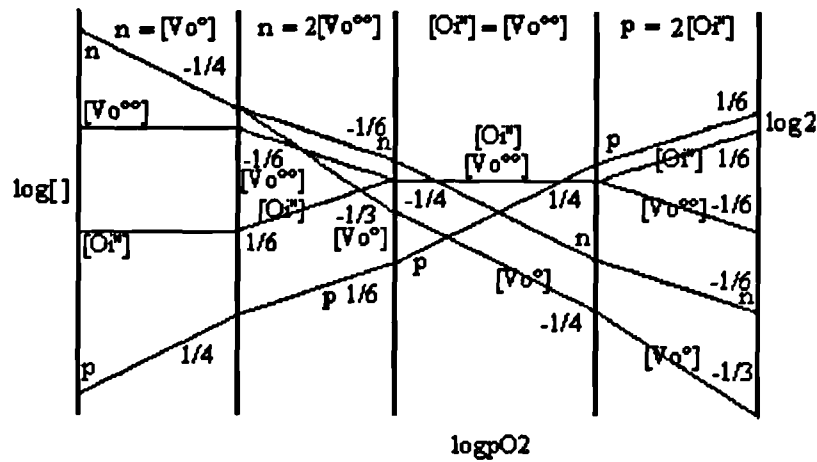


FIG.3.4.1a BROUWER DIAGRAM FOR CERIUM OXIDE; LOW TEMPERATURE CASE

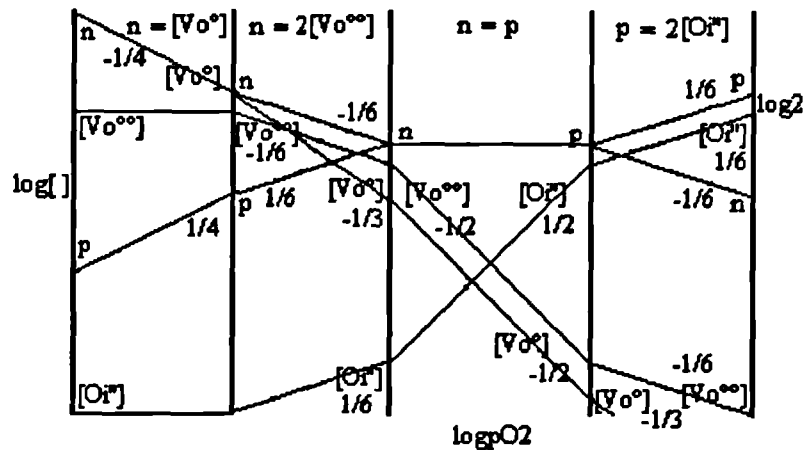


FIG.3.4.1b BROUWER DIAGRAM FOR CERIUM OXIDE; HIGH TEMPERATURE CASE

Similar diagrams can be constructed for higher and lower valent doped cerium oxide. In these cases the central intrinsic region characterised either by frenkel defects or as

a semiconductor will be characterised by the dopant, having the brouwer approximations of the neutrality condition as given here.

$$\text{Y doped ceria} \quad [Y_{Ce}'] = 2[V_{O^{\bullet\bullet}}] \quad [50]$$

$$p = [Y_{Ce}'] \quad [51]$$

$$\text{Nb doped ceria} \quad n = [Nb_{Ce}^{\circ}] \quad [52]$$

$$[Nb_{Ce}^{\circ}] = 2[O_i^{\bullet\bullet}] \quad [53]$$

and the resulting oxygen pressure relationships are shown on the diagrams.

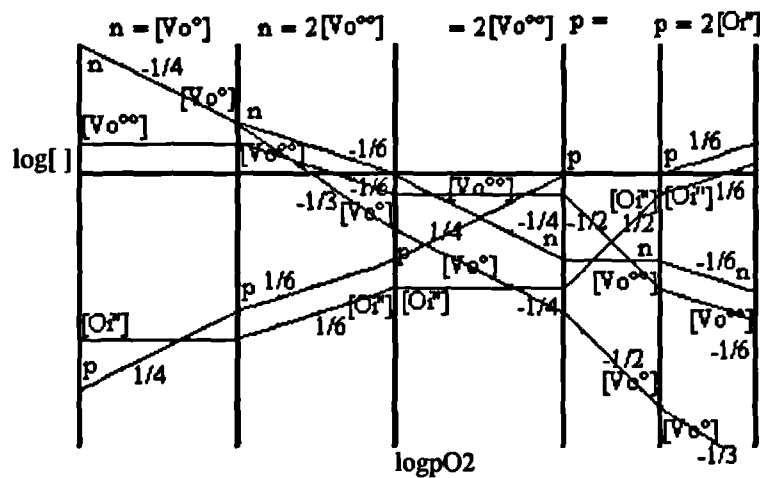


FIG.3.4.1c BROUWER DIAGRAM FOR LOWER VALENT DOPED CERIA

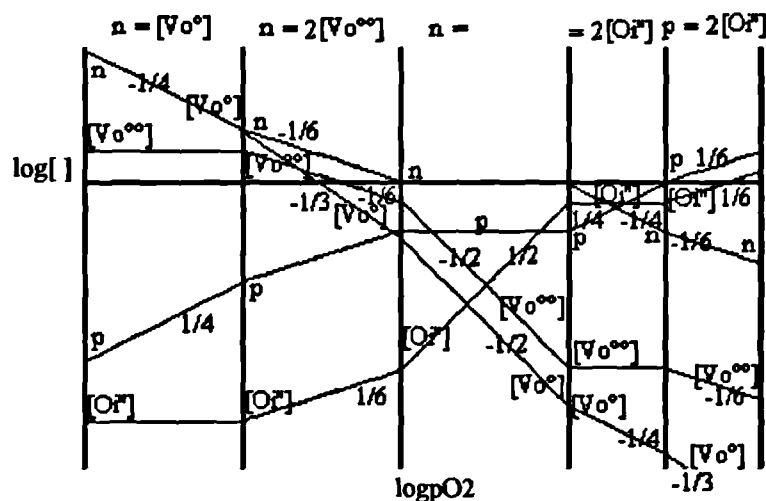


FIG.3.4.1d BROUWER DIAGRAM FOR HIGHER VALENT DOPED CERIA

3.4.2 MORE COMPLEX MODELS

In reality, cerium oxide exhibits large intermediate regions in which one particular species is not predominant. This originally lead to some confusion, as the slopes of $\log \sigma$ and $\log(\text{weight loss})$ v. $p\text{O}_2$ were not those predicted for the oxygen vacancy defect compensation model. For this reason, cerium interstitials were suggested (82-84). Kevane (127) tried to solve the equations without using the Brouwer approximation, and found that there are a wide range of $p\text{O}_2$ for ceria over which a slope of $-1/5$ could be observed. Tuller and Nowick (79) used this solution when analysing their conductivity data. The equation for n as follows can be formed by combining a neutrality condition of

$$n = [V_{\text{O}}^{\circ}] + 2[V_{\text{O}}^{\infty}] \quad [54]$$

with the equations 26 and 27:

$$n^3 - K_3(T) p\text{O}_2^{-1/2} (K_4(T) n + 2) = 0 \quad [55]$$

Tuller and Nowick (79) indicate that analysis of the equation shows that at near stoichiometry doubly ionised oxygen vacancies are expected to predominate giving a $\partial \log n / \partial \log p\text{O}_2 = -1/6$, and at large deviations from stoichiometry singly ionised vacancies predominate giving a $\partial \log n / \partial \log p\text{O}_2 = -1/4$. This can also be seen in the brouwer diagram, but the above equation covers the transition region between these extremes that doesn't appear on the diagram. Tuller and Nowick indicate that in the transition regions, conductivity measurements would be more reliable than thermogravimetric measurements in determining defect structure; the thermogravimetric measurements depend on the total number of oxygen vacancies, not only those contributing electrons.

Shingler (60) proposed a model having a more complex neutrality condition for higher valent doped ceria, considering both oxygen interstitials and cerium vacancies. He rejected Tuller's (81) assumption that interstitial oxygen would be the compensating defect. He considers

$$2[O_i^{\bullet}] + n = [NbCe^{\circ}] \quad [56]$$

$$[O_i^{\bullet}] + n = [NbCe^{\circ}] \quad [57]$$

$$2[V_{\text{Ce}}^{\bullet}] + n = [NbCe^{\circ}] \quad [58]$$

$$[V_{Ce}'] + n = [Nb_{Ce}^{\circ}] \quad [59]$$

for niobium doped ceria. A summary of the predictions of this model are given.

TABLE 3 4 2 SUMMARY OF MODEL PREDICTIONS (60)

DEFECT	SLOPE	WIDTH OF TRANSITION REGION (ORDERS MAG. PO ₂)	SHAPE DEPENDENCE ON DOPANT CONCENTRATION
V _{Ce} '	-1	4 to 5	N
V _{Ce} ''	-0.5	4 to 5	Y
O _i '	-0.5	8 to 10	N
O _i ''	-0.25	8 to 10	Y

He suggested that the width of the transition region may be used to determine the defect type, and that

$$2[O_i''] + [O_i'] + n = [Nb_{Ce}^{\circ}] \quad [60]$$

$$2[V_{Ce}''] + [V_{Ce}'] + n = [Nb_{Ce}^{\circ}] \quad [61]$$

could also be considered. His experimental data were unable to verify the validity of such a model, or be used to identify the compensating defect as precipitation of a second phase disrupted results. However, the transition region was seen to be somewhat smaller than that predicted for oxygen interstitials.

Thus far, the defect models have considered variations between composition and oxygen pressure only. Patterson(128) and Tuller(81) have considered 3-dimensional plots for $\log\sigma$, $\log pO_2$ and $1/T$. The domains between ionic, electrolytic and electronic behaviour can be separated by straight lines in $\log pO_2$ $1/T$ space. It is first necessary to define the difference between electrolytic and ionic behaviour. Ionic behaviour is found at the point where $t_i > 0.5$. The electrolytic domain is that region in which the proportion of ionic conductivity is high enough for the material to be used as an electrolyte. Patterson defines this as being where σ_i is one hundred times greater than σ_e or σ_p

$$\sigma_T = \sigma_i + \sigma_p + \sigma_e \quad [62]$$

$$\sigma_i T = A \exp\{-\Delta h_m/kT\} \quad [63]$$

$$\sigma_e T = B \exp\{-E_H/kT\} pO_2^{-1/n} \quad [64]$$

$$\sigma_p T = C \exp\{-E_p/kT\} pO_2^{1/n} \quad [65]$$

where A, B and C are independent of temperature and pressure, and n gives the relationship with oxygen pressure. The domain boundaries may be calculated from the above. For the ionic domain

$$\ln pO_2 = -n[\Delta h_m - E_p]/kT + n \ln[A/C] \quad [66]$$

$$\ln pO_2 = n[\Delta h_m - E_H]/kT - n \ln[A/B] \quad [67]$$

The electrolytic domain boundaries may be similarly calculated by introducing a factor of 100. At high temperatures where a p-n transition is observed, the domain boundary may be calculated from

$$\ln pO_2 = -n[E_H - E_p]/2kT + [n \ln[B/C]] \quad [68]$$

Unfortunately, in cerium oxide the preexponential factors A, B and C are not always independent of oxygen pressure and temperature, as mobilities of both electrons and ions vary. Therefore, extrapolation in this manner is not straightforward. A discussion of other defect models and of oxygen pressure relationships found experimentally follows.

Panlener et al (129) carried out thermogravimetric measurements indicating a -1/5 slope pO_2 dependence found experimentally for electrical conductivity was consistent with a model having ΔH_{O_2} dependent on x for CeO_{2-x} . Oxygen vacancies were accepted as the defect. After considering combinations of singly and doubly ionised vacancies, and quadruply ionised vacancy pairs, they suggest that the -1/5 pO_2 dependence at near stoichiometry is due to doubly ionised vacancies. In a later work Dawicke et al (130) show this near stoichiometric -1/5 dependence could be due to the presence of both charge compensating vacancies introduced by reduction, and vacancies introduced by di- or trivalent impurities in the oxide. Why the number of the former vacancies would not be suppressed by the impurities is not clear.

Hillert and Jansson (131) have proposed a two sublattice thermodynamic model. They do not use Kroger-Vink notation. The proposed sublattices consist of $Ce^{4+}O^{2-}$ and $Ce^{3+}V_O$ respectively. The model predicts the miscibility gap that can be seen in the phase diagram. Additionally the model predicts a slope of -1/6 between oxygen pressures of 10^{-4} and 10^{-10} , thus there is some deviation between the experimental

data and the model, when the data has a fit of $-1/5$. However, because of the scatter in the experimental data the observed match may still be good. In view of the species being considered in the model (doubly ionised oxygen vacancies), a predicted slope of $-1/6$ is consistent with other models for the same species. Hillert and Jansson suggest that their model could be used for solutions of different oxides. Experimental data of Riess et al (132) by a coulometric titration technique as opposed to thermogravimetric data showed that for $10^{-4} < x < 10^{-3}$ $\ln x = [-1/4] \ln pO_2 + k$ and for $10^{-3} < x < 10^{-2}$ $\ln x = [-1/6] \ln pO_2 + k$, where k is a constant.

Tuller and Nowick (79) experimented on a single crystal. They assumed the total conductivity to be equal to the electronic conductivity. This would only be a safe assumption at high temperature or low oxygen pressure, when comparing a maximum ionic conductivity at 0.1 S/cm and a maximum total conductivity of 1 S/cm over $\ln pO_2$ 1/T space. However, Tuller suggests that on reduction, oxygen vacancies interact, reducing the level of ionic conductivity (section 3.2). It has also been suggested that there is a critical temperature below which this ordering takes place for small x . The miscibility gap in the phase diagram is predicted. Tuller's results show a $-1/6$ dependence followed by a smooth transition to a $-1/4$ dependence with decreasing pO_2 . A shallow $\sigma_{\max}$ was reached at 900' and 1000'C at a pO_2 of 10^{-17} and 10^{-16} respectively. The data of Naik and Tien on Nb doped ceria show a similar $\sigma_{\max}$ but reached at higher pO_2 and/or lower T . Slopes of $-1/6$ and $-1/5$ were noticed. It should be noted however, that in this case similar means a value of at least two times the undoped value, even at low oxygen pressure. $\sigma_{\max}$ appeared to be stable over a wider pO_2 before decreasing than for the undoped ceria.

3.4.3 DOUBLE DOPING

Kroger (125) states that addition of foreign atoms to a material that give rise to charge centres affect the concentration of native defects in the material, and that where more than one foreign atom is present, the effects can be summed; if they introduce the same charge the overall effect is enhanced, and if the charges are opposing, then the effect is diminished. Association of the defects together, or with native imperfections can introduce associates that must themselves be treated as single charged entities. Where charged foreign species are present in sufficiently large number, then intrinsic defects become negligible.

Charged foreign atoms affect the solubility of each other in the host lattice where there is more than one species, since these atoms introduce defects into the lattice Kroger gives 3 cases:

1. Concentrations of both are too low to dominate the neutrality condition; there is no effect unless they combine.
2. Only one of the foreign species dominates the neutrality condition, affecting the solubility of the other.
3. Both dominate the neutrality condition, and the solubility of both is affected.

Interaction is such that the solubility is decreased if both foreign species give rise to centres of the same charge, and increased where the charges are opposite. Initial studies on cerium oxide simultaneously doped with both lower (Y^{3+}, In^{3+}) and higher (Nb^{5+}) cations were carried out at Imperial College (156,157). Results were inconclusive as an AC impedance technique was used to measure conductivity; the conductivities were later found to be considerably higher using a 4 probe technique.

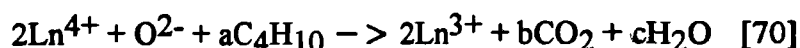
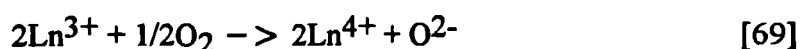
Wang et al (111) recently examined the effect of adding Nb or Ta to CeO_2 doped with trace amounts of In^{3+} . They found that addition of the higher valent ion reduced the number of (InV_O) associates for 300 to 500 ppm of Nb or Ta. The effect was found to be the same for both ions, and was therefore attributed to the charge of the cation rather than the specific cation. Wang noted that the ion had to be added in excess of what was expected given the number of pairs, and assumed that unintentional impurities had introduced additional oxygen vacancies. The compensating oxygen introduced with the Nb or Ta dopant is believed to occupy any oxygen vacancies present.

It was hoped, in this study, that the low solubility of Nb in cerium oxide could be increased by doping with lower valent atoms also, and that such a procedure would lead to improved expansion-contraction properties during oxidation and reduction, and possibly increase the σ_{max} in $\ln pO_2$ 1/T space.

3.5 CATALYTIC PROPERTIES

Nonstoichiometry is believed to be an important factor in the catalytic properties of a ceramic (60). There is a large amount of research in this field looking at cerium oxide based catalysts, and using cerium metal or oxide as additives in other catalysts such as precious metals (77, 133-140), in addition to those papers already discussed in section 2.4. The work of Hattori et al (133) is the most interesting.

Cerium oxide was found to be the most active catalyst, from the series of lanthanide oxides, in the production of CO₂ during the oxidation of butane. At 400° and 450°C the yields of CO₂ on CeO₂ were far higher than on any other lanthanide oxide. As the temperature was increased the difference became less marked, but CeO₂ always gave the highest yield. Both the conversion of oxygen and yield of CO₂ increased with sample weight. Of the series of lanthanide oxides, lanthanum was found to have the lowest activity. The activity decreased from Ce to Gd, and again from Tb to Lu; Tb having the highest yield after Ce. Hattori surmised that ionisation of the Ln³⁺ to Ln⁴⁺ was important, as had been previously suggested by other researchers. For the oxidation of butane



Thus ceria is only active in a reducing atmosphere, where a large number of Ce³⁺ ions are available. The ionisation potential difference between 4fⁿ and 4fⁿ⁻¹ subshells consists of a coulomb attraction energy, and the interaction between the 4f electrons. The latter is divided into a repulsion energy and an exchange energy. The high activity of cerium oxide corresponds to the smaller coulomb attraction between the Xe shell and the 4f electron; the Xe shell for Ce has a smaller charge and larger ionic radius than for the succeeding lanthanide oxides. Cerium oxide also has a zero exchange energy in both charged states, there being only 1 or 0 electrons in the 4f shell. Tb also has a zero exchange energy, but a larger coulombic interaction. The 4th ionisation potential of La₂O₃ is extremely high, as it involves breaking into the Xe shell. The reaction products were CO₂, CO, CH₄, C₂H₄, C₃H₆ and various butenes. CeO₂ gave the lowest yield of CO and negative yields of butenes, traces having been present in the butane reactant.

Mackrodt et al (139) found that a catalyst composed of Ce(75%), Pr (8%) and La(17%) oxides had an activity fortyfour times higher than that of pure ceria for the catalytic combustion of methane. These studies were carried out at temperatures close to the sintering temperature. The La was required to prevent sintering of the catalyst at those temperatures. Ceria has been used by Yao et al (137) in automotive catalysts. Here it was the Ce^{4+} to Ce^{3+} reaction that was important. Ceria enhances the CO removal from exhausts under oxygen deficient conditions by supplying lattice oxygen that is then replaced in oxygen rich conditions. Otsuka et al (140) use CeO_2/Ce metal to decompose water relying on the same properties.

Thus it would appear that lattice oxygen and the oxidation/reduction between Ce^{4+} and Ce^{3+} are important in controlling the catalytic properties of cerium oxide, and go some way to explaining why no carbon deposition was found by Mogensen (71-73). Provided that oxygen is supplied at a sufficient rate through the electrolyte to the catalyst, it seems that there should be no problem with carbon deposition on a ceria anode in a fuel cell. However, it is unlikely that carbon deposition can be avoided under high temperature reducing conditions when the cell is not in use.

4. EXPERIMENTAL METHOD AND APPARATUS

This chapter is divided into sections dealing with the relevant experimental techniques and apparatus used. There is also a section dealing with initial experiments, and their influence on the main body of experimental work that was carried out

4.1 SAMPLES

All samples used are listed below.

INTENDED COMPOSITION	SAMPLE NAME
(initial samples)	
$\text{Ce}_{0.89}\text{In}_{0.05}\text{Nb}_{0.06}\text{O}_{2-x}$	I6
$\text{Ce}_{0.925}\text{In}_{0.035}\text{Nb}_{0.04}\text{O}_{2-x}$	I4
$\text{Ce}_{0.9075}\text{In}_{0.0475}\text{Nb}_{0.045}\text{O}_{2-x}$	I45
$\text{Ce}_{0.895}\text{In}_{0.05}\text{Nb}_{0.055}\text{O}_{2-x}$	I55
$\text{Ce}_{0.935}\text{Y}_{0.03}\text{Nb}_{0.035}\text{O}_{2-x}$	Y35
$\text{Ce}_{0.98}\text{Y}_{0.02}\text{O}_{2-x}$	Y0
(prepared by previous workers (156-157))	
$\text{Ce}_{0.965}\text{Y}_{0.03}\text{Nb}_{0.005}\text{O}_{2-x}$	Y05
$\text{Ce}_{0.96}\text{Y}_{0.03}\text{Nb}_{0.01}\text{O}_{2-x}$	Y1
$\text{Ce}_{0.955}\text{Y}_{0.03}\text{Nb}_{0.015}\text{O}_{2-x}$	Y15
$\text{Ce}_{0.95}\text{Y}_{0.03}\text{Nb}_{0.02}\text{O}_{2-x}$	Y2
$\text{Ce}_{0.895}\text{Y}_{0.05}\text{Nb}_{0.055}\text{O}_{2-x}$	Y55
$\text{Ce}_{0.82}\text{Y}_{0.1}\text{Nb}_{0.08}\text{O}_{2-x}$	Y8
$\text{Ce}_{0.835}\text{Y}_{0.1}\text{Nb}_{0.065}\text{O}_{2-x}$	Y6
(high purity)	
$\text{Ce}_{0.965}\text{Y}_{0.03}\text{Nb}_{0.005}\text{O}_{2-x}$	I
$\text{Ce}_{0.96}\text{Y}_{0.03}\text{Nb}_{0.01}\text{O}_{2-x}$	E
$\text{Ce}_{0.955}\text{Y}_{0.03}\text{Nb}_{0.015}\text{O}_{2-x}$	G
$\text{Ce}_{0.95}\text{Y}_{0.03}\text{Nb}_{0.02}\text{O}_{2-x}$	D
$\text{Ce}_{0.945}\text{Y}_{0.03}\text{Nb}_{0.025}\text{O}_{2-x}$	J
$\text{Ce}_{0.94}\text{Y}_{0.03}\text{Nb}_{0.03}\text{O}_{2-x}$	A
$\text{Ce}_{0.935}\text{Y}_{0.03}\text{Nb}_{0.035}\text{O}_{2-x}$	B
$\text{Ce}_{0.93}\text{Y}_{0.03}\text{Nb}_{0.04}\text{O}_{2-x}$	C
$\text{Ce}_{0.925}\text{Y}_{0.03}\text{Nb}_{0.045}\text{O}_{2-x}$	H
$\text{Ce}_{0.92}\text{Y}_{0.03}\text{Nb}_{0.05}\text{O}_{2-x}$	F

4.2 SAMPLE PREPARATION

4.2.1 POWDER PREPARATION

The ceramic powders were prepared by a coprecipitation technique. The name given is self-explanatory, but there are a number of ways that it has been carried out by different workers. Readey et al (141), preparing zirconia, started with soluble chloride salts, a solution of which was dropped into excess ammonia solution. Wan and Duh (142-143), preparing a $\text{ZrO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3$ mixed oxide, started with chlorides and nitrates, and dripped ammonia solution into a solution of the starting materials, gradually increasing the pH. Shei (144), making a superconducting material, dissolved nitrates, including copper, in nitric acid and dripped this solution into a precipitating agent. In this case the precipitating agent was prepared by dissolving triethylamine in oxalic acid. This was better for his powders, as copper tends to form complexes with ammonia. Khurana et al (145) also dripped their cation solution into excess precipitating agent sodium hydroxide.

The basic idea is as follows: a homogeneous solution of metal cations in the required proportions is precipitated simultaneously. Thus coprecipitation of cations in ceramic preparation produces a good homogeneous material, compared to that produced by a mixed oxide method that relies on mechanical mixing of solid powders and cation diffusion during calcining. As has been shown above, workers have achieved this either by dripping the cation solution into the precipitating agent (usually an alkali) or by dripping the precipitating agent into the cation solution. Lessing (146) pointed out that the pH of the solution containing the precipitate affects both the point and extent of precipitation of each cation. This is backed up Duh and Wan (143), who found that the final pH they reached affected the surface area of the powders produced, the density of sintered specimens and the achieved concentration of additives. The powders used in this study were prepared by adding the cation solution to excess ammonia solution.

The following were used to prepare the initial samples: (Aldrich Chemicals) $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 99.9%; $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ 99.9%; $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ 99.9%; NbCl_5 99+%. The following were used to prepare the later high purity samples: (Johnson Matthey) $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 99.99% (2/5/<1ppm Si/Al/Ca); $\text{Y}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ 99.99% (10/5/1); NbCl_5 puratronic (2/<0.3/0.5).

The water content of the yttrium nitrate was found to by thermal decomposition to be $x = 5.7$. The relative amount of each of the above salts required for a particular

composition of powder was calculated, assuming that nothing would be lost during preparation. The nitrates were dissolved in warm distilled water and the chloride in concentrated hydrochloric acid. The chloride solution was then added to the nitrate solution. This was stirred continuously using a magnetic stirrer. The most important consideration is that the precipitating cations are completely insoluble in the precipitating agent. Examination of the Pourbaix diagrams (147) for each of the cations (figs 4.2a-d) shows that cerium and yttrium hydroxides form, which are insoluble in alkaline conditions. Niobium oxide is insoluble across the entire range of pH. There may be some niobate formation, but this is unconfirmed. Indium behaves rather differently, forming a hydrated oxide that is soluble at high pH. However, according to Remy (148), whilst being soluble in excess caustic alkalis, the material is insoluble in ammonia solution, forming no complexes. Consequently, it was to be expected that all cations should precipitate as insoluble oxides or hydroxides in excess ammonia solution.

The cation solution was dripped slowly into excess ammonia solution, which was being stirred continuously, and a gel-like precipitate formed. This was then centrifuged and washed in ammonia solution (pH~13) in order to remove any remaining chloride ions. The gel was then refluxed in butanol for the initial samples, and heptanol for the high purity samples for between 1 and 2 hours. Research (141, 149) has shown that mixing the precipitate with alcohol results in softer agglomeration of powders. It has been suggested (149) that water molecules form hydrogen bonds both with chemical groups on the surface of the powder particles and between themselves, thus forming bridges between particles. When the water is replaced by alcohol, the alcohol molecules bond to the powder surface, but these bonds are terminal, as the alcohol cannot bond to another alcohol molecule at the same time. It has also been found that the heavier the alcohol the softer the agglomeration (150). Softer agglomeration of powders is preferable because these compact more easily. Refluxing with an alcohol of higher boiling point than water causes the alcohol molecules to replace the water molecules on the powder surface.

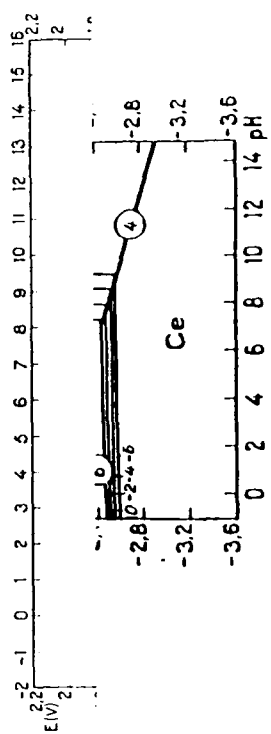
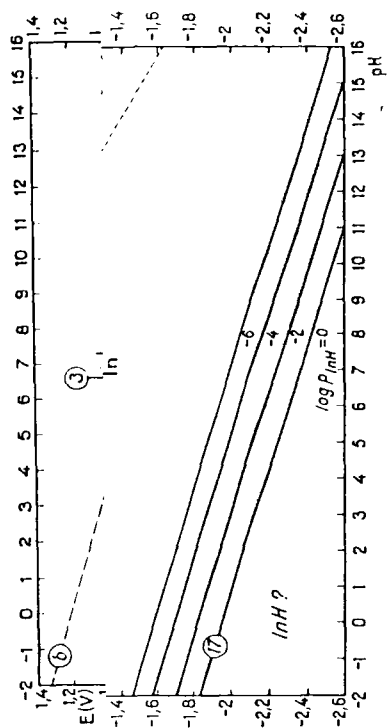
The refluxed material, still gel-like, was centrifuged and dried for two days in a Buchi furnace at a temperature sufficiently high enough to evaporate the alcohol (110-160°C depending on the alcohol used). This dried material was ground with a pestle and mortar and ballmilled in ethanol for two days, in a polythene bottle and with two sizes of calcia stabilised zirconia milling balls. The resulting slurry was dried under an infra red lamp and ground to a fine powder. The powder was calcined at 850°C for 8 hours in order to convert any hydroxides to oxides. Initial samples were prepared with glass

beakers and centrifuge tubes. The high purity samples were prepared with polypropylene beakers and spatulas, and polyallomer centrifuge tubes available from BDH.

4.2.2 SINTERING OF SOLID SAMPLES

Sintering is very important, in that it affects the porosity and grain structure of the final solid sample. A number of sintering studies have been made, mainly referring to zirconia (151-154) but also alumina (155). A summary of the pertinent results is given. There are three main types of pore in a green material: macropores, coarse micropores and fine micropores. Macropores are not eliminated during sintering, but have the same shrinkage as the bulk. Coarse micropores increase during sintering, and fine micropores are eliminated. There are two mechanisms involved: approaching particle centres is caused by atom transport by either grain boundary or lattice diffusion with the grain boundaries acting as a vacancy sink; pore coalescence occurs when material is transferred from one pore surface to another by any of grain boundary diffusion, lattice diffusion and surface diffusion, vaporisation and condensation. Large pores in a sample inhibit grain growth, as do second phase particles. Alumina, silica and titania have been used as sintering aids. These tend to form an intergranular glassy phase however, which can be undesirable. It is important to eliminate macropores and coarse micropores in the pressing stage of preparation.

All initial samples were pressed dry, heated at a ramp rate of 5°C/min and held at 1550 or 1600°C for 6 hours, then cooled to room temperature at a rate of 5°C/min. Most of the powders were sintered in the form of pellets having a diameter of 10mm, though some bar shaped samples were also made. The high purity samples were pressed with acetone, to ensure a hard compact that did not disintegrate during handling. These samples were pressed in bar form in Tokyo, and had to be carried to a furnace across the other side of the campus. They were fired in a vertical siliconite furnace, having a recrystallised alumina tube, at 1500°C for 12 hours. The furnace was cooled to 1200°C to allow exchange of samples. Each changeover took about 40 minutes.



4.3 INITIAL INVESTIGATIONS

At the start of the project, investigations were an extension of those carried out by previous workers (156-157) participating in short projects at Imperial College.

Cerium IV Oxide was doped with both lower (In^{3+} , Y^{3+}) and higher (Nb^{5+}) valent cations, in order to improve the electronic conductivity at low $p\text{O}_2$. These materials were fabricated using the methods described in section 4.2. Samples prepared by the earlier workers were also used. All samples are listed at the start of this chapter (section 4.1). The materials were characterised by a number of techniques as is described. Data relating to the lattice parameter, thermal expansion coefficient and conductivity of these samples will not be discussed in this section, but in chapter 5.

4.3.1 ELECTRON MICROSCOPY

Sintered pellets were polished to 1μ using diamond paste. They were then thermally etched by placing in a furnace at 1200°C for 20 minutes. After carbon coating, they were examined on either the Jeol T200 or the JSM35-CF microscope.

TABLE 4 3.1a ELECTRON MICROSCOPY AT IMPERIAL COLLEGE

SAMPLE	MICROSCOPE/EXAMINATION	RESULT
I4	JSM35, quantitative analysis before and after grinding further	m. Ce(96.5)In(1)Nb(2.5) sp. Ce(56)In(13.2)Nb(30.8)
I45	JSM35, quantitative analysis before and after grinding further	m. Ce(97.3)In(0.2)Nb(2.5) sp. Ce(56)In(0.1)Nb(43.9)
I55	JSM35, quantitative analysis before and after grinding further	m. Ce(97.3)In(0.2)Nb(2.5) sp. Ce(52.9)In(0.5)Nb(46.6)
I6	JSM35, quantitative analysis before and after grinding further	m. Ce(95.5)In(1.1)Nb(3.4) sp. Ce(54.9)In(1.7)Nb(43.4)
Y55	JSM35, quantitative analysis, only one spot examined	m. Ce(92.4)Y(4.5)Nb(3.1) sp. Ce(42)Y(20.4)Nb(37.6)
Y0	T200, backscattered	no second phase

m.=matrix sp.=second phase

Several spots of each sample were analysed during quantitative analysis unless otherwise indicated. In some cases analysed samples were ground further and re-examined to check the homogeneity of the composition. In these cases no difference was found on comparing the results.

A second phase was found in all samples containing indium, and the proportion of indium was very much lower than had been expected. In most cases it can be considered negligible. However, in sample I4, the indium appeared to have segregated predominantly to the second phase. The composition of those second

phase spots varied $1\% < \text{In} < 50\%$ with respect to the other cations. The result given is the average. The second phase can be seen in the photographs (figs 4.3.1a-f), and T200 qualitative analysis data is also included.

Two samples were examined on a Hitachi 9000 transmission electron microscope with STEM and a KEVEX thin film analyser while in Tokyo. They were prepared by grinding with 0.5μ alumina paste to a thickness of $70\text{--}150\mu$ and dimple grinding to a thickness of $20\text{--}40\mu$ using a Gatan Nissei model 656N dimple grinder. The samples were then inserted into a molybdenum or copper mesh and put in an ion beam thinner until the first hole was visible. The supervision and assistance of Professor T. Yano, and Dr. Kato is acknowledged here.

TABLE 4.3.1b ELECTRON MICROSCOPY AT TOKYO INSTITUTE OF TECHNOLOGY

SAMPLE	EXAMINATION	RESULT
Y35	STEM with thin film analysis, photographs	no second phase, but amorphous Si-Al-O grain boundary phase
Y0	STEM with thin film analysis, diffraction mode, HRSTEM, photographs	Si-Al-O grain boundary phase

No second phase was found in either of these samples, but a ternary point/grain boundary phase was found. Analysis proved that this was rich in silica and alumina and was amorphous. The analyses and photographs can be seen in figs(5.3.1g-l). The presence of this phase in both samples led to the belief that it was due to general impurity and would be present in all samples. Examination of sample Y0 under high resolution conditions indicated that the phase may run the entire grain boundary length. Examination of the high resolution photographs (figs5.3.1m-o) shows a possible glassy phase with a few areas of short range order.

4.3.2 X-RAY DIFFRACTION

Pellet samples, both polished and unpolished were examined on a Philips diffractometer to check whether the material was single phase. Initial studies indicated that there were additional peaks, i.e. peaks over and above those given for ceria (JCPDS), for all samples examined, including those containing no niobium. In the Indium containing samples, there were sufficient extra peaks, and the same extra peaks for each sample, for a CeNbO_4 type phase to be identified. However, in samples where the niobium concentration was low, it was thought unlikely that such a phase should exist, and none had been found by electron microscopy. The computer software suggested a number of materials that could be responsible, but because the number of additional peaks was small in these cases, a match was difficult to find.

The only likely material suggested was aluminium, from which the sample holder was made. Examples of the x-ray diffraction patterns obtained and comparison with JCPDS data can be seen in figs 5.3.2a-d. The experiment was repeated using a glass sample holder, and after polishing of samples. The number of excess peaks was reduced.

4.3.3 DISCUSSION

In those samples in which a second phase was found both by x-ray diffraction and SEM examination, that phase is believed to be a CeNbO_4 type phase. This is the phase that was found in niobia doped ceria by Shingler (60) and Naik and Tien (79). InNbO_4 and YNbO_4 (158) are similar compounds. YNbO_4 has the same structure as CeNbO_4 and that of InNbO_4 is slightly different because of the smaller ion size. The CeNbO_4 structure is capable of accommodating an oxygen excess (159) and can be described in terms of a distorted fluorite (160). The ionic charges in the compound have been found to be 5+ for niobium and 3+ for cerium (161). The variable valency of the cerium ion allows the oxygen excess to be accommodated. An oxygen excess may also be introduced by doping with higher valent cations (162).

In this case it is likely that cerium ions are replaced with the ternary ions yttrium and indium, having no effect on stoichiometry. It was noticed however, that in sample I4 the high indium content in the second phase appeared to be accompanied by a decreased niobium content, probably because of the smaller ion size. The charge deficit may be balanced by a change to 4+ in the charge of some of the cerium ions, or by a deficit of lattice oxygen. In either case the phase would be highly defective. Examination of the second phase compositions in table 4.3.1a show the cerium content to be higher than the sum of the niobium and indium contents in each case. Given that the second phase spots are small this could well be attributed to a contribution from the matrix cerium.

On considering the lack of indium in the majority of samples studied, it was suggested that the material may have been lost as a vapour phase In_2O during sintering (163). Those samples containing little indium had a marked tendency to react with the alumina tray used, whereas sample I4 did not stick at all. Alternatively, although indium oxide does not form complexes with ammonia, it does have an affinity for organic complex formation (148), and it is possible that the In may have formed complexes with the alcohol used during the refluxing stage of the powder preparation. In recent work by Wang et al (111) on ceria doped with trace amounts of In, it was found that 25-50% of In was lost during calcination at 1550-1600°C. The

evaporated In was partly absorbed by the alumina sample holder, and the rest deposited on the furnace. They also observed that In was more often to be found in nonrepresentative regions of the material than in the bulk. Whatever the case, there was no difference in the preparation procedure for sample I4 as compared to the others. The difficulty in getting indium to stay in the sample, and its preference for a second phase, when this was achieved, meant that study of the Ce-In-Nb Oxide system was discontinued.

The intergranular phase found in TEM investigations has been found by previous researchers (60, 106-107) and has been found to affect the conductivities of the materials. Since it was intended that extensive conductivity measurements be made, it was decided that a series of samples should be made from material as near as possible free from silica and alumina impurities.

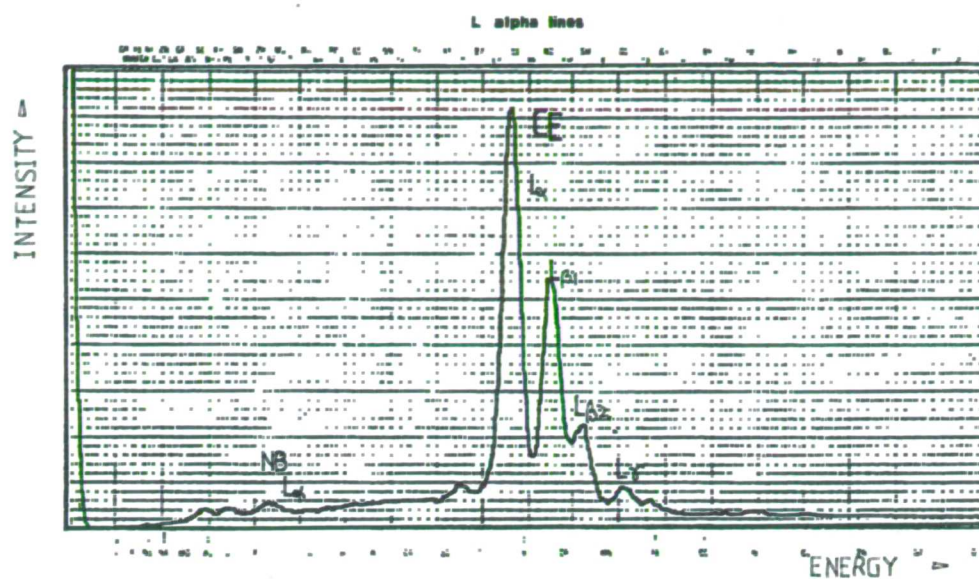


FIG.4.3.1a EDAX ANALYSIS OF SAMPLE I6 AT X1500

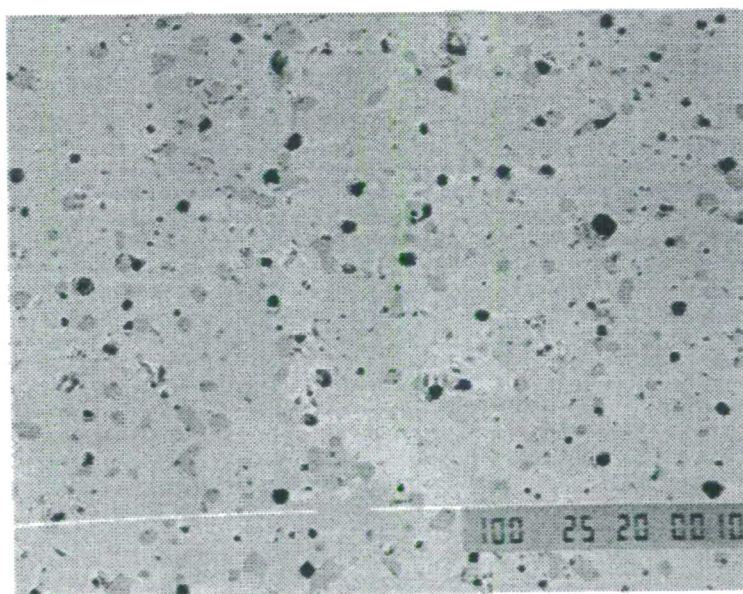


FIG.4.3.1b SEM BACKSCATTERED MICROGRAPH OF I6 AT X500

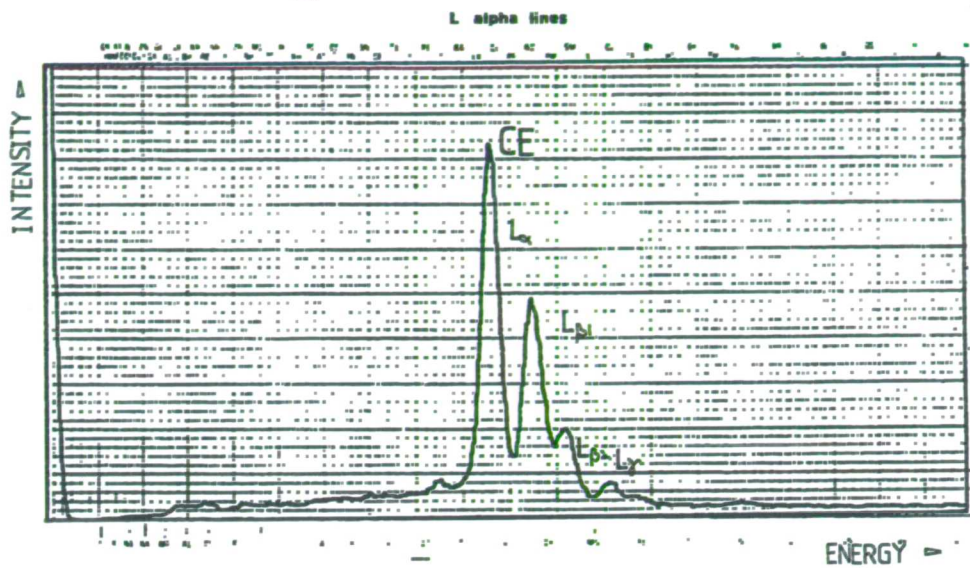


FIG.4.3.1c EDAX ANALYSIS OF MATRIX OF SAMPLE I6 AT X20000

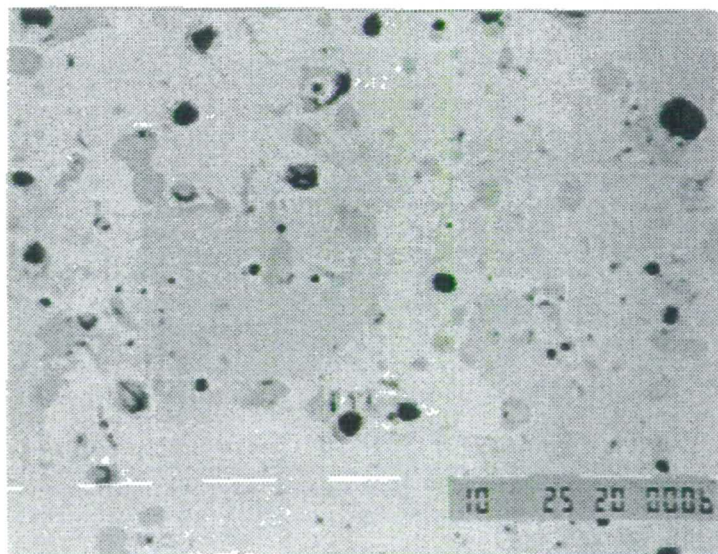


FIG.4.3.1d SEM BACKSCATTERED MICROGRAPH OF I6 AT X1000

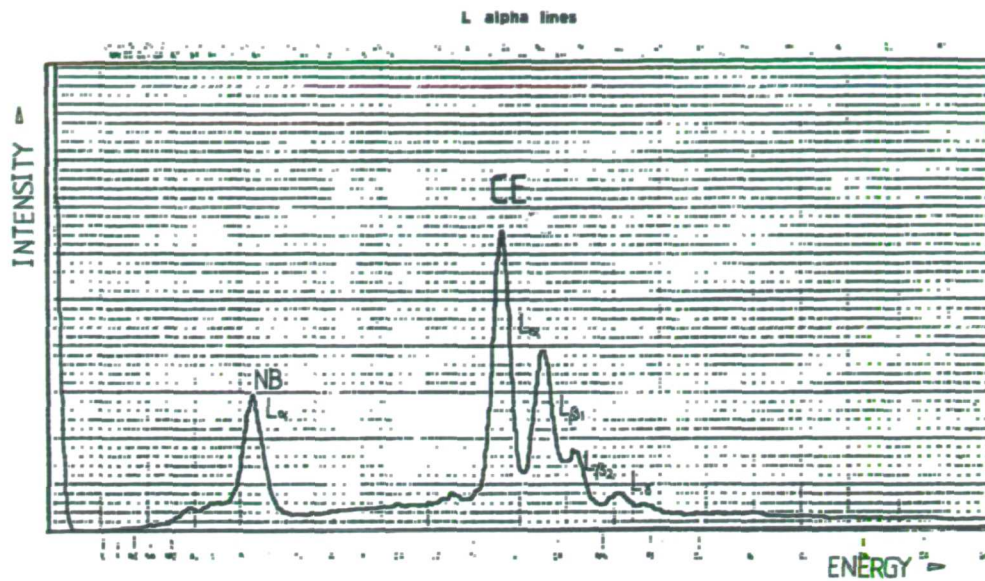


FIG.4.3.1e EDAX ANALYSIS OF SECOND PHASE OF SAMPLE I6 AT X20000

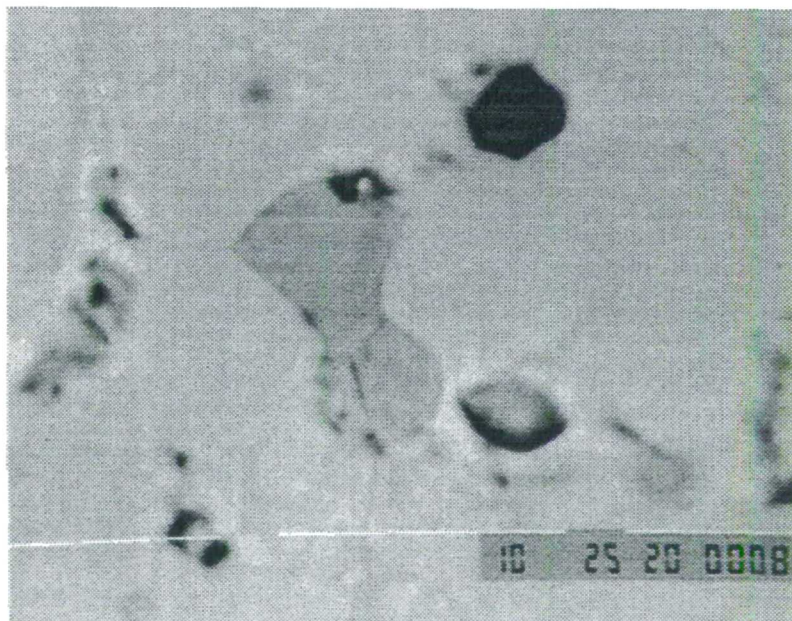


FIG.4.3.1f SEM BACKSCATTERED MICROGRAPH OF I6 AT X3500

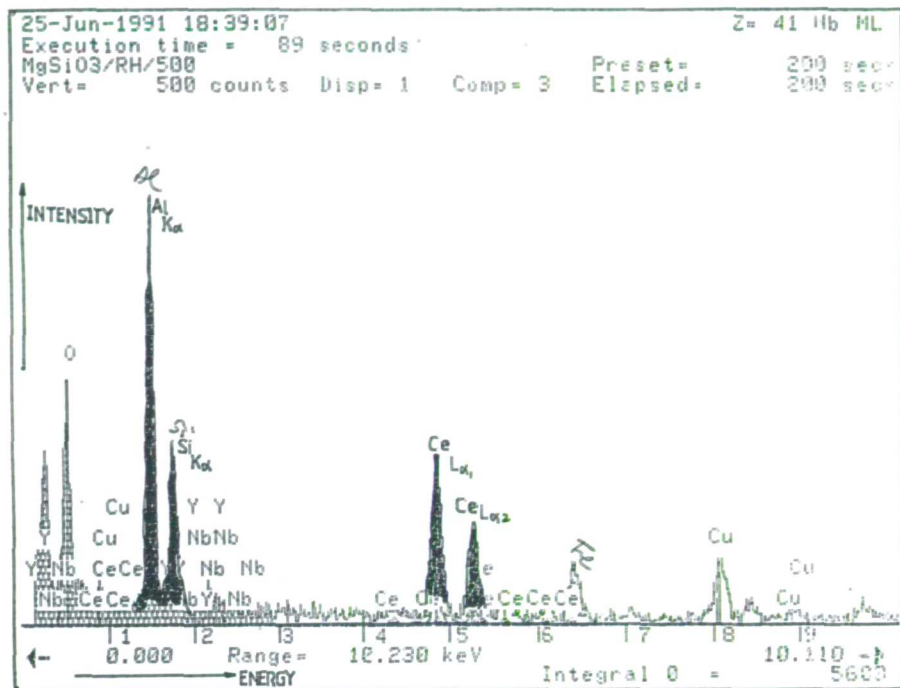


FIG.4.3.1g EDAX THIN FILM ANALYSIS OF THE TRIPLE POINT PHASE , SAMPLE Y35



FIG.4.3.1h SAMPLE Y35 TRIPLE POINT PHASE, X50000



FIG.4.3.1i SAMPLE Y35 TRIPLE POINT PHASE, X50000

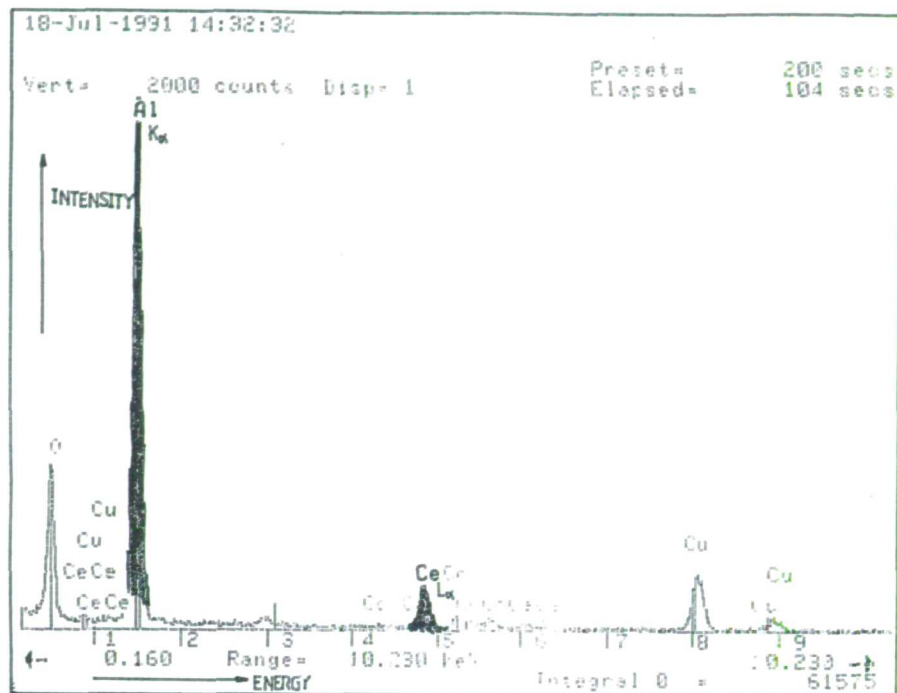


FIG.4.3.1j EDAX THIN FILM ANALYSIS OF THE TRIPLE POINT PHASE , SAMPLE Y0



FIG.4.3.1k SAMPLE Y0 TRIPLE POINT PHASE, X50000

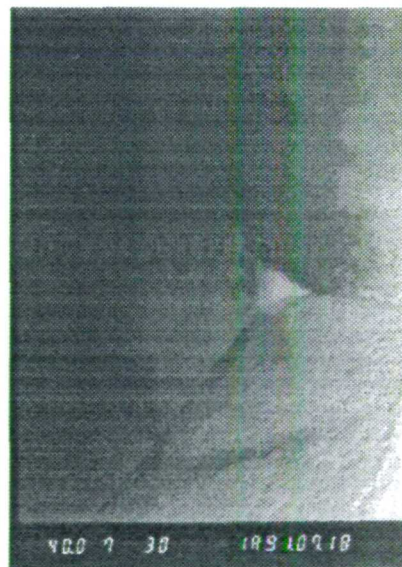


FIG.4.3.1l SAMPLE Y0 TRIPLE POINT PHASE, X40000

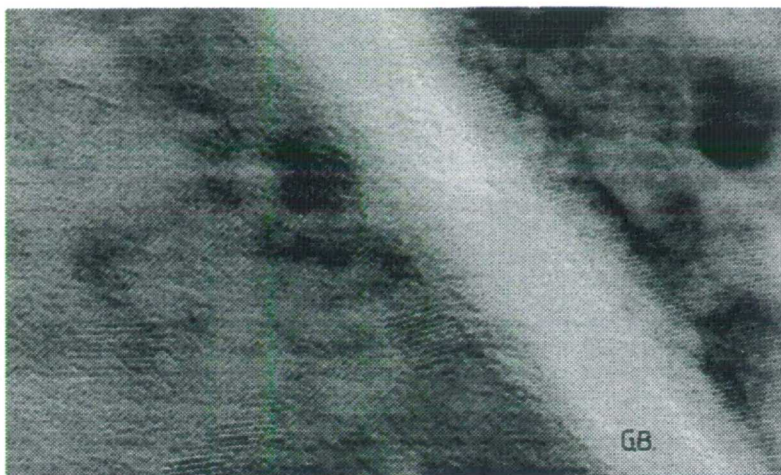


FIG.4.3.1m HRTEM MICROGRAPH GRAIN BOUNDARY SAMPLE Y0, 1cm $\approx$ 3.4nm

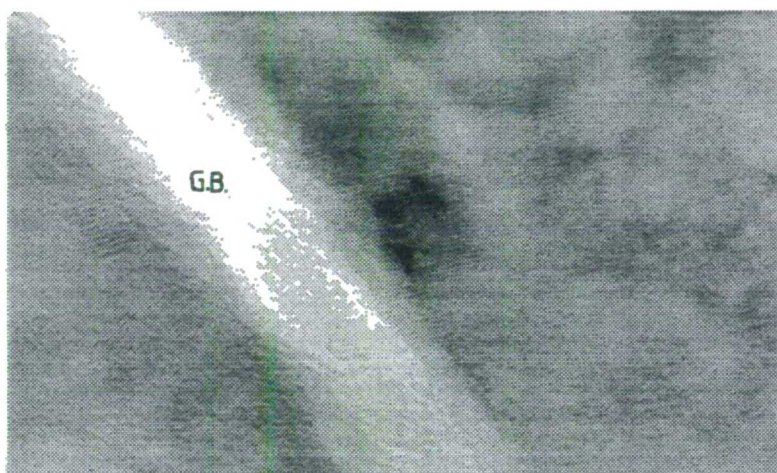


FIG.4.3.1n HRTEM MICROGRAPH GRAIN BOUNDARY SAMPLE Y0, 1cm $\approx$ 3.4nm

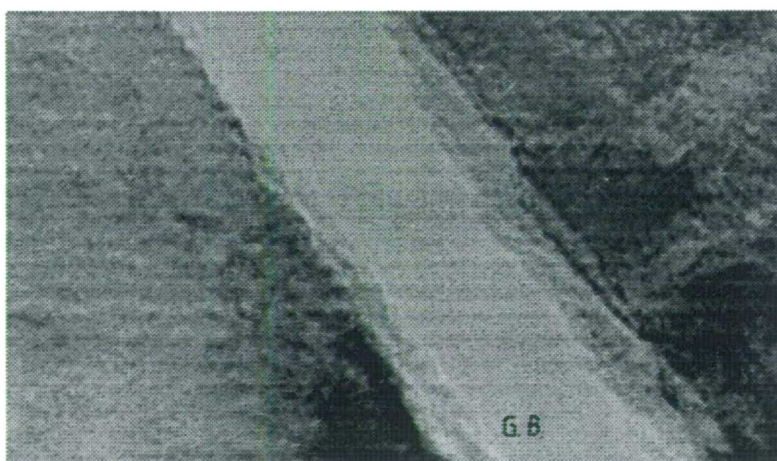


FIG.4.3.1o HRTEM MICROGRAPH GRAIN BOUNDARY SAMPLE Y0, 1cm $\approx$ 3.4nm

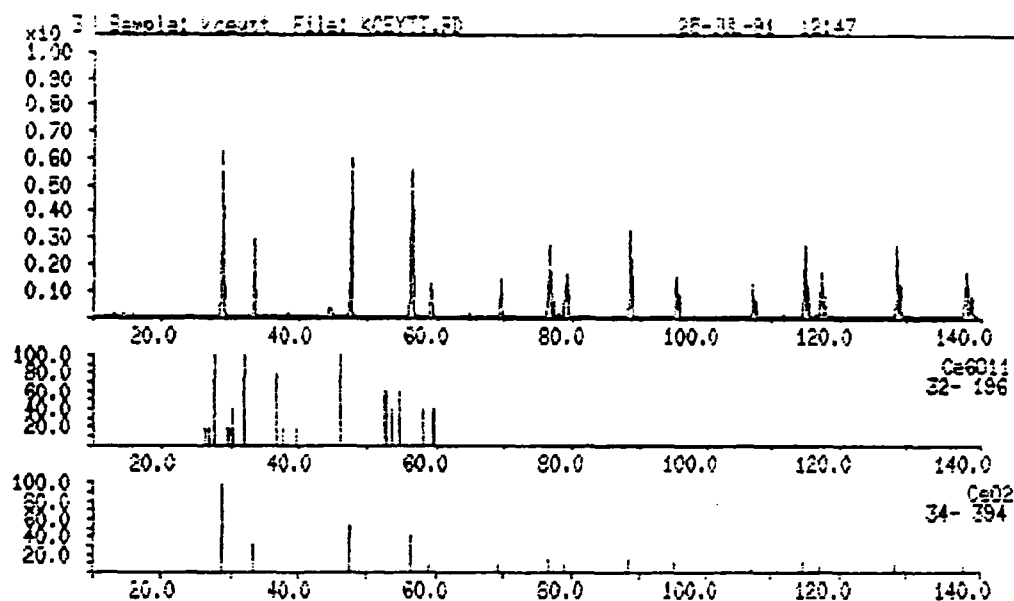


FIG. 4.3.2a XRD TRACE FOR SAMPLE Y0 COMPARED WITH Ce₆O₁₁

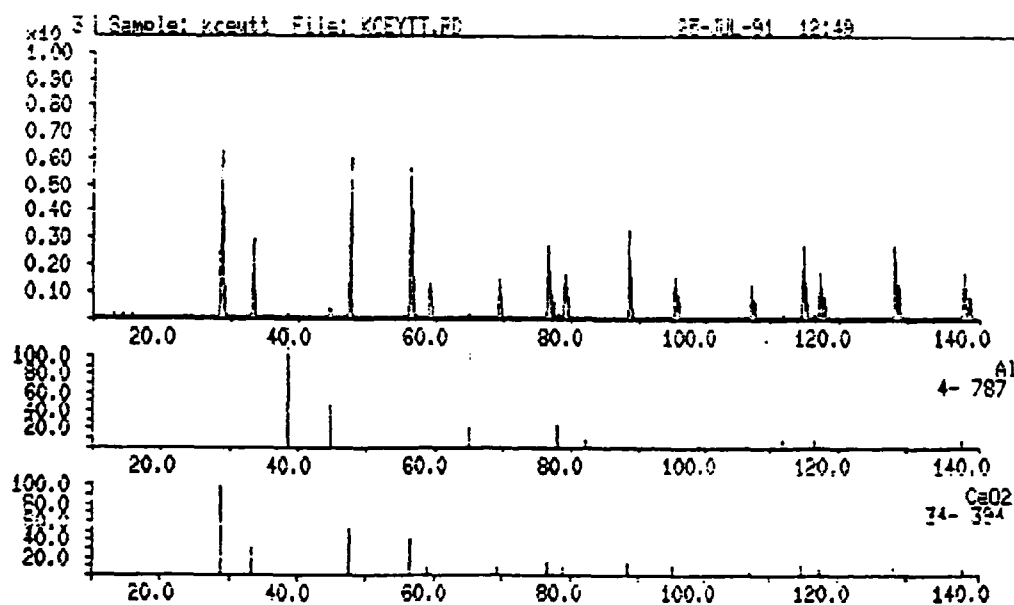


FIG. 4.3.2b XRD TRACE FOR SAMPLE Y0 COMPARED WITH Al

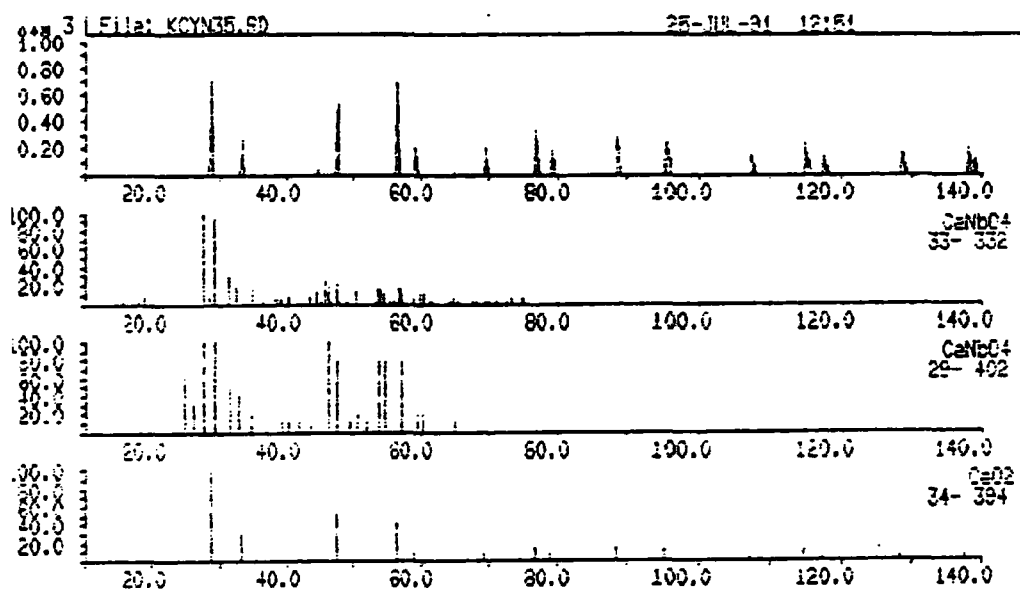


FIG. 4.3.2c XRD TRACE FOR SAMPLE Y35 COMPARED WITH CeNbO_4

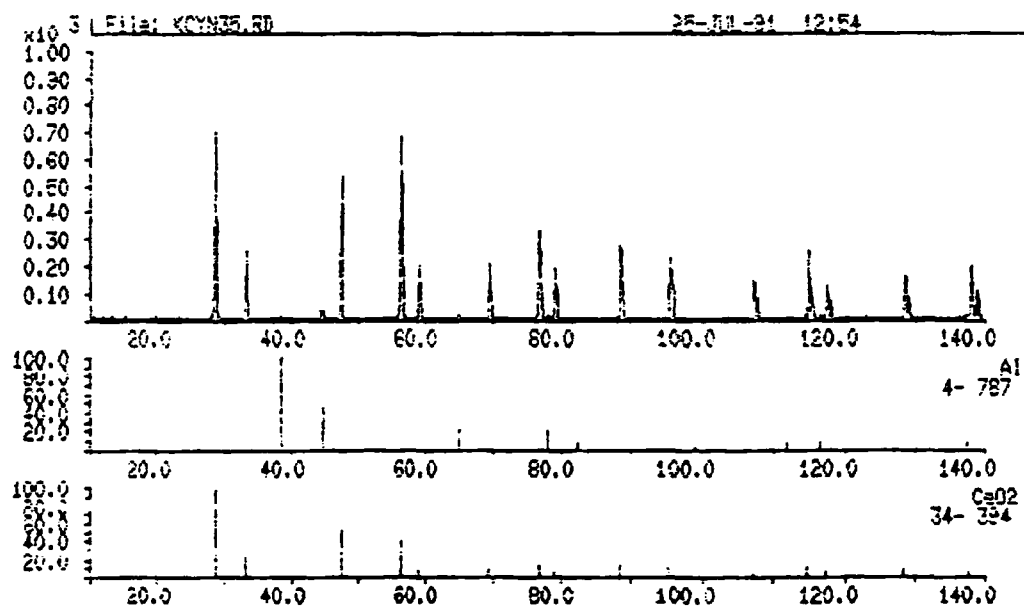


FIG. 4.3.2d XRD TRACE FOR SAMPLE Y35 COMPARED WITH Al

4.4 EXPERIMENTAL RIG FOR THERMOGRAVIMETRIC AND CONDUCTIVITY EXPERIMENTS

Thermogravimetric and conductivity experiments were carried out at the Research Laboratory for Nuclear Reactors at the Tokyo Institute of Technology under the guidance of Prof. T.Maruyama and Prof. Y.Saito. The following people were involved in the master design of the rig whilst I was in London: Prof. Saito, Prof. Maruyama, Dr.B.Onay and masters student Shin Uchino. Some alterations and changes were initiated by myself, once in Tokyo, and construction of the rig was carried out by myself and Shin Uchino with assistance from Dr. Onay (particularly with glassblowing). The aim was to produce a rig on which the thermogravimetric and conductivity experiments could be carried out simultaneously. The experimental rig was firmly secured to guard against earthquake. Thermogravimetric experiments were carried out primarily by Shin Uchino, under my supervision. Conductivity experiments were carried out by me.

4.4.1 GAS SYSTEM

The gas system was designed such that there were two wings, each with their own circulation unit, and which could be sealed off from the rest of the system. The gas used in the system was carbon dioxide, and this could be reduced locally in each wing with an oxygen pump. The system needed to be vacuum tight. A schematic diagram is given below.

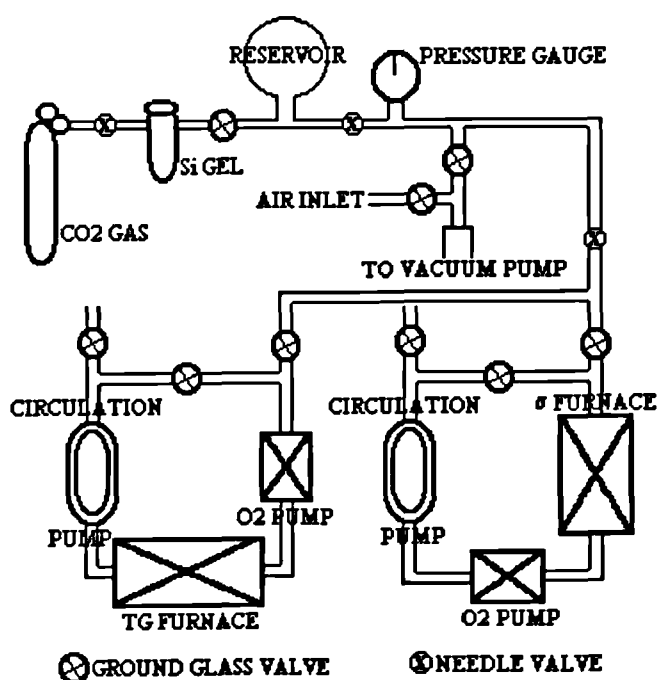


FIG.4.4.1a GAS SYSTEM

The circulation pump was supplied by Misuzu company. The gas is circulated when an ac electricity supply applied to the magnetic coil forces the piston to move up and down. See the diagram below.

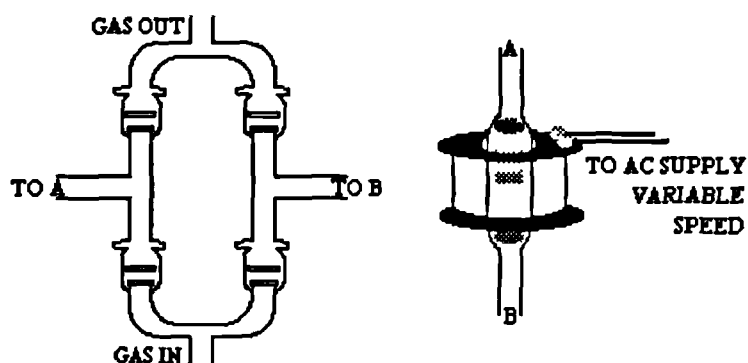


FIG. 4.4.1b CIRCULATION PUMP

The speed of the pump was controlled by varying the ac frequency.

4.4.2 OXYGEN PUMPS AND SENSORS

The oxygen pressure was controlled by reducing the carbon dioxide gas via a zirconia electrolyte according to the equation:

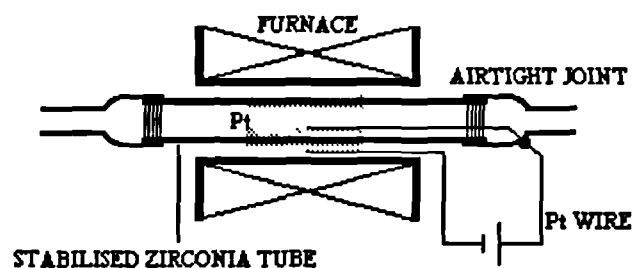


FIG. 4.4.2a OXYGEN PUMP

This can be done using an oxygen pump, and gives better control of the oxygen pressure, particularly in the intermediate pressure range, than mixing gases (164-165). The oxygen pumps were made as shown in fig. 5.5.2a. Ytria or calcia stabilised zirconia tubes were given inner and outer electrodes by painting with platinum paste, and securing a platinum mesh fused to platinum wire onto the painted surface. This was heated slowly to 1000°C held for ten minutes at that temperature and cooled. The

tubes were sealed into the glass system by winding the ends with cotton thread, fitting a made-to-fit glass head at each end and sealing the joint with araldite epoxy resin.

During pump operation, a voltage is applied to the electrodes. The reaction can be driven in either direction, depending on the electrode polarity. A galvanostat/potentiostat was used to apply the voltage. The reactions that occur at each electrode are:



at the inner surface and



at the outer surface.

The oxygen sensors operate on the same principles as the pump. The difference in oxygen pressure across the electrolyte results in a potential, which can be measured by attaching a voltmeter across the electrodes. The oxygen pressure can then be calculated from the following equation:

$$E = RT (\ln (0.21/p\text{O}_2)) / 4F \quad [4]$$

where E is the measured potential, 0.21 is the oxygen pressure of the air environment in atmospheres, and $p\text{O}_2$ is the pressure in the system.

The sensors were constructed in a manner similar to that of the pumps and can be seen in fig. 4.4.2b.

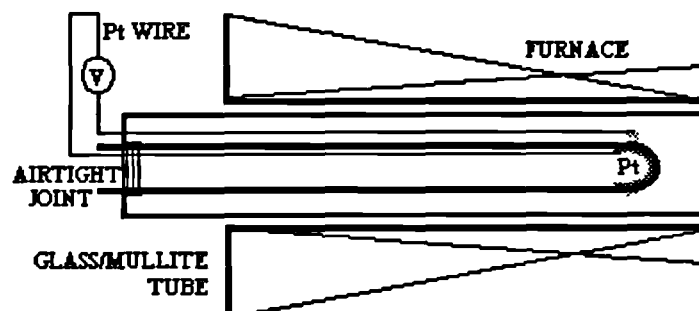


FIG. 4.4.2b OXYGEN SENSOR

4.4.3 THERMOGRAVIMETRIC BALANCE

A shimadzu TGA-41 thermobalance was incorporated into the system, and some adjustments made to the basic design. The operating principles of the balance are as follows. Two photoelectric diodes receive light from a lamp situated in the balance mechanism through a shutter on the beam of the balance. This allows the position of the beam to be precisely determined. A schematic diagram is given.

The balance is described as having a special alloy taut band. The beam is made of quartz glass. This has a low coefficient of thermal expansion minimising apparent weight changes. As the furnace used to heat the sample was very much larger than that supplied with the balance, the temperature was controlled separately, and a TG31 weight measurement unit was used. The TG41 unit would not operate unless it could also control the furnace temperature. The oxygen pressure was also controlled separately. The error in measurements with respect to the balance sensitivity was given in the manual as 2% of the full scale for ranges of 1 and 2mg, and 1% of the full scale for all ranges between and including 5 and 2000mg.

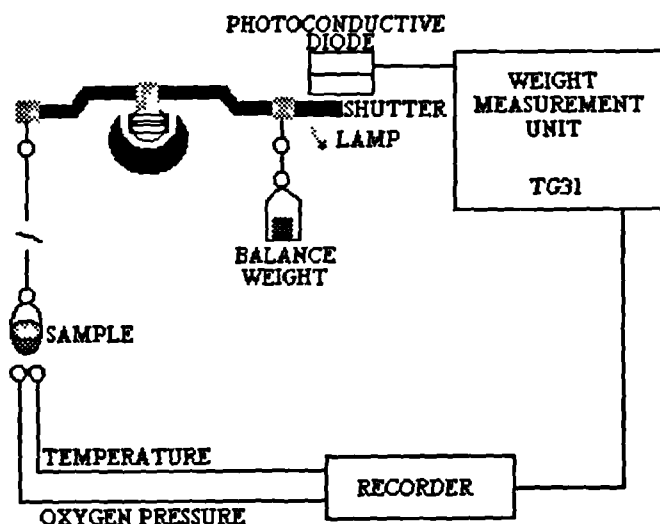


FIG. 4.4.3a SCHEMATIC DIAGRAM OF BALANCE MECHANISM

There were a number of problems with the balance after examination of the pure ceria sample, and during examination of samples I and E. These were solved before examination of samples B and C. Unfortunately there was insufficient time to repeat the earlier experiments. Before experiments were carried out, the balance was carefully calibrated using weights having a weight known to the fourth significant

figure. The balance was run blank under experimental conditions to check for any apparent weight changes. The only effect observed, and which was to be expected, was a displacement in the zero position when the circulation pump was turned on. This displacement did not appear to alter as the temperature was changed, and remained stable over the course of a day. The displacement also returned to the original position following a jolting earthquake. For the majority of experiments the balance was set at a range of 250mg with a sample weight of approximately 3g. Some earlier measurements were carried out with a range of 2.5mg and a sample of between 0.2 and 0.3g.

TABLE 4.4.3
SAMPLES EXAMINED
C, I, E, B, WAKO CeO ₂ 99.9%

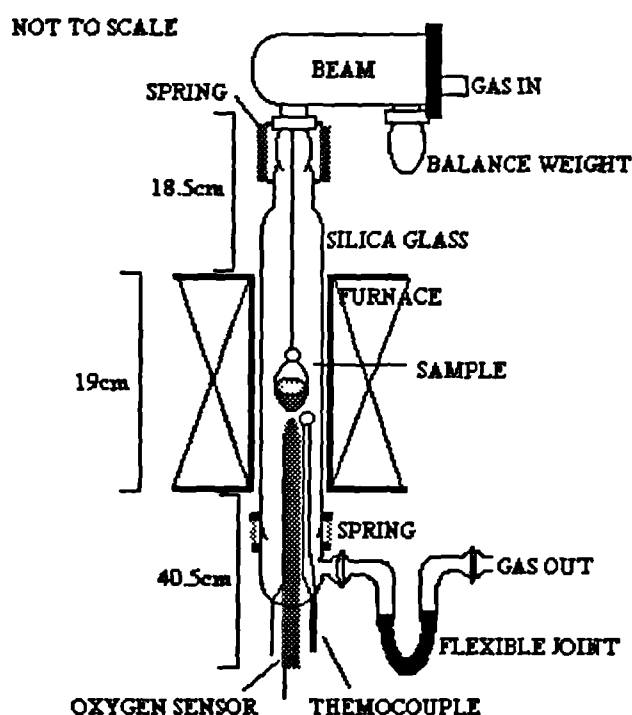


FIG. 4.4 3b RIG FOR TG. EXPERIMENTS

The sample holder was made of high purity recrystallised alumina. Bevan and Kordis (91) reported that cerium oxide can react with a platinum metal holder under similar experimental conditions. The powders used were ground from presintered bar samples, apart from the wako powder. The sample was carefully weighed to ± 1 of the fourth significant figure. The samples were loaded onto the rig and the joints

sealed with apiezon high temperature vacuum grease. The vacuum tightness was checked by evacuating the system.

Air was then reintroduced, and the sample was heated to the required temperature. Experiments were carried out at 800, 900, and 1000°C. After heating, the balance was zeroed, evacuated and carbon dioxide was flushed through. That wing of the gas system was then sealed, and the gas circulated. Measurements were carried out at oxygen pressures between 10^{-12} and 10^{-21} atmospheres. At each pressure at which a measurement was taken, the system was first allowed to equilibrate. Equilibrium was defined as unchanging weight and pO_2 measurements with time. The temperature was held constant for a series of measurements taken in both the reducing and oxidising directions for each sample and at each temperature.

4.4.4 CONDUCTIVITY SYSTEM

It was originally intended that seebeck coefficient and conductivity measurements be carried out as close together as possible. To do this, a rig similar to that used by Nowotny et al (166) was decided upon.

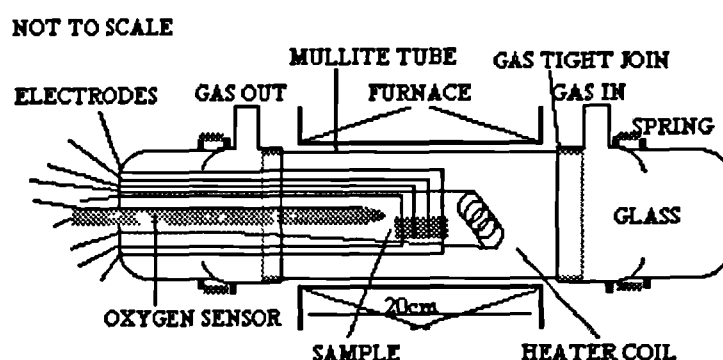


FIG.4.4.4a RIG FOR CONDUCTIVITY EXPERIMENTS

The inner high purity recrystallised alumina tube supporting the sample and oxygen sensor is not shown in the diagram. For each of the experiments the voltage was applied as shown in the circuit diagrams(fig. 4.4.4.b).

Conductivity experiments were carried out at the same temperatures and over the same oxygen pressure range as the thermogravimetric experiments. The samples used were barshaped. A voltage was applied to the sample using a Riken Denshi standard voltage generator. For the most part applied voltages were between 20 and 500mV. The current was calculated from the measured voltage across a known resistor. At

constant temperature and pO_2 a series of measurements were taken for each sample under equilibrium conditions, using different applied voltages of positive and negative polarities. The voltage measured across the sample was plotted against the current for each measurement, giving a straight line plot. Because of temperature variation within the furnace, the line did not usually go through the origin. The resistance of the sample was found from the gradient of the line.

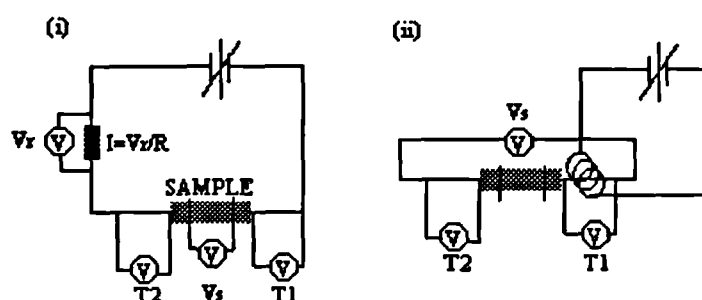


FIG. 4.4.4b (i) CONDUCTIVITY (ii) SEEBECK CIRCUIT DIAGRAMS

The seebeck measurements were not particularly successful. It was not possible to take measurements over a series of temperature differences. The heater in the rig did not increase the difference in temperature. It was found that the difference remained more or less constant, but the average temperature of the sample increased. Seebeck measurements are based on the theory that an applied temperature difference across a material induces a corresponding potential difference. This is known as the Seebeck effect. The reverse is also true, and is known as the Peltier effect. The seebeck coefficient is given by dividing the difference in voltage by the difference in temperature. Measurement of the seebeck coefficient enables better interpretation of conductivity results. Assuming that the mobility of charge carriers remains constant, the conductivity is proportional to concentration of charge carriers. Where defects interact, the mobility alters. In seebeck data the mobility of charge carriers is not significant (166-167). Comparison of data for both types of experiment allows the mobility to be calculated.

4.4.5 WIRING OF AND SUPPLY OF POWER TO THE RIG

The laboratory contained several 110V sockets and two junction boxes with 1x200V30A and 2x100V20A supplies. The conductivity furnace was the only piece of equipment to be connected directly to 200V. This was necessary because of the size of the furnace. One line was taken from the 200V, and put through a transformer to give two additional 100V lines.

All electrode leads were plugged into a socket board, and were connected to chart recorders and multimeters via that board. The potentiostat/galvanostat and constant voltage generator were also connected to the relevant electrodes through a socket board. This can be seen in the photographs of the rig supplied (fig. 4.4.5m).

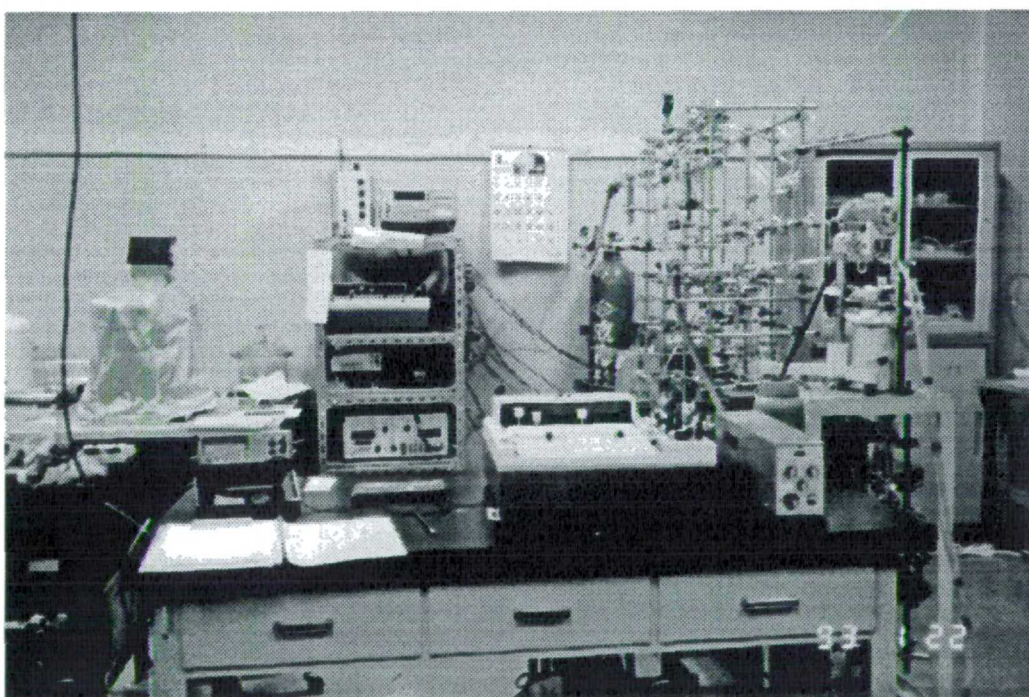
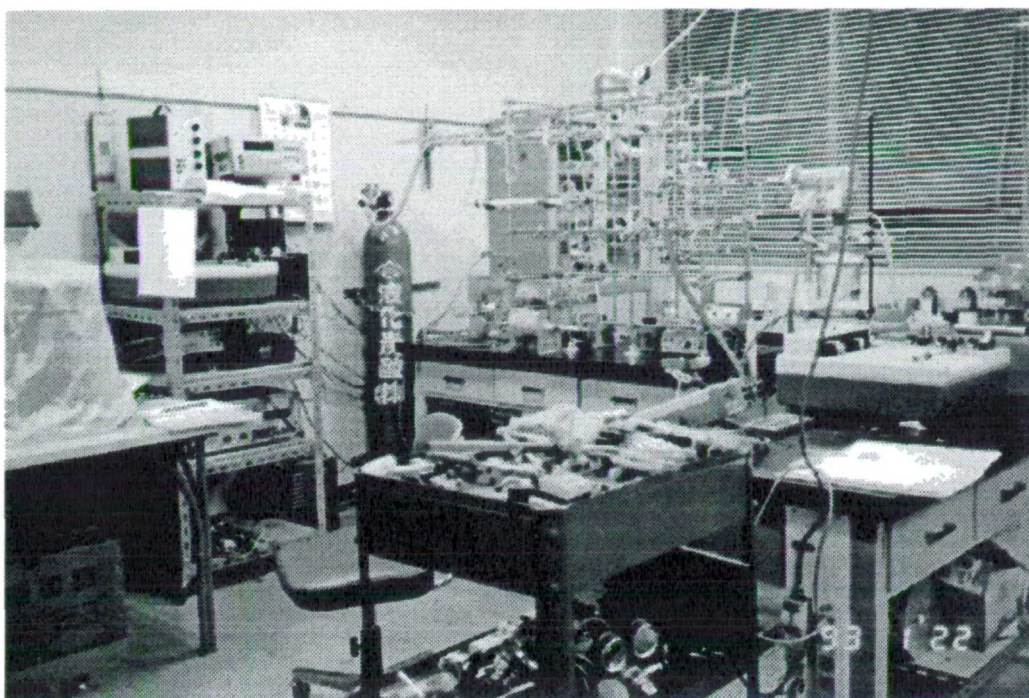
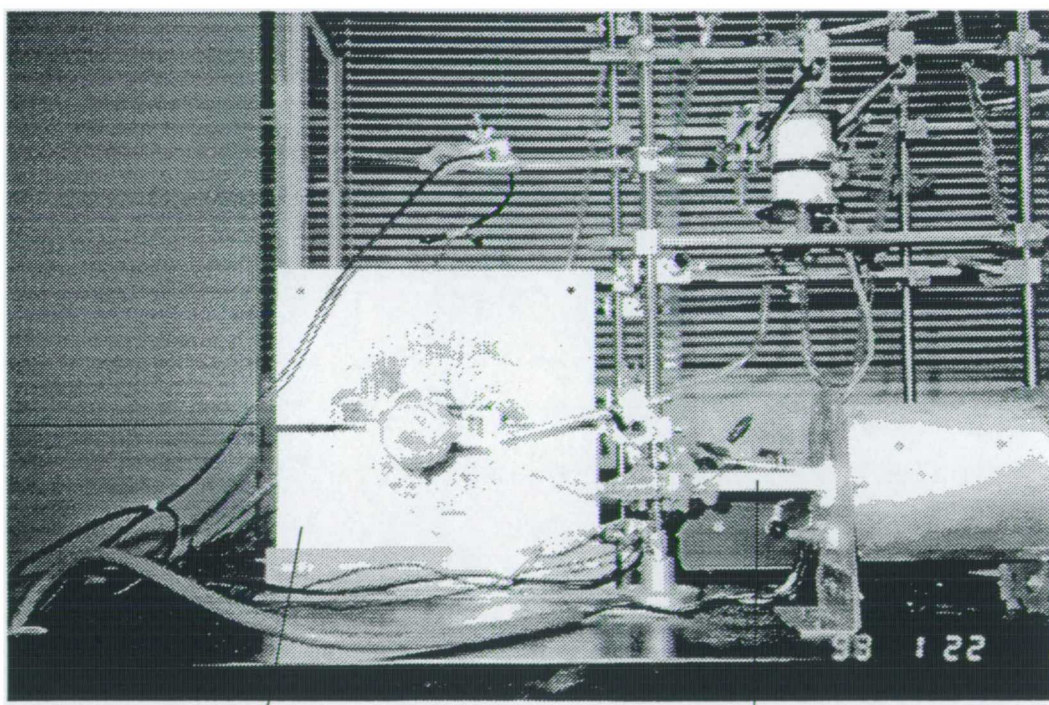
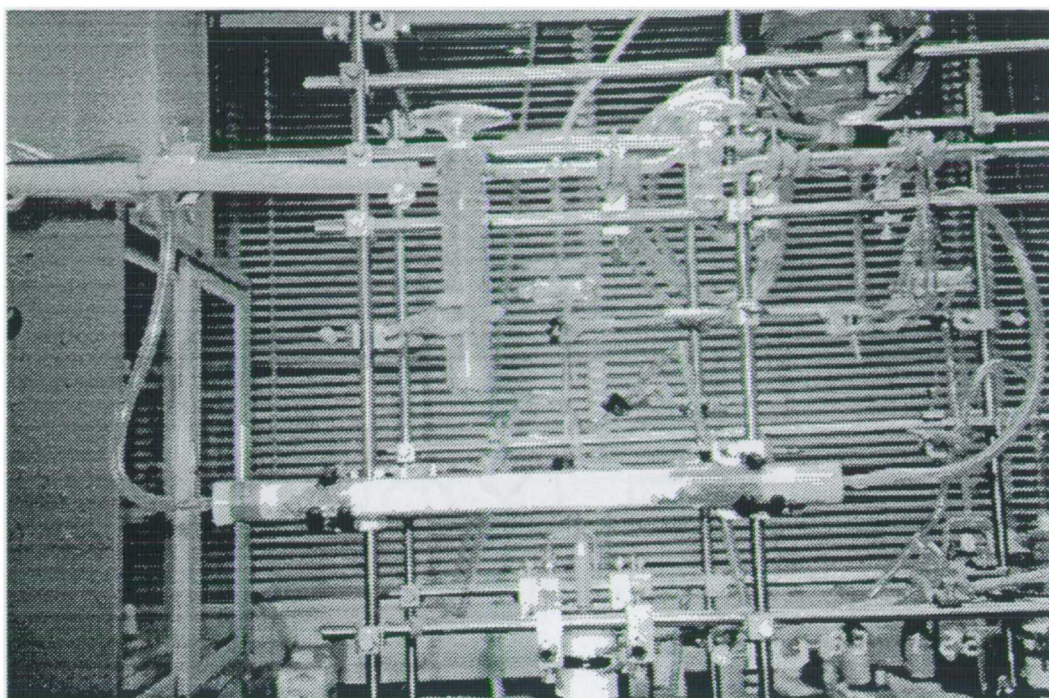


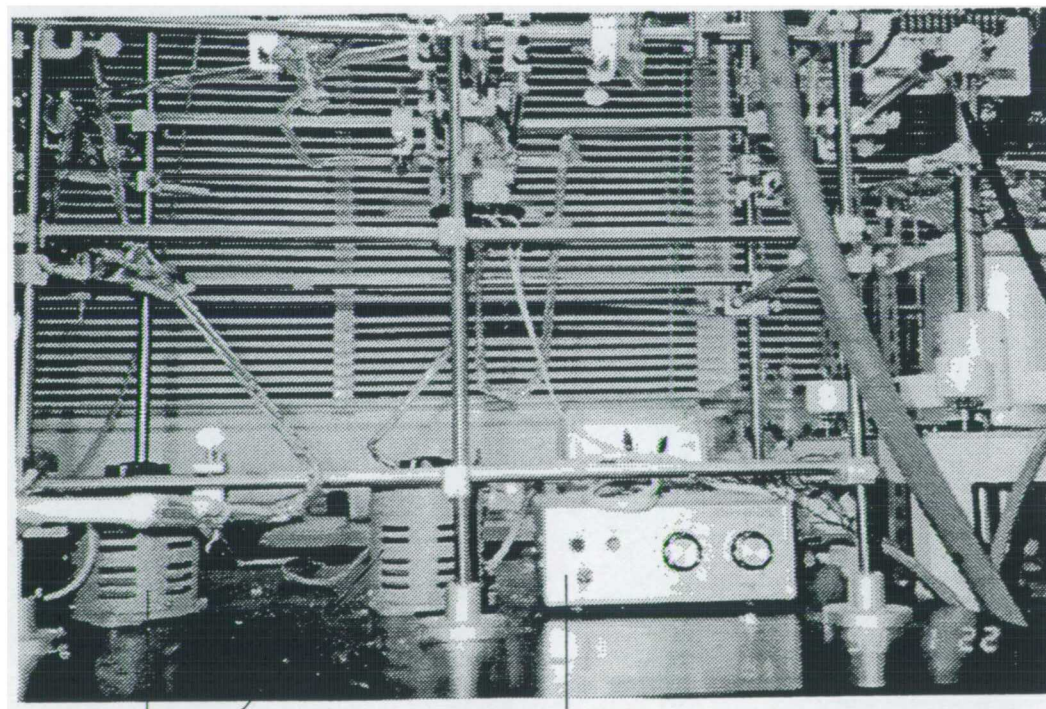
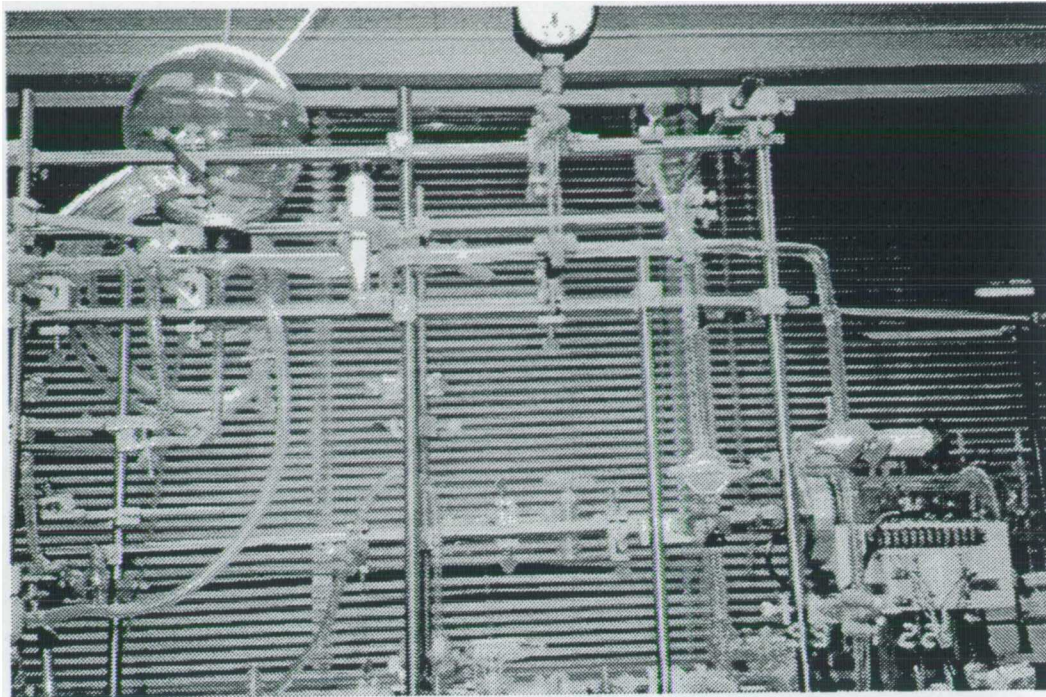
FIG 4.4.5 a,b FRONT AND SIDE VIEWS OF EXPERIMENTAL EQUIPMENT



COND FURNACE

O₂ PUMP

FIG 4.4.5 c,d FRONT LEFT, CONDUCTIVITY FURNACE AND OXYGEN PUMP



AC FREQ CONTROL

CIRC CONTROL

FIG 4 4.5 e,f FRONT RIGHT; T.G. CIRCULATION PUMP CONTROL

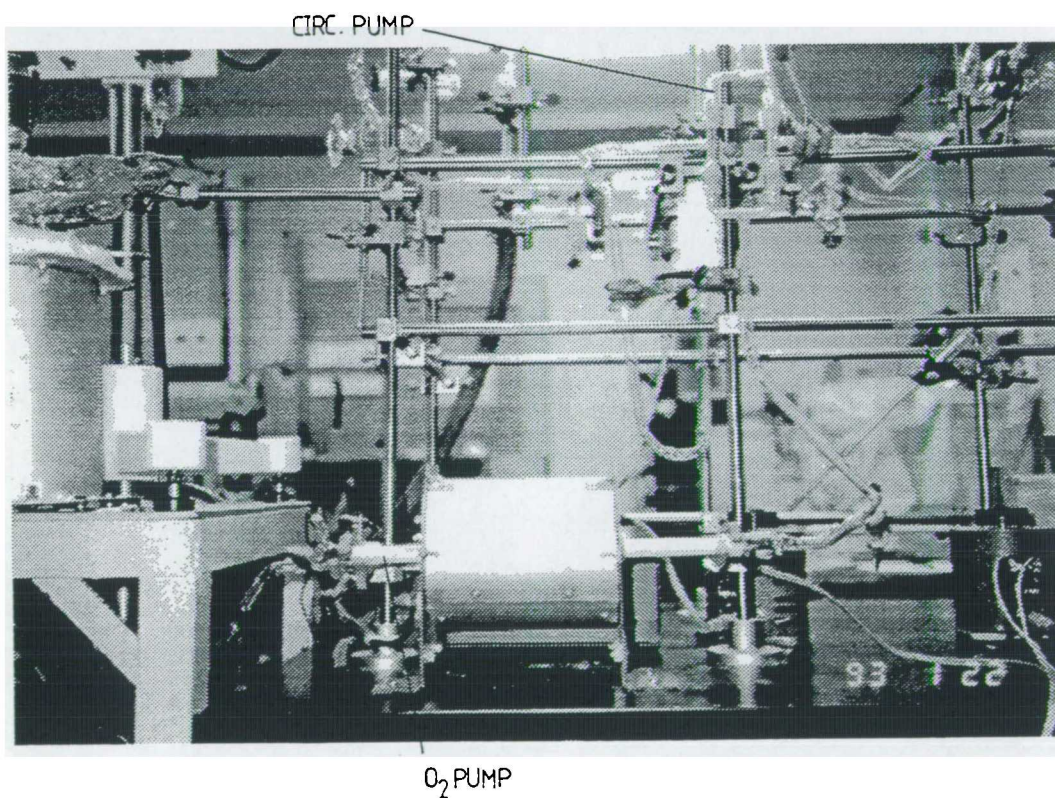
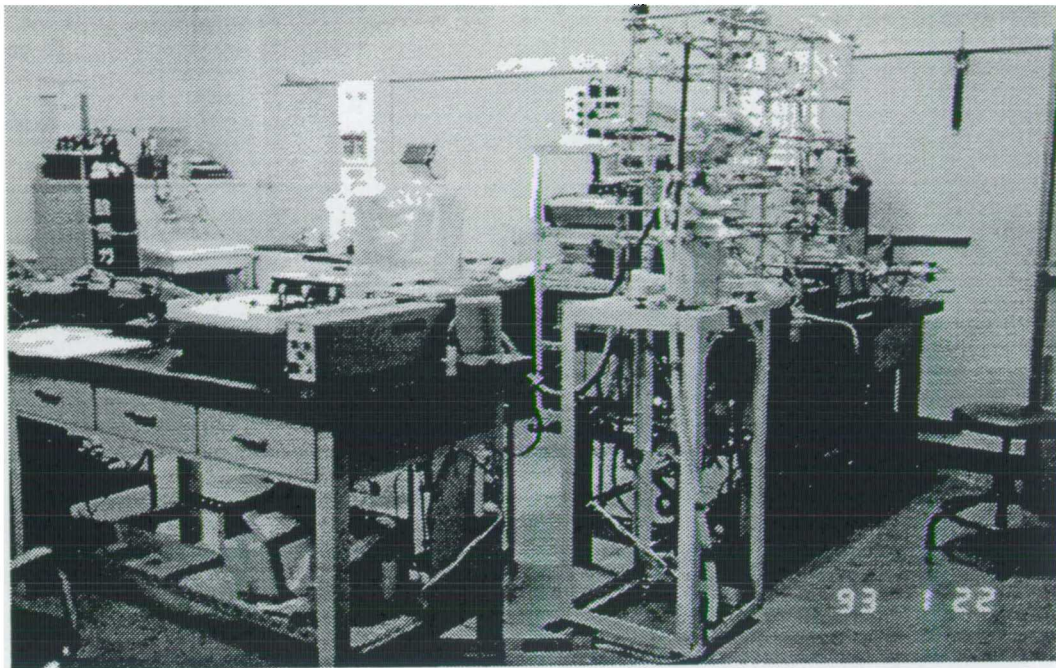
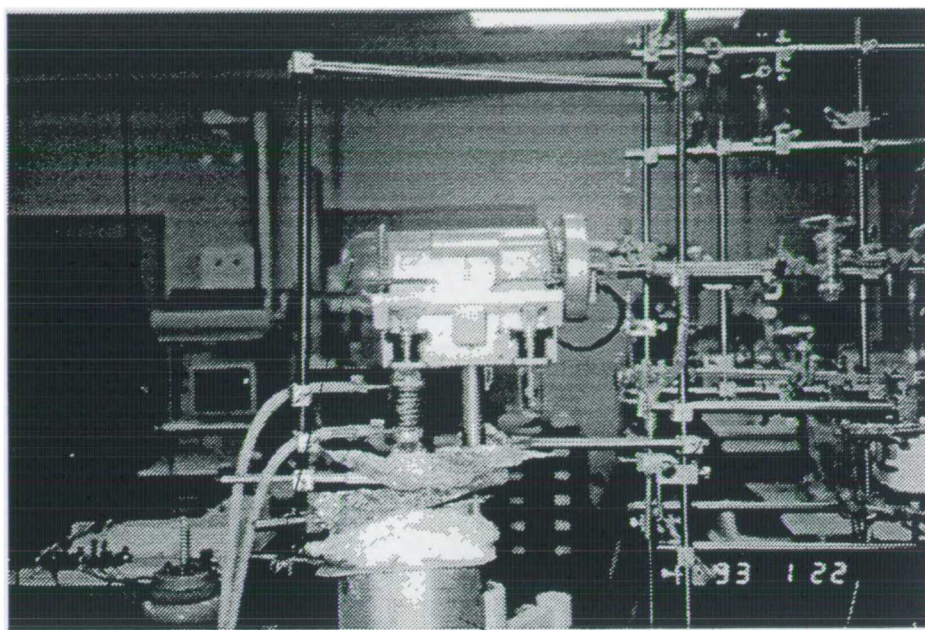
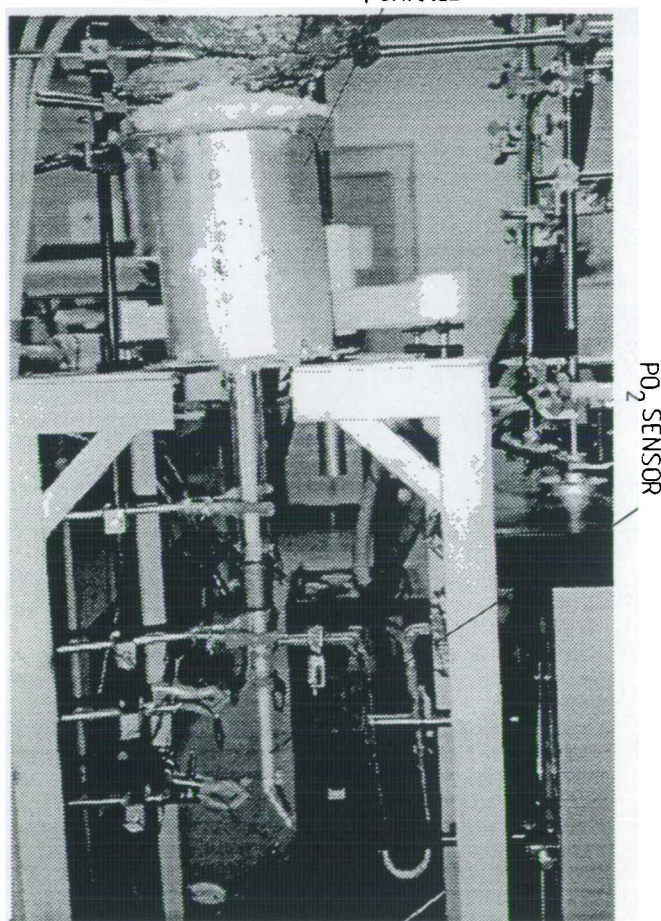


FIG 4.4.5 g,b REAR SIDE VIEW; T.G. OXYGEN AND CIRCULATION PUMPS



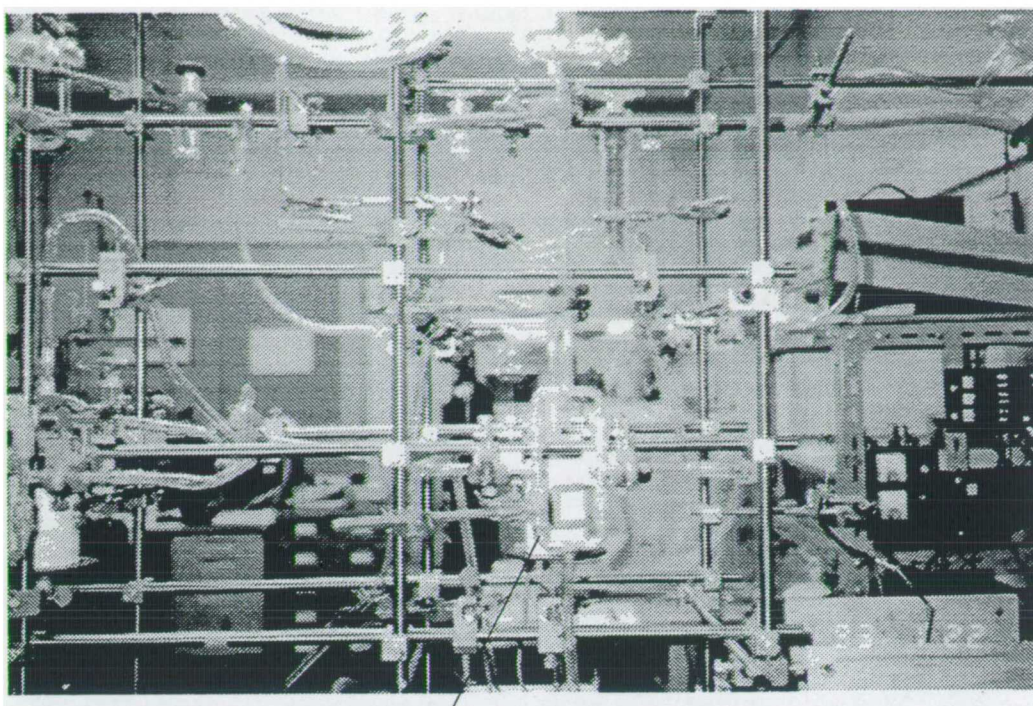
BALANCE

FURNACE

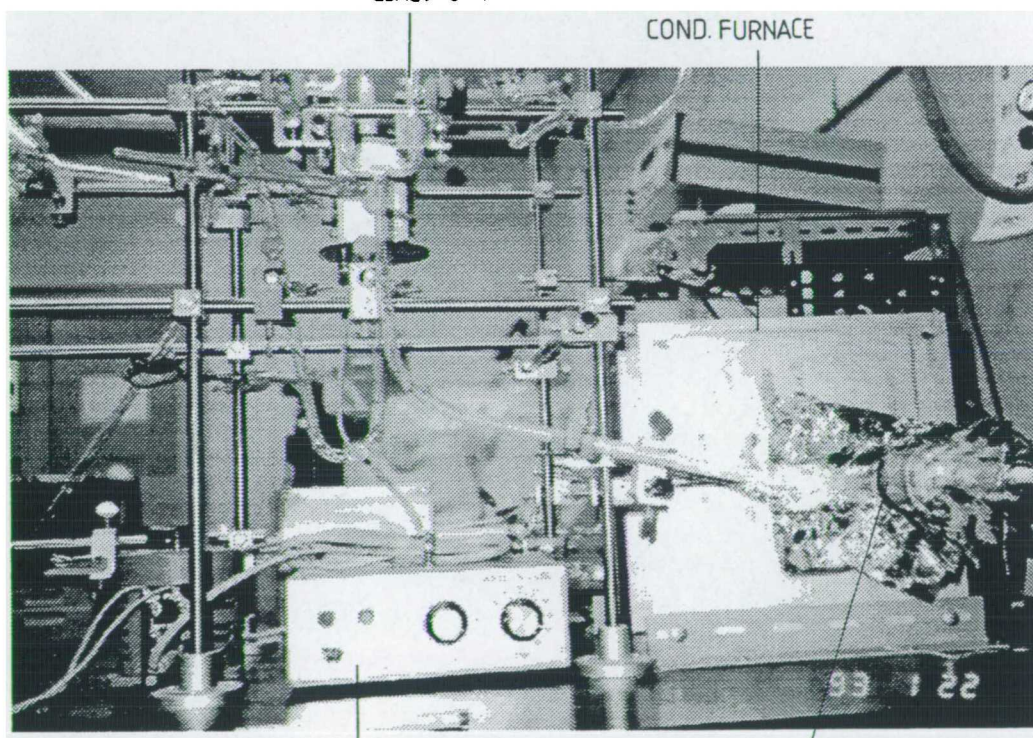


PO₂ SENSOR

FIG 4.4.5 i,j REAR RIGHT; TG BALANCE AND REACTION TUBE



CIRC. PUMP



COND. FURNACE

PUMP CONTROL

REACTION TUBE

FIG 4.4.5 k, l REAR LEFT; CONDUCTIVITY CIRCULATION PUMP, CONTROL AND REACTION TUBE

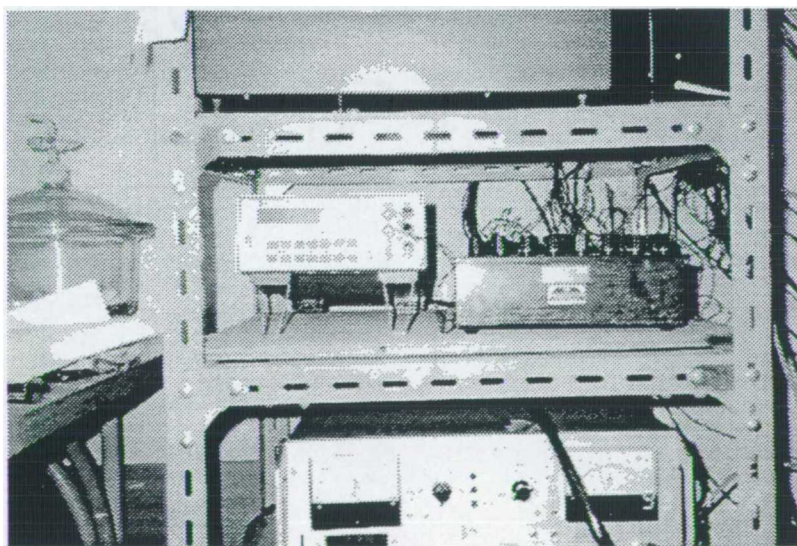
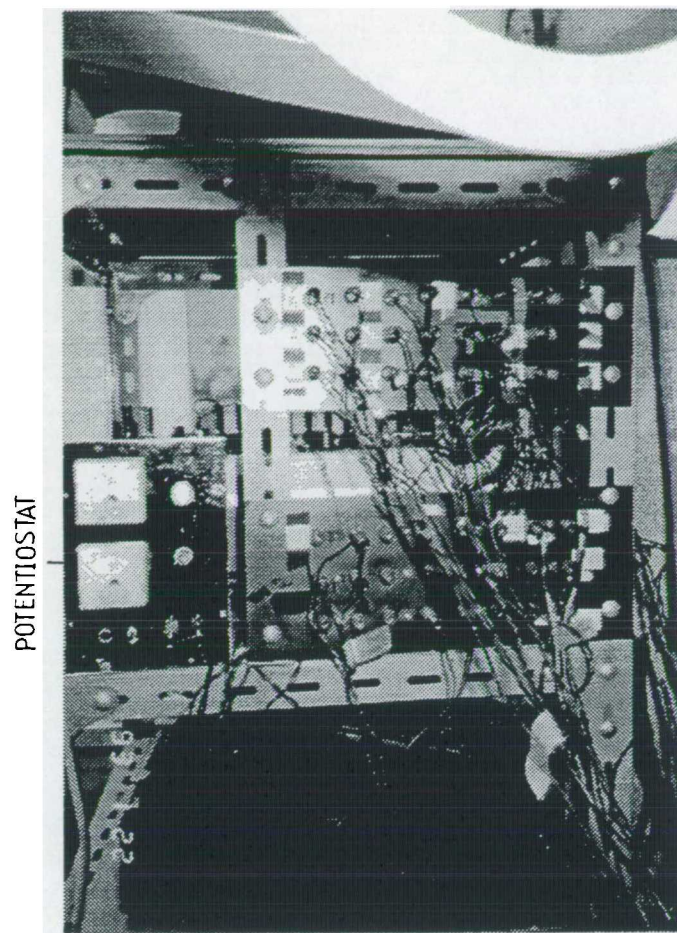


FIG 4.4.5 m,n SOCKET BOARD FOR ELECTRODES, THERMOCOUPLES ETC. FOR BOTH EXPERIMENTAL RIGS

4.5 CHARACTERISATION

4.5.1 LATTICE PARAMETER AND XRAY DIFFRACTION

Lattice parameter measurements were done in Tokyo using a Philips diffractometer equipped with APD1700 software. Presintered samples were ground to a powder, and mixed with an equal quantity of high purity silicon (Johnson Matthey 99.9999%) used as a standard against which the diffraction peaks were calibrated. The measurements were made, as near as possible, at constant temperature. The diffractometer was run on a step program with an active time of 2 hours and 50 minutes covering $87-139^{\circ}2\theta$. The lattice parameter was calculated using the software with a refinement procedure. The results are accurate to the third decimal place.

TABLE 4.5.1 SAMPLES USED FOR LATTICE PARAMETER MEASUREMENTS		
SAMPLE	OXYGEN ANNEALED	HIGH PURITY
Y0	Y, N	N
E	N	Y
Y15	Y, N	N
Y2	Y	N
J	N	Y
A	N	Y
Y35	N	N
C	N	Y
H	N	Y
F	N	Y

Several samples had been annealed in oxygen at 1000°C for 5 hours. The following samples were examined for evidence of a second phase: Y2, Y15, Y1, Y55 on a Philips diffractometer in London.

4.5.2 ELECTRON MICROSCOPY

The following samples were examined using Jeol T200, JeolT220 and JSM35-CF scanning microscopes as specified in table 4.5 2

4.5.3 COMPOSITION ANALYSIS

Samples were listed with their intended compositions at the beginning of this chapter. This is not necessarily the actual composition of the finished powder. Five of the higher purity powders were sent to the analytical laboratory of the Geology Dept. at Imperial College for analysis. The technique used was Induction Coupled Plasma. A small quantity of each powder had to be fused with silica, in order for measurements to be made.

TABLE 4 5 2 SEM SAMPLES

SAMPLE	PREPARATION	TYPE OF EXAMINATION
Y55, Y0 Y15	polish to 1micron, thermal etch 1200°C 20min	T200, secondary and backscattered images, no photographs
C, I	disp. in ethanol	T220, powders. photographs x500- x5000
IE,G,A,B, C,H,F	polish to 1micron, set in resin	T200, secondary and backscattered images, no photographs
multilayer	polish to 1/10 micron hit with hammer	JSM35 cross-section and EDAX linescan, T200 secondary and backscattered with photographs T220 fracture surfaces, with photographs

4.6 MATERIAL PROPERTIES

4 6.1 COEFFICIENT OF THERMAL EXPANSION

The coefficient of expansion was measured for I6 and I55 in air and forming gas atmospheres over 25-1000°C. A dilatometer with an alumina rod was used. The expansion coefficient of the rod, given as $8.4 \times 10^{-6} \text{ K}^{-1}$ by the manufacturers, was taken into account when making the calculations. The following is the equation used.

$$(L-L_0)/L_0\Delta T + 8.4 \times 10^{-6}$$

where L_0 is the initial length, and L the achieved length. ΔT is the temperature difference.

4.6.2 OXYGEN DIFFUSION

Samples examined: Y0, Y05, Y55, Y6

The diffusion coefficients were measured using secondary ion mass spectrometry. The samples were polished by me, but the rest of the work; ion exchange and SIMS was carried out by Dr. S.Carter. Samples were preannealed at the same temperature as the O18 exchange was to be carried out in dry O16 at 0.7atm. The preannealed time was longer than the O18 exchange time. Exchange was carried out at temperatures from 700 to 900 in an atmosphere enriched with O18 (70% O18, 5% O16, 25%N) at 1 atm.

SIMS (atomika 2000 or 6500) was used to obtain the O18 depth distribution profiles using a Xe beam at 10 keV. Ordinary depth profiling was carried out for depths to 10m, and a linescanning technique was used on cross sections perpendicular to the original polished surfaces. A large Xe^+ beam traverses the required length

The values of D^* and k (diffusion and surface exchange coefficients) were obtained by fitting the experimental data to

$$(C_x - C_{bg}) / (C_g - C_{bg}) = \text{erf}[x/2(D^*t)^{1/2}] - \exp(hx + h^2 D^* t) \times \text{erfc}[x/2(D^*t)^{1/2} + h(D^*t)^{1/2}]$$

where

C_x = isotopic concentration at depth x

C_g = concentration in exchange gas

C_{bg} = background concentration

$h = k/D^*$

t = diffusion time

4.6.3 CONDUCTIVITY

This section deals with the early conductivity experiments carried out at Imperial College.

TABLE 4.6.3 CONDUCTIVITY SAMPLES

SAMPLE	TECHNIQUE
I6	AC impedance in air, van der Pauw 4 point square method in air- variation with temperature
Y1	4 point contact method in air and forming gas- variation with temperature

AC impedance was used to measure the conductivity of I6, but it was found that the electronic conductivity was too high. In the van der Pauw 4 point square method contacts can be interchanged giving a series of voltages for a given set of conditions (170). The average of these can be taken. The 4 contact method is the same technique described in section 4.4.4.

4.6.4 CATALYSIS FOR THE OXIDATION OF METHANE

Catalysis experiments were carried out on powders of samples I and C. The BET (Brunauer Emmett Teller) surface areas of the powders were measured using a Monosorb Surface Area Analyser (Quantachrome Corp.). The adsorbing gas was nitrogen, and the coolant liquid nitrogen. The samples were first degassed 8 consecutive adsorption-desorption runs were carried out for both samples. The average was taken from runs 3-5 for C, and 3-8 for I. The sample weights were 0.6894g and 0.8712g respectively.

Dr. H.Middleton carried out the first catalysis experiment, sample C. The remainder of the experiments were performed by myself, with some assistance from Dr. Middleton. 1g (± 0.01) of powder was used for each experiment. The powder was placed in a U-tube connected to the gas system. Because the powders were very fine, care had to be taken in packing them. If too closely packed, the gas would be unable to flow through the sample, and a back pressure would build up.

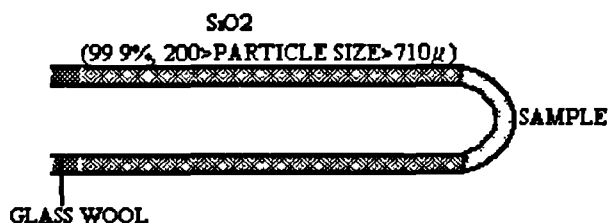


FIG. 4.6.4a CATALYSIS SAMPLE

On leaving the sample, the gas could be injected into a gas chromatograph for compositional analysis. A Pye Unicam PU4500 chromatograph with a PU4810 computing integrator (Philips) was used.

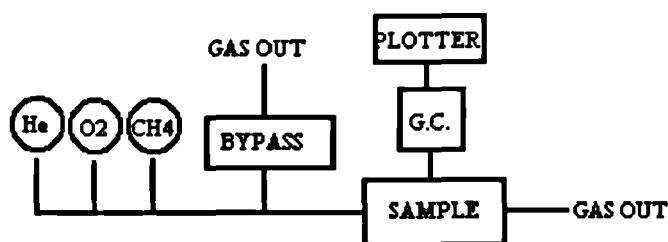


FIG. 4.6.4b FLOW CHART OF APPARATUS

The experimental system was designed and built by Dr. Middleton. The initial ratio of gases was 5:1 $\text{CH}_4:\text{O}_2$ and 10:1 $\text{He}:(\text{CH}_4 + \text{O}_2)$. The gases were mixed at a flow rate of 50ml/min. 15ml/min was put through the sample, and the remainder through the bypass. Measurements were made under constant temperature conditions from 25-1000°C for both samples. The gas chromatograph could be calibrated for CH_4 , CO , CO_2 , and O_2 with the speciality gas supplied for the purpose, but unfortunately not for H_2 .

A series of carbon deposition experiments was performed on sample I using the system without the chromatograph. It had been claimed that carbon deposition did not occur on ceria samples (4) and the aim of the experiments was to determine whether there were conditions under which deposition would occur. Methane and helium were mixed at a ratio 75:25. The flow rates remained the same as those used previously. The sample was left at constant temperatures of 500-900°C for up to 10 hours at a time. The sample was quenched by rapid cooling of the furnace. A qualitative examination was made of the sample appearance. The experiment was repeated in 100% methane at 800°C.

4.7 COSINTERING EXPERIMENTS

A variety of multilayer studies were carried out as shown.

TABLE. 4.7 COSINTERED SAMPLES

SAMPLE	SLURRY TYPE	SUBSTRATE	STUDIES	SINTER
C, H	tapecasting (a)	zirconia, ceria-gadolinia	reduction, SEM	air, H ₂
H	ethylcellulose/di-butylphthalate (b)	as above	reduction	air
YSZ	as above	H, ceria-gadolinia		air
H	ethylcellulose/terpinol (c)	ceria-gadolinia		air

Samples were prepared by painting the slurry onto a presintered substrate and/or green substrate. A variety of sintering conditions were used, selection of which depended on the substrate material. In general, the temperatures were 1450°C for zirconia substrate samples, and 1600°C for ceria-gadolinia substrate samples. The zirconia powder was Tosoh TZ8Y and the ceria-gadolinia Rhone-Poulenc 80-20. Because of organics present in the slurries all samples were heated at 0.5°C/min up to 200°C and thereafter at 5°C/min. The length of time spent at the maximum temperature was varied. Samples were cooled at 10°C/min, or at 5°C/min to 900°C and thereafter at 10°C/min. All samples were sintered in a horizontal tube furnace.

Experiments were also carried out on cermets based on silver (silver paint). It had been suggested (168) that silver would be a good material because it conducts protons. Proton conduction has been found to be beneficial in fuel cell components (70). The melting point of silver is too low, at 962°C (169), to be cosintered at the usual temperatures. A miscible alloy such as silver-palladium (mp. from 962-1555 (169)) would be an alternative, but was not used in this case. Silver paint was mixed

with varying amounts of sample H and painted onto green and presintered zirconia pellets. All samples were sintered at 900°C.

5. RESULTS AND DISCUSSION

5.1 INTRODUCTION

This chapter is divided into sections dealing with the different types of experiment and is drawn together at the end. It was originally intended that conductivity and thermogravimetric experiments be carried out on all high purity samples at 800, 900, and 1000°C over the pO₂ range 10⁻¹²-10⁻²⁰. This would have enabled the activation energies for conduction and reduction to have been calculated and compared, and changes in these values with sample composition would have been noted. However, continual problems with the experimental rig, and with the samples, has meant that far fewer data than had been anticipated were collected, and such comparisons are not possible here.

5.2 MATERIAL CHARACTERISATION

5.2.1 LATTICE PARAMETER

The graph of lattice parameter versus composition is given. Note that the JCPDS files give a value of 5.41134Å for ceria containing some yttrium (amount unspecified, #34-394). This is fairly close to the value given here for Y0; 5.4118Å. Remembering that the Y content was the same for all samples (intended composition 3%) other than Y0 (2%), the decrease in lattice parameter with increasing niobium content is to be expected. Niobium is a significantly smaller ion (78), and causes the lattice to contract. This is opposed to the results of Shingler (60) who found an increase. If both results are correct, this can be explained as follows. Ytria-doped ceria contains oxygen vacancies which can be filled by the excess oxygen introduced by further doping with niobia. Doping with niobia alone introduces an oxygen excess which can be accommodated either by oxygen interstitial atoms, or cation vacancies. The presence of both cation vacancies, and a smaller ion may be expected to reduce the lattice parameter. If oxygen interstitials are the compensating mechanism, the presence of interstitial atoms will serve to encourage lattice expansion, whilst the smaller ionic radius will work against this. If doping with niobium alone causes an expansion of the lattice, then it would appear that the effect of the interstitial atoms is the greater. This being so, a reversal of the decrease in lattice parameter with increasing niobium concentration should be expected once the niobium content is greater than the yttrium content.

The data here show that there may be a reversal above this point, but the accuracy of the data (to the third decimal place) means that the result is not wholly conclusive. There is also the possibility that the decline in the rate of decrease represents a solubility limit, rather than be leading to a reversal. No conclusive evidence of a second phase was found in these samples (section 5.2.2). When examining the data with a knowledge of the actual composition of the high purity powders, a reversal would be expected to occur around samples Y2 and J, or at 2.5%Nb as plotted here. The scale here is of intended composition. Actual compositions of the non-high purity samples were not measured, and it may be that the lattice parameters of the two sets of samples cannot be so easily compared. The presence of lower valent and other impurities may affect the results, and the difference between actual and intended composition of the two sets may also be different, although the same method of preparation was used.

TABLE 5 2.1 LATTICE PARAMETER	
SAMPLE	LATTICE PARAMETER
Y0	5 41118
E	5.40803
Y15	5.40646, 5.40667
Y2	5 40611
J	5 40628
A	5 40701
Y35	5 40604
C	5.40378 ...5.40702
H	5.40674
F	5 40712

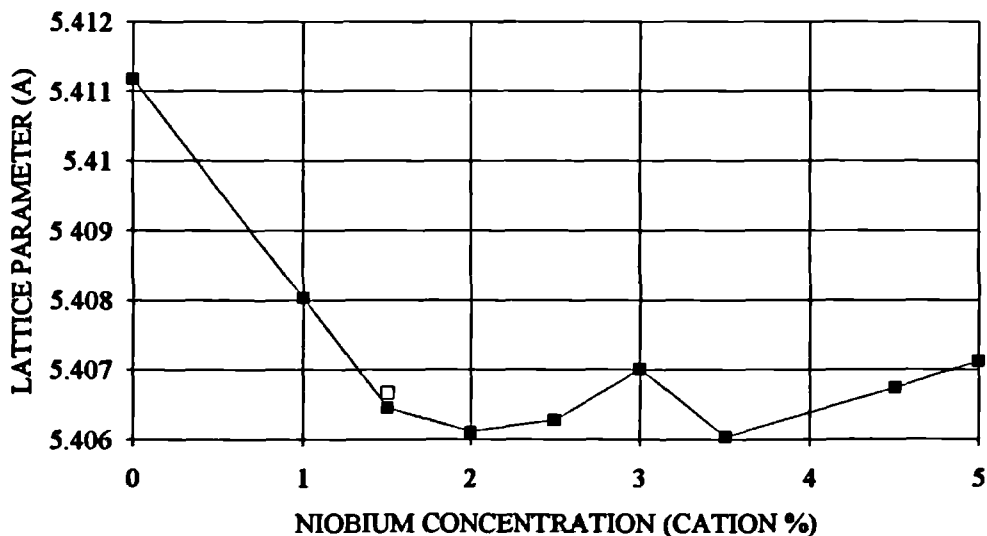


FIG. 5.2.1 VARIATION IN LATTICE PARAMETER WITH NIOBIUM CONCENTRATION

The lattice parameter of sample C has been discounted here. Whilst the parameters of the other samples proved reproducible to the third decimal place, the data for sample C resulted in a wide range of parameters, affected by the peaks used for the calculation.

5.2.2 COMPOSITION

Backscattered and secondary electron images with EDAX for the initial samples have already been discussed in section 4.3. This section will deal with the high purity samples. Sintered bars of each of the samples were polished to 1μ using a hyprez diamond spray, and examined on a JEOL T200 microscope in both secondary and backscattered image modes. No second phase was visible in either mode. The result was rather surprising, particularly for samples H and F, where some second phase might have been expected. Sample F showed a variation in shade of green across the sample when examined by eye, and this was originally attributed to a second phase. However, such variation in shade has since been found in zirconia-doped india samples during work carried out in the department by J.M. Bae. In this case also, no evidence of a second phase was found during SEM examination. The high purity samples were also examined by x-ray diffraction, and no evidence of a second phase was found. Shingler (60) states that in his samples, evidence of a second phase was found during x-ray diffraction, but not by SEM. In this case, since no evidence was found by either method, it is assumed that any second phase present is minimal.

TABLE 5.2 2a ICP COMPOSITION

SAMPLE	INTENDED COMPOSITION %			ACTUAL COMPOSITION %		
	Ce	Y	Nb	Ce	Y	Nb
A	94	3	3	91.746	3.761	4.494
B	93.5	3	3.5	91.075	3.737	5.188
C	93	3	4	90.522	3.758	5.72
E	96	3	1	94.396	3.893	1.711
I	96.5	3	0.5	95.038	3.9	1.061

The actual composition of five of the samples was found by the induction coupled plasma method. To do this, a small amount of the sample had to be fused with silica. The compositions of the powders are given here, and compared to the intended composition. The data are accurate to $\pm 0.1\%$ for samples A and C, but were not repeated for the remaining samples.

As can be seen, there is a large difference in the intended and actual compositions. All samples studied are deficient in cerium, and contain more niobium:yttrium than was originally intended. Plots of intended Nb, and Ce v. actual Nb give a good straight

line, and extrapolation of the data allows the composition of the remaining samples to be estimated.

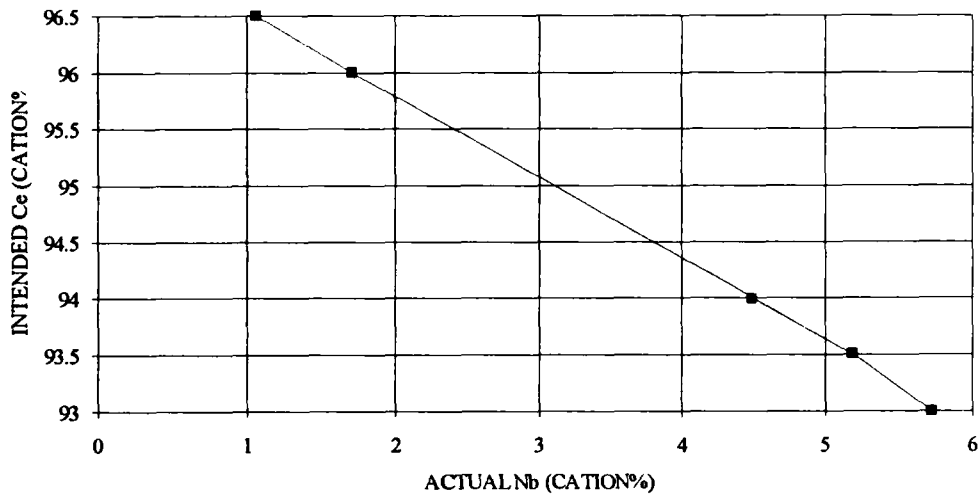


FIG. 5.2.2a PLOT OF ACTUAL v. INTENDED COMPOSITION

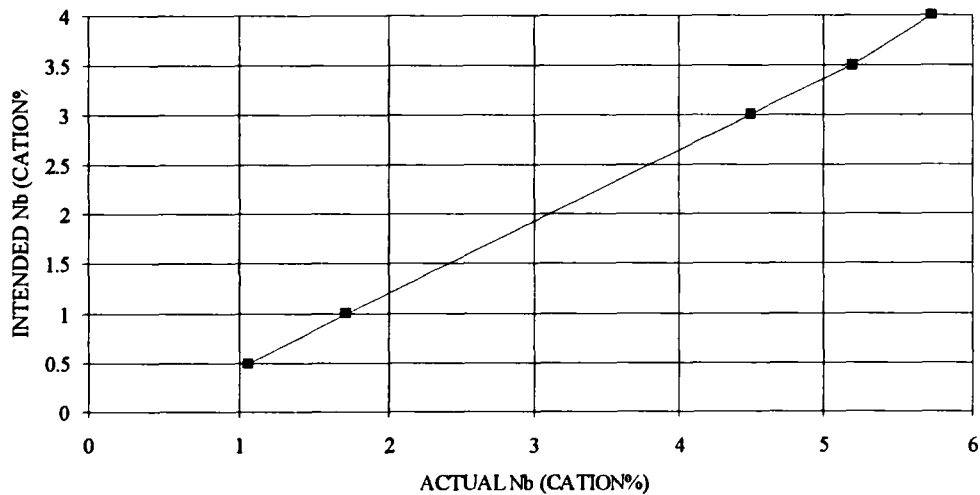


FIG. 5.2.2b PLOT OF ACTUAL v. INTENDED COMPOSITION

Given these results, it is still more surprising that no evidence of a second phase was found in sample C, H or F. As discussed in chapter 3, the solubility limit of niobium in ceria was found to be between 1.2 and 1.3% cations. In this case the difference in Y and Nb content is 3.2% cations, more than twice the expected value. It may well be that the data cannot be extrapolated well (the last point is off-line), or a second phase may have been present, that was not detected. The presence of yttria may promote the solubility of niobium over and above that which would be expected. However, since a second phase was found in sample Y55 (section 4.3), where the intended

composition was one with only a 0.5cation% difference between the concentrations of Y and Nb, the latter is extremely unlikely.

TABLE 5 2 2b ESTIMATED COMPOSITION

SAMPLE	INTENDED COMPOSITION %			ESTIMATED COMPOSITION %		
	Ce	Y	Nb	Ce	Y	Nb
G	95.5	3	1.5	93.7	3.7	2.6
D	95	3	2	93.1	3.65	3.25
J	94.5	3	2.5	92.45	3.7	3.85
H	92.5	3	4.5	89.85	3.8	6.35
F	92	3	5	89.2	3.8	7

5.2.3 DENSITY

The densities of the samples to be used in the electrical conductivity experiments were measured. The weight of the samples was measured when suspended in water, with the samples completely wetted, and then after drying out, at a measured temperature (172). The density was calculated from the following equation.

$$\rho = W_{(\text{dry})} \times \rho_L / (W_{(\text{wet})} - (W_L - W_w)) \quad [1]$$

where ρ_L is the density of water (171) at the temperature that the measurements in water were made, $W_{(\text{dry})}$ the weight of the dry sample, $W_{(\text{wet})}$ the weight of the wetted sample, W_L the weight suspended in water, and W_w the weight of the wire from which the sample was suspended. These were measured to $\pm 0.0005\text{g}$. For each sample the density was measured twice, and the average densities are given in table 5.3.2a.

TABLE 5 2 3a SAMPLE DENSITY

SAMPLE	(%Nb)	DENSITY (g/cm3)
I	0.5	6.4
E	1	7
G	1.5	6.7
D	2	5.8
J	2.5	5.6
A	3	7
B	3.5	6.4
C	4	7
H	4.5	6.9
F	5	6.4

There is no obvious pattern in variation of density with composition, and it is therefore concluded that the final density depended more upon the pressing of the

sample than composition. Because of problems with the press, it was not possible to monitor the pressure used from sample to sample, so some variation may be expected.

TABLE 5.2.3b SAMPLE DENSITY AS A PERCENTAGE OF THE THEORETICAL

SAMPLE	THEORETICAL DENSITY (g/cm ³)	% T.D.
E	7.14	98
G	7.14	93.8
D	7.13	81.3
J	7.12	78.9
A	7.11	98.5
B	7.1	90.1
C	7.09	98.2
H	7.08	97.5
F	7.07	90.5

The theoretical densities of the samples were calculated from the lattice parameters given in section 5.2.1, and account for variation in weight of the unit cell, with composition. The intended compositions were used in these calculations. Errors will arise as the actual composition is different, and any second phase present will introduce other unit cells that have not been considered. The sample density as a percentage of the theoretical is given in table 5.2.3b. Conductivity results can be adjusted according to the % theoretical density, enabling direct comparison of results between samples.

5.2.4 SURFACE AREA ANALYSIS AND POWDER SIZE

BET surface area analysis was carried out on two powders, C and I, to aid comparison of data from the catalysis experiments. It was found that sample C had a surface area of 8.27m²/g (± 0.4) and sample I a surface area of 18.72m²/g (± 0.9). The fineness of the powder affects the surface area to be measured, so the two powders were then examined on JEOL T200 and T220 microscopes.

Examination of the photographs shows a large variation in particle shape and size. From the pictures it appears that the particle size of sample I is larger than that for sample C, though both powders show evidence of particle agglomeration. The particles of sample C were much harder to focus on, and required greater magnification. The photographs of sample C show what may either be large very porous particles or agglomerates of smaller submicron particles. Individual submicron particles can also be seen. The agglomerates or larger particles for sample I seem to be much more solid. Again small submicron particles are also visible

The difference in surface area of the powders may be attributed to the different shapes and sizes of the particles. The fineness of powder C could mean that the powder was packed more solidly in the reaction tube during the surface area measurement. The larger particles of I mean that packing would not have been so close and more surface area was available. Some initial problems found by Dr. Middleton in packing the reaction tube for the first catalysis experiment were attributed to the fineness of the powder. That there were no problems during subsequent experiments indicates only that problems were expected, and more care taken. With this in mind, there may be some difference in packing and therefore surface area between the catalysis and surface area experiments. Although several surface area measurements were made for each sample, and the average taken, all measurements were taken on one packing of both samples.

Variation in powder characteristics across the range of samples, may also account for the variable densities of sintered samples. Sample C is denser than I, though as the lattice parameter of I was not measured, the % of theoretical density could not be calculated, but is expected to have been around 90-92% as compared to 98% for C. The surface areas of the other powders were not measured, so that any correlation between powder characteristics and sample density cannot be confirmed. However, as discussed in section 4.2.2, a more compactible powder should result in fewer pores and hence a density closer to the theoretical.

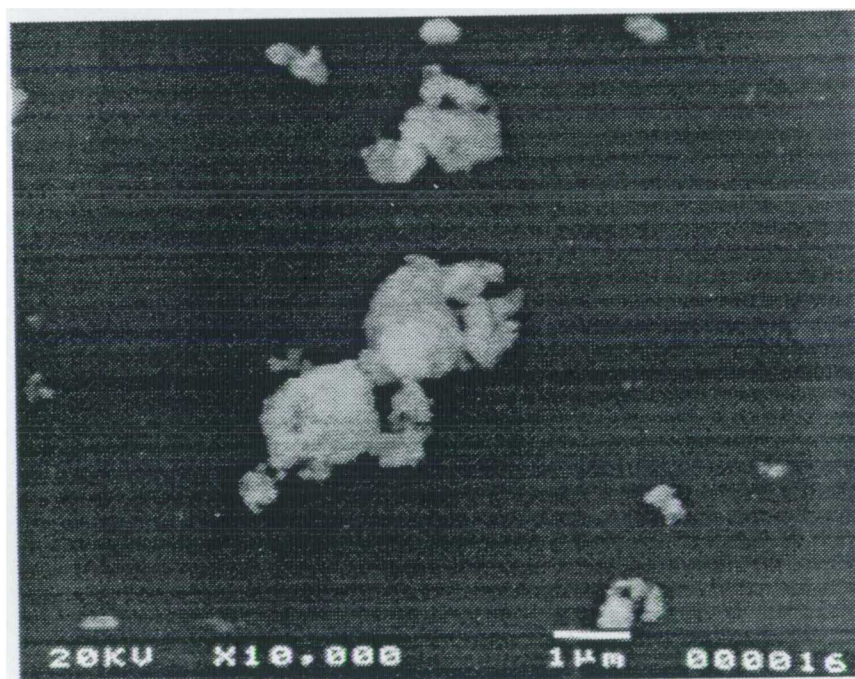
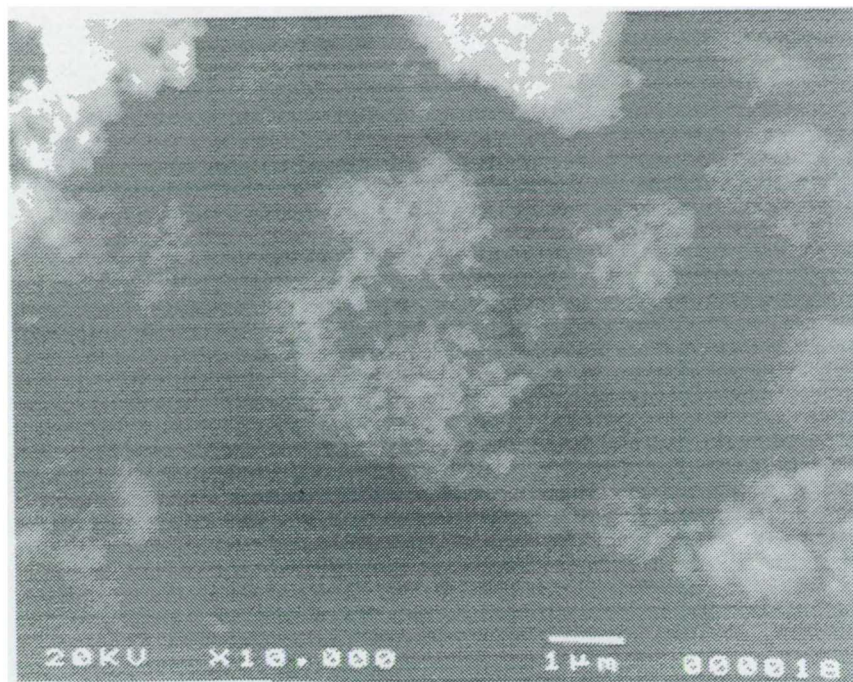


FIG 5.2 4a,b SEM SECONDARY ELECTRON MICROGRAPHS, POWDER C

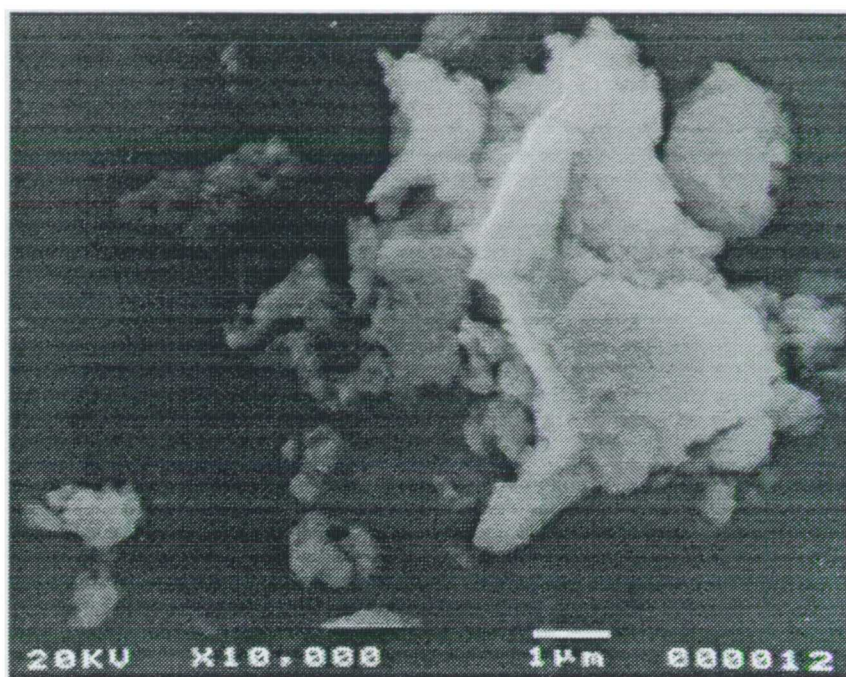


FIG 5 2 4c,d SEM SECONDARY ELECTRON MICROGRAPHS POWDER I

5.3 MATERIAL PROPERTIES

5.3.1 COEFFICIENT OF THERMAL EXPANSION

The coefficient of expansion was measured for two of the india-doped samples, I5 and I55. In air the results compare well with data for pure ceria.

TABLE 5 3 1a COEFFICIENT OF THERMAL EXPANSION			
SAMPLE	TEMPERATURE RANGE (°C)	EXPANSION COEFFICIENT (K ⁻¹)	
		AIR	FORMING GAS
I5	25 - 1000	1.23E-05	
	25 - 600		1.41E-05
	700 - 900		6.47E-05
	COOLING		BROKE
I55	25 - 1000	1.30E-05	
	25 - 800		1.35E-05
	860		BROKE

The value is slightly higher than that normally given for pure ceria, but is consistent with a model where oxygen interstitial ions are introduced by the niobium. As the temperature increases, the Ce⁴⁺ to Ce³⁺ transition becomes more favourable, and some excess oxygen may be lost. The presence of Ce³⁺ ions may cause an additional expansion in the lattice. Steele (174) reports that for perovskite materials, the greater the number of oxygen vacancies, the greater the unit cell dimensions and hence the greater the coefficient of thermal expansion. He indicates that the thermal expansion coefficient merely reflects the vibrational amplitudes of the atoms or ions in a material. The amplitude increases with increasing temperature. Where defects cause an expansion in the unit cell dimensions, they also allow larger amplitudes of vibration for the remaining atoms. This would also explain the larger value here. Whilst it is true that the presence of interstitial ions is likely to reduce the vibrational amplitudes in those local areas containing the ions, they would be increased in the remainder of the crystal. Samples with a smaller lattice parameter (section 5.2.1) may be expected to have a coefficient of expansion smaller than that for pure ceria.

In forming gas, there is a large reduction in the sample with increasing temperature. At lower temperatures the coefficient is fractionally larger than that in air, and at higher temperatures, considerably larger where it was possible to measure it. Here in a reducing atmosphere, Ce⁴⁺ → Ce³⁺, and the sample loses oxygen. Loss of oxygen causes an expansion in the lattice (86-90). Both Ce³⁺ ions and oxygen vacancies favour lattice expansion because Ce³⁺ ions are larger than Ce⁴⁺ ions, and the absence of oxygen on an oxygen site means that shielding of centres of positive charge is reduced, and there is a greater repulsion between ions. The repulsion is

reduced if the vacancy is situated adjacent to the Ce^{3+} , and such complex formation has been discussed (section 3.2.1).

Calculations have been made from the data of Sims (88-90) and Mogensen (72) to give theoretical values for the expansion coefficient for samples heated in a reducing atmosphere. For these calculations it is assumed that samples do not begin to reduce until they reach 800°C. Sims' data covered 25 - 1000°C in air, and Mogensen's from pO_2 10^0 to 10^{-20} at 1000°C. The Mogensen data has been fitted to the Sims sample at 1000°C, and calculations of expansion coefficient made over the temperature range 800 - 1000°C.

TABLE 5.3.1b CHANGE IN SAMPLE LENGTH WITH pO_2 AND T.

TEMP. (°C)	%EXP.	%EXP.	pO_2	LENGTH (microns)
25	0		0.21	3474.7
800	0.86		0.21	3504.6
1000	1.108	0	0.21	3513.2
1000		0.75	$1.00E-15$	3539.5
1000		1.54	$1.00E-18$	3567.3
1000		2.16	$1.00E-20$	3589.1

The result for sample I5 is between that for a pO_2 of 10^{-15} and 10^{-18} , which is consistent with the atmosphere of forming gas, indicating that doping has had little effect on the expansion - contraction behaviour of ceria in a reducing atmosphere.

TABLE 5.3.1c

THEORETICAL EXPANSION COEFFICIENT 800-1000°C AT pO_2 SHOWN

pO_2	EXPANSION COEFFICIENT
$1.00E-15$	$4.92E-05$
$1.00E-18$	$8.95E-05$
$1.00E-20$	$1.21E-04$

Given the enormous expansions, it is not surprising that a sample, subject to the compressive stresses of the dilatometer, was found to break. The sample also undergoes compression on cooling. It is not clear whether the broken samples are a result of the expansion - contraction in the ceria, or the second phase. If the fracture is as a result of the expansion - contraction, then it is not very hopeful that the material may be used successfully in a fuel cell above 800°C. $CeNbO_4$ is difficult to fabricate and tends to break up when subjected to changes in pO_2 (162)

5.3.2 THERMOGRAVIMETRIC DATA

The data given here are shown alongside the data from the literature, at three temperatures, and plotted in three ways: weight loss, composition, and oxygen loss. Experiments were carried out in both the oxidising and reducing directions at each temperature for each sample, and points are plotted on the graphs on order of measurement. In each case for samples E and I, a large spread in the data was visible, due to problems with the balance that were later corrected. The data for E and I are therefore excluded from this discussion. The thermogravimetric data were measured within $\pm 3^\circ\text{C}$ of 800°C , 899°C for all samples. At higher temperature the thermogravimetric data were measured within $\pm 3^\circ\text{C}$ of 969°C for sample C, and 993°C for the remaining samples. Since the experiments were not repeated, an estimate of accuracy with respect to sample composition cannot be made, but the powders were expected to be homogeneous. There was a good correlation in the data compared between oxidising and reducing directions.

The literature data plotted were all reported as measured at 800°C , 900°C and 1000°C (105,123,129), apart from the data of Bevan and Kordis (91). Their data were measured at 1023°C , 916°C and 779°C . The section and figure headings are given to the nearest 100°C for simplicity. For the niobium doped samples in the literature, and the $[\text{Nb}] > [\text{Y}]$ samples two models were used to determine composition from weight loss data (figs.5.3.2.1c-f). 1 assumes an interstitial oxygen ion, and 2 a $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ charge compensating mechanism.

5.3.2.1 1000°C

Significant reduction of the cerias at this temperature begins at a $p\text{O}_2$ of 10^{-13} . A greater weight loss was found on sample B than C with reducing $p\text{O}_2$. The weight loss of pure ceria is severe at low $p\text{O}_2$, going through a steep transition at 10^{-14} - 10^{-16} . Such a transition was not found in the doped samples. The data here would appear to support that of Naik and Tien for doped and pure ceria in fig. 5.3.2.1b. At higher pressures both B and C show a greater weight loss than pure ceria. Doping with ions of either valence seems to inhibit the steep transition found in reduction of pure ceria.

The experimental data measured here for pure ceria is closest to that of Bevan and Kordis (91). Examination of the literature data shows that the Bevan and Kordis data gives the steepest weight loss for pure ceria. The sample doped with 1% CaO in the literature, behaves in a manner similar to that for pure ceria, retaining the steep slope between 10^{-14} and 10^{-16} . The data for pure ceria from Naik and Tien (123) does not

agree well with the remaining data for pure ceria. Both the higher and lower valent doped materials show a shallower decrease in n with decreasing pO_2 when compared to pure ceria. In the following graphs for all temperatures pO_2 is measured in atmospheres.

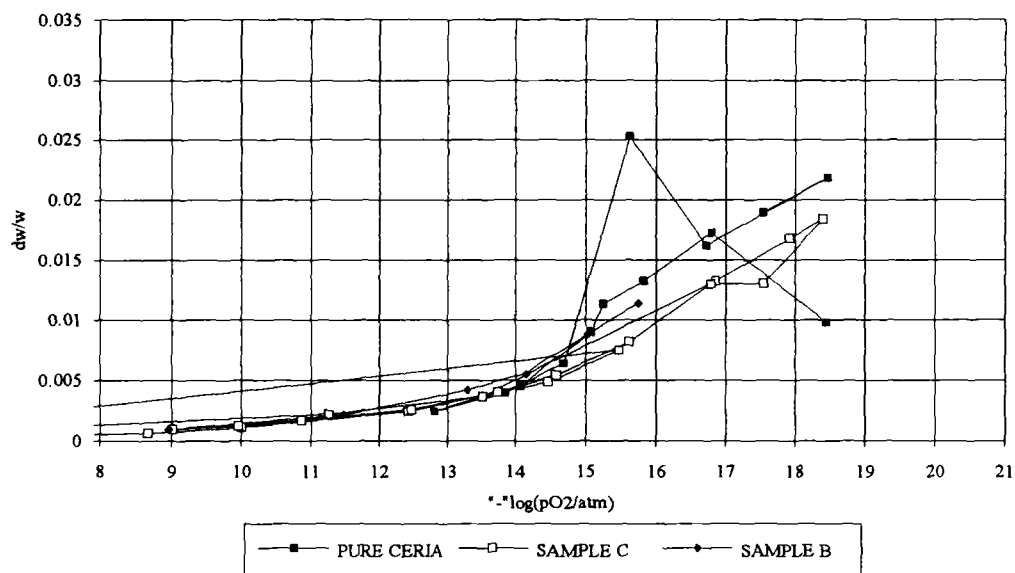


FIG. 5.3.2.1a 1000°C WEIGHT LOSS v. OXYGEN PRESSURE

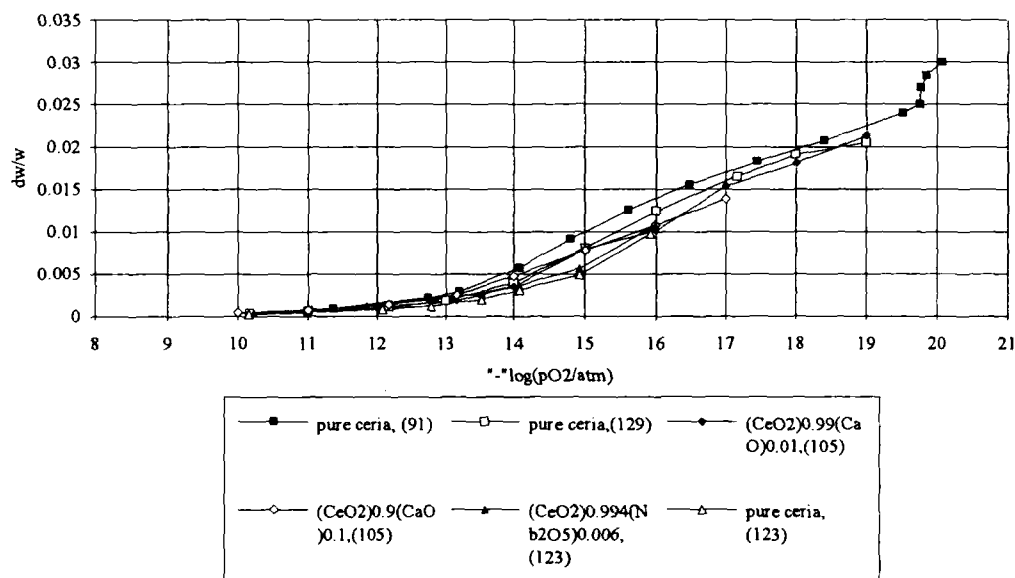


FIG 5.3.2.1b 1000°C WEIGHT LOSS v. OXYGEN PRESSURE
(REFERENCES GIVEN IN LEGEND)

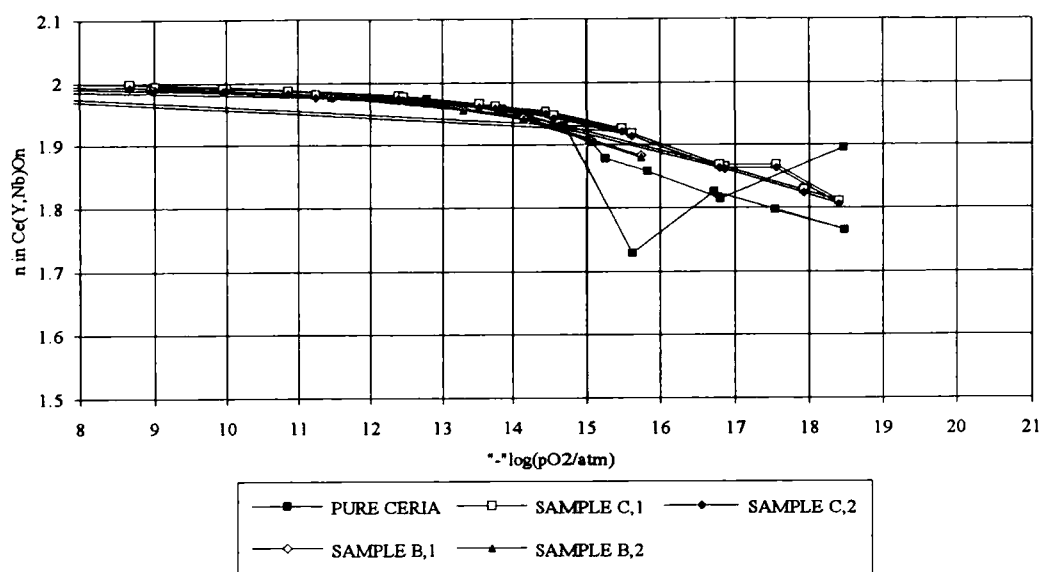


FIG. 5.3.2.1c 1000°C COMPOSITION v. OXYGEN PRESSURE

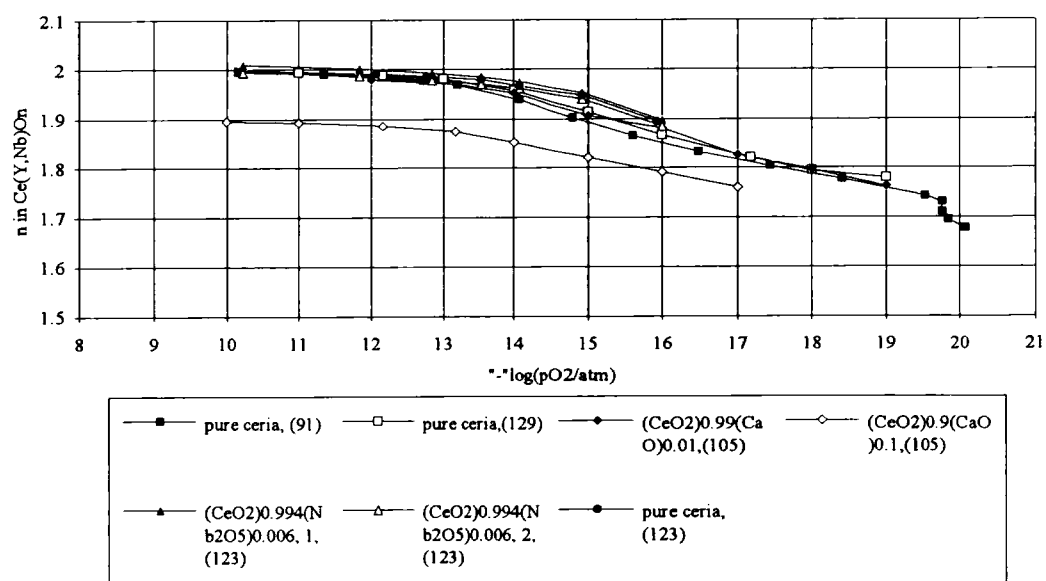


FIG. 5.3.2.1d 1000°C COMPOSITION v. OXYGEN PRESSURE (REF. IN LEGEND)

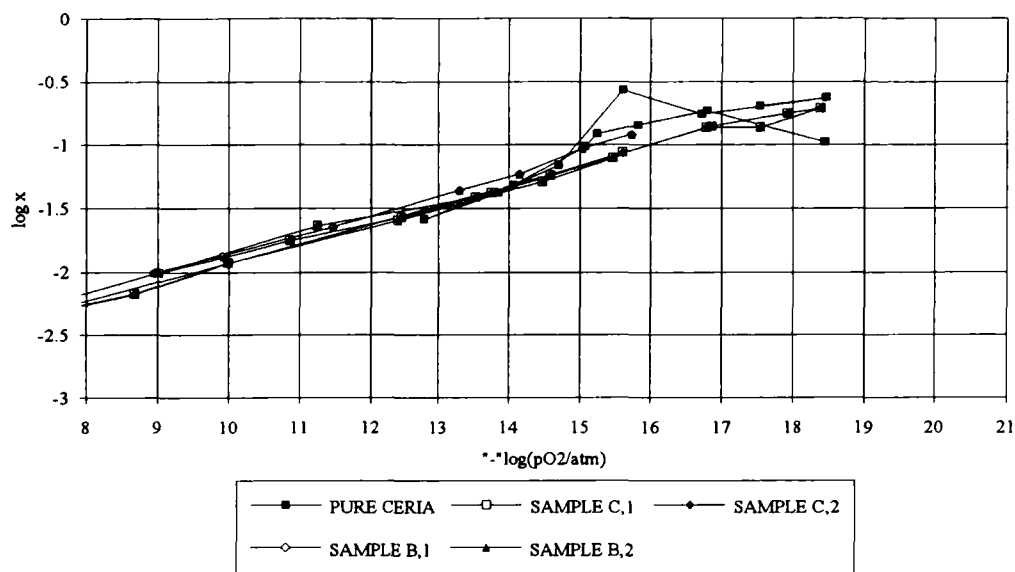


FIG. 5.3.2.1e 1000°C LOG(OXYGEN LOSS) v. OXYGEN PRESSURE

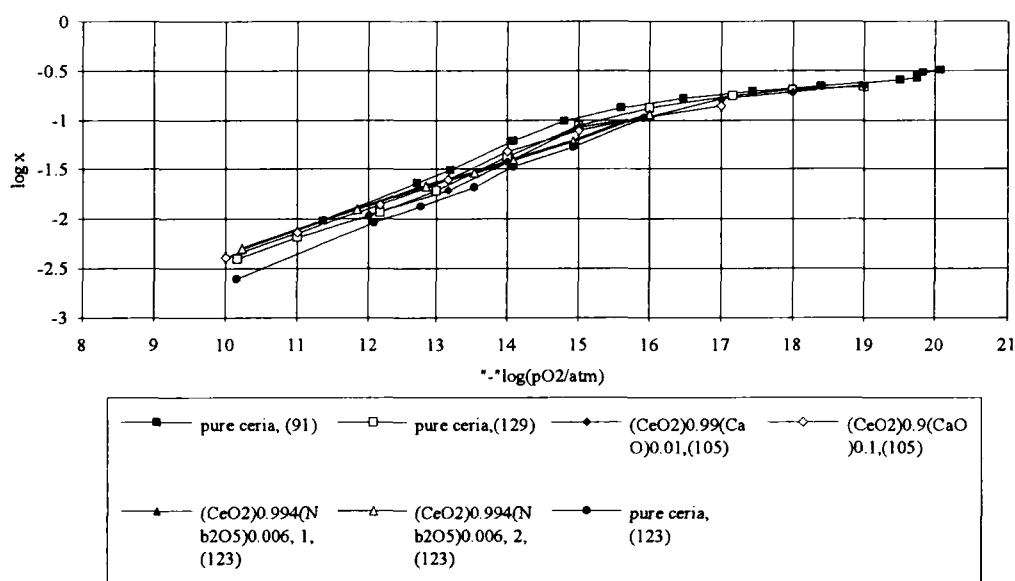


FIG. 5.3.2.1f 1000°C LOG(OXYGEN LOSS) v. OXYGEN PRESSURE (REF. IN LEGEND)

5.3.2.2 900 °C

Significant reduction of the cerias begins at a pO_2 of 10^{-15} at this temperature. The slope for pure ceria goes through a steep transition at around a pO_2 of 10^{-16} , a lower pressure than the transition at 1000°C. The results are different to those at 1000°C in that the lower valent doped materials in the literature suffer a greater initial weight loss than the undoped material. In the experimental data, both samples B and C suffer

a greater initial weight loss than pure ceria, as does the niobia-doped sample of Naik and Tien when compared to their data for pure ceria (123).

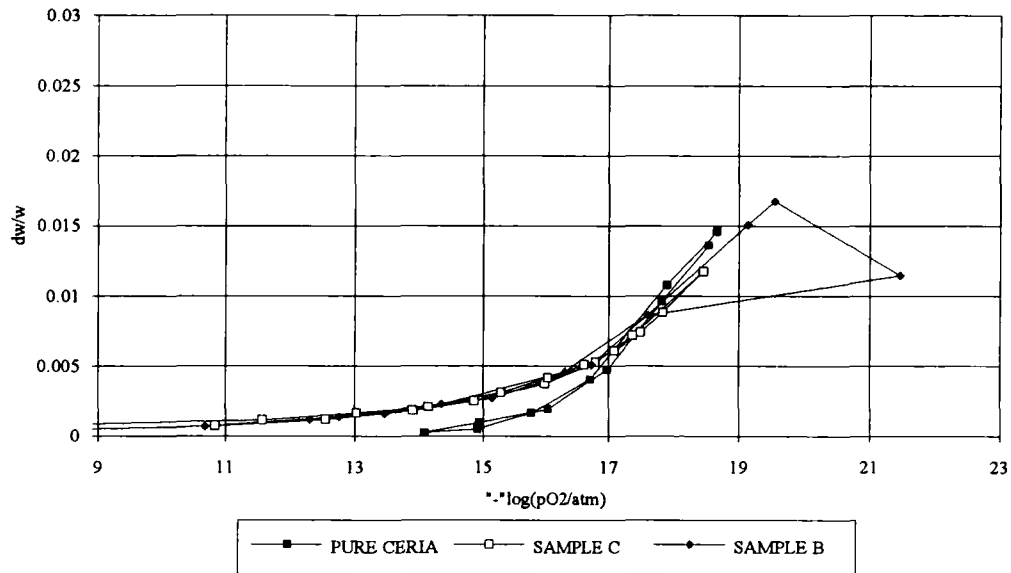


FIG. 5.3.2.2a 900°C WEIGHT LOSS v. OXYGEN PRESSURE

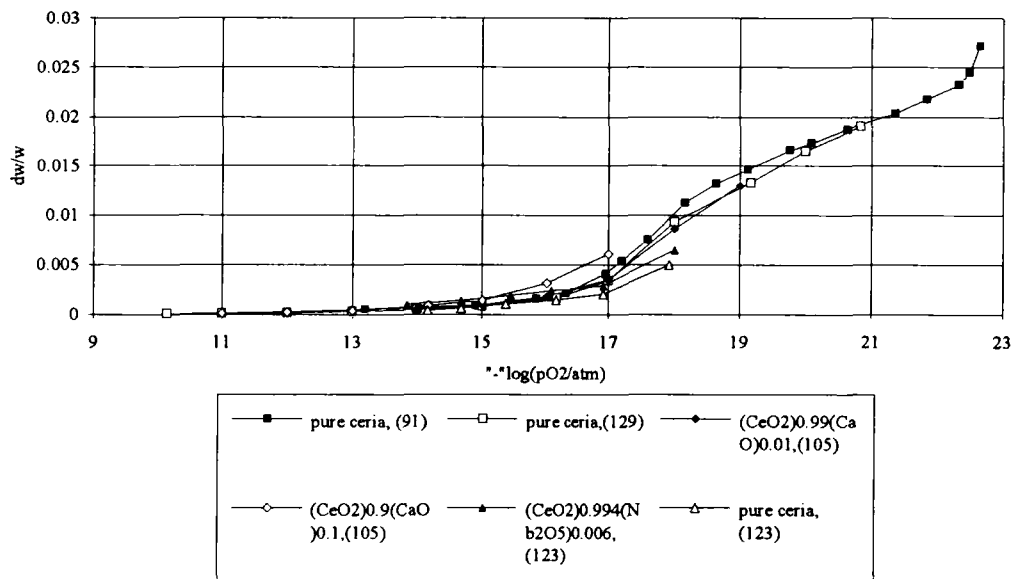


FIG. 5.3.2.2b 900°C WEIGHT LOSS v. OXYGEN PRESSURE (REF. IN LEGEND)

The experimental data for pure ceria is close to that of Bevan and Kordis in the literature. The reduction in Naik and Tiens pure ceria data is much less than that for the Gerhardt data and the Bevan and Kordis data.

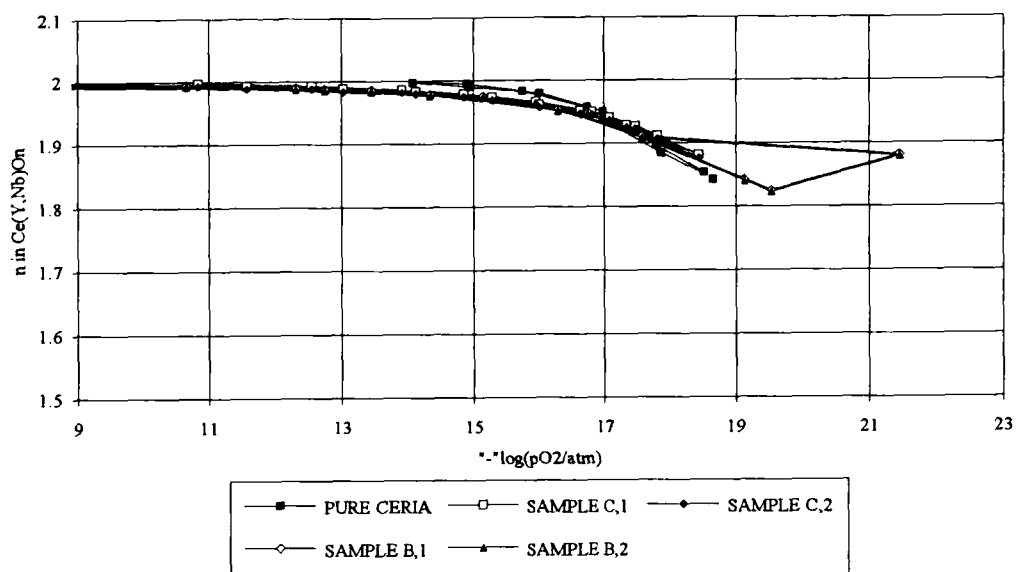


FIG. 5.3.2.2c 900°C COMPOSITION v. OXYGEN PRESSURE

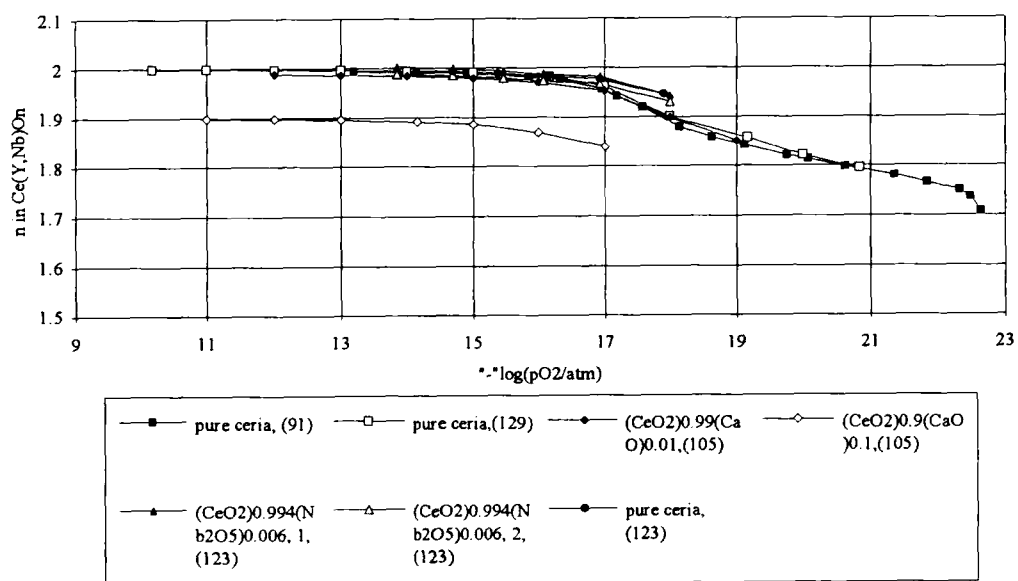


FIG. 5.3.2.2d 900°C COMPOSITION v. OXYGEN PRESSURE (REF IN LEGEND)

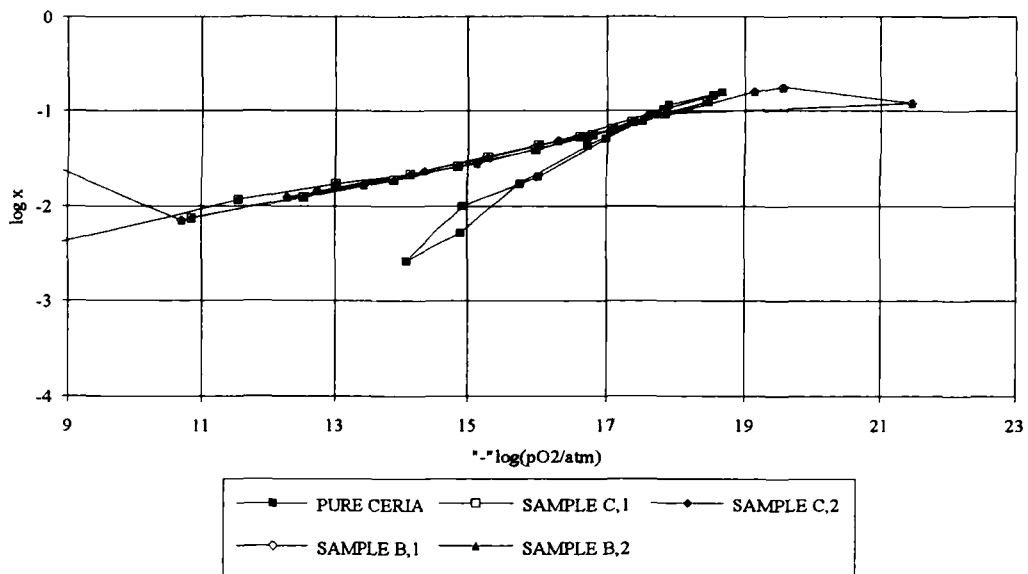


FIG. 5.3.2.2e 900°C LOG(OXYGEN LOSS) v. OXYGEN PRESSURE

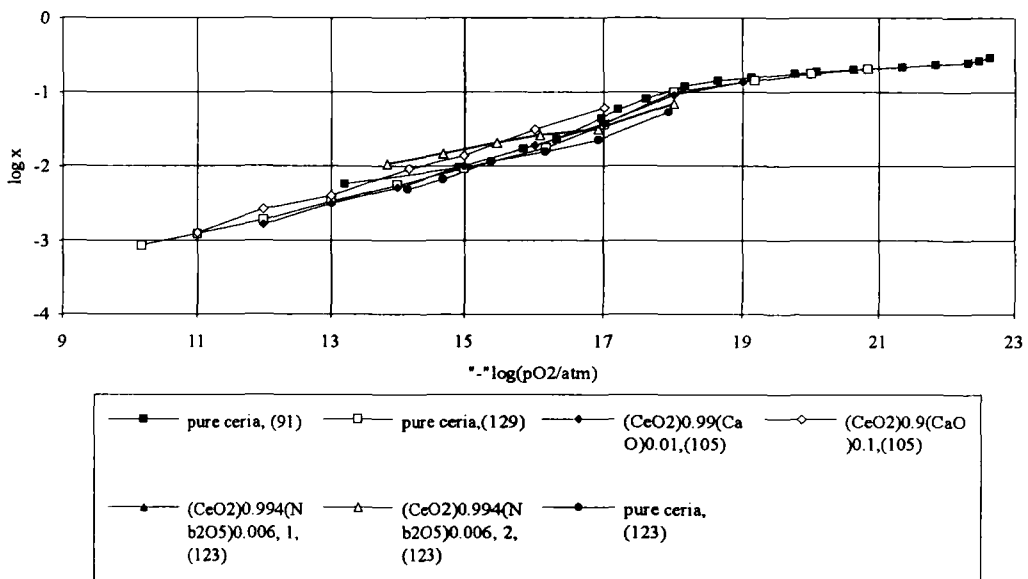


FIG. 5.3.2.2f 900°C LOG(OXYGEN LOSS) v. OXYGEN PRESSURE

Down to oxygen pressures as low as $10^{-17.5}$ samples B and C lose more oxygen than pure ceria. At oxygen pressures below this, pure ceria loses more oxygen. At this temperature, in the literature, the behaviour of all the lower valent cerias is close to that for pure ceria, all having similar slopes, whilst the slope for the higher valent doped sample is shallower. This is reflected to some extent in my data.

5.3.2.3 800' C

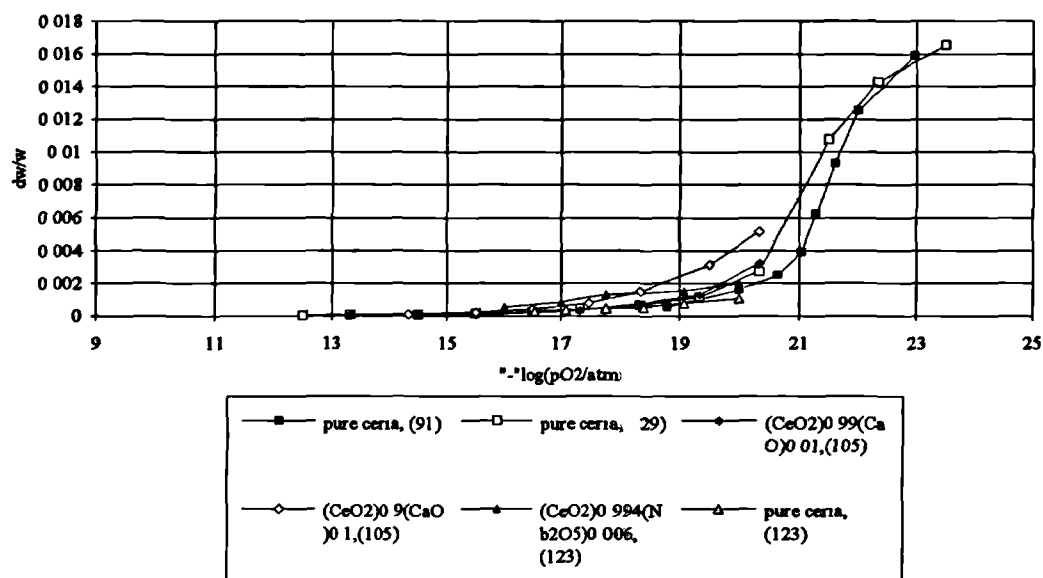


FIG. 5.3.2.3a 800'C WEIGHT LOSS v. OXYGEN PRESSURE (REF. IN LEGEND)

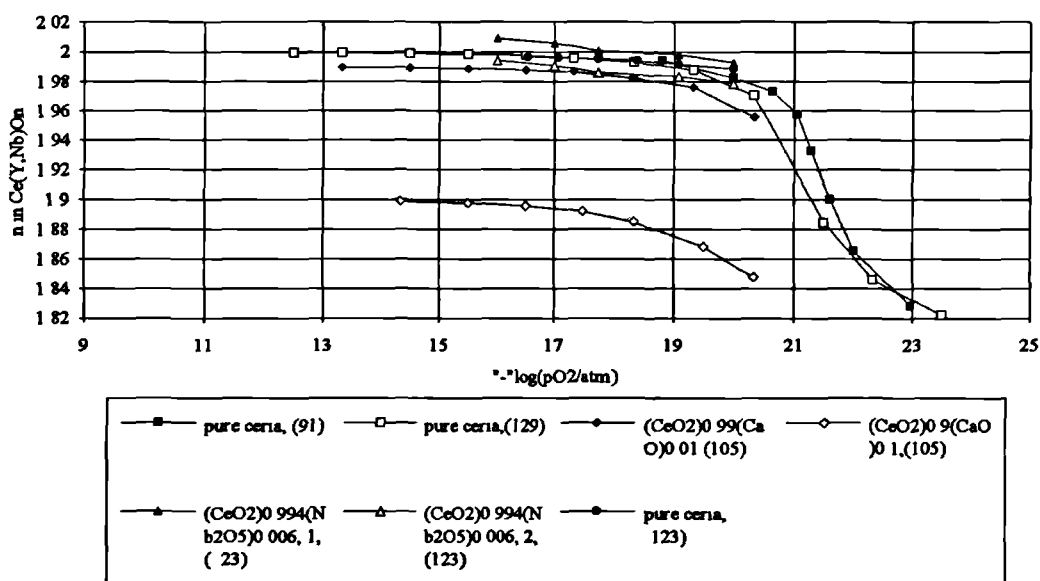


FIG. 5.3.2.3b 800'C COMPOSITION v. OXYGEN PRESSURE (REF. IN LEGEND)

At this temperature, there was no significant weight loss until oxygen pressures below about 10^{-19} . Because of this, very few measurements were made. The experimental data showed a similar low pressure of reduction, but as measurements were only made on samples E and I, the exact values are meaningless. For this reason the graphs are not plotted here. Niobia doped ceria exhibits a higher weight loss in this initial stage of reduction, as at 900°C.

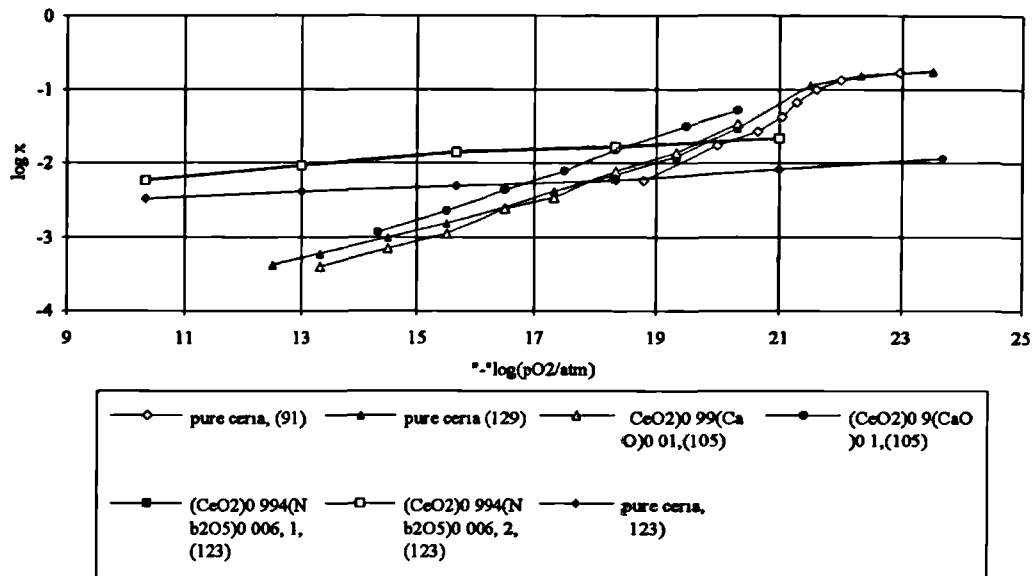


FIG. 5.3.2.3c 800°C LOG(OXYGEN LOSS) v. OXYGEN PRESSURE (REF. IN LEGEND)

The 10%CaO-doped material in the literature exhibits an initially steeper slope than ceria doped with smaller quantities of lower valent dopant. The slopes of the pure ceria samples were steeper at oxygen pressures lower than 10^{-20} , but data was not available for the remaining materials below this pressure.

5.3.2.4 SUMMARY OF FINDINGS

Simultaneous doping with niobium and yttrium does not appear to have a significant effect on the results when compared to the data for the singly doped materials. This would be in keeping with the theory of double doping proposed by Kroger, and discussed in section 3.4.2. Doping up to the quantities examined, does not appear to have a significant effect on the extent of oxygen loss from the material. Thus, it cannot be expected to greatly reduce the expansion - contraction that the material undergoes during reduction and oxidation. Doping does seem to eliminate the steep reduction found between oxygen pressures 10^{-14} and 10^{-16} at 1000°C , and at 10^{-16} at 900°C , which may be of benefit. The region corresponds to the miscibility gap given in the phase diagram, and if there are no phase changes, stresses in the material reducing could be decreased. Both higher and lower valent dopants appear to have this effect. Doping with a higher valent dopant or where $[Nb] > [Y]$, seems to cause an initial higher rate of oxygen loss when compared to pure or lower valent materials at temperatures of 900°C and below. The situation at 1000°C is not so clear. My experimental data shows a similar initial weight loss, whilst the data in the literature

shows greater losses for a number of other materials. However, at this temperature, the values are close, and when examining the Naik and Tien data separately, it can be seen that their data for pure ceria shows a smaller loss. The Naik and Tien data (123) for pure ceria is in poor agreement with the other data throughout. Naik and Tien (123) suggest that this additional initial weight loss in niobium doped materials was due to loss of interstitial oxygen in addition to lattice oxygen. This author believes that the interstitial oxygen will leave the lattice more readily, rather than in addition to lattice oxygen. Reduction of a cerium ion and subsequent loss of an interstitial oxygen is believed to cause less distortion in the lattice than reduction of the cerium ion, and loss of a lattice oxygen, it is thus energetically more favourable. This means that interstitial oxygen will be lost at a greater rate than lattice oxygen, resulting in an initial larger weight loss in higher valent doped samples. Loss of interstitial oxygen will work to decrease the lattice parameter, whilst reduction of cerium ions will work to increase it. Because initially there are negligible oxygen vacancies in this material, shielding of positive centres in the crystal is better than in a lower valent doped material, and expansion - contraction of the lattice in this region may be improved. However, given the results for the coefficient of expansion in section 5.3.1, this effect is clearly not sufficient above 800°C.

5.3.2.5 THERMOGRAVIMETRIC MODEL

Before thermogravimetric experiments were carried out, a series of simple models for the higher purity sample compositions, based on the results of Bevan and Kordis (91) were produced. Because of the nature of the dopants, a number of assumptions had to be made about the initial stoichiometries in air. It was assumed that in all samples, yttrium doping resulted in the formation of doubly ionised oxygen vacancies and niobium doping introduced oxygen ions which would fill those vacancies until $[Nb] = [Y]$. The samples were divided into two groups; those for which $[Y] \geq [Nb]$ (I,E,G,D,J and A), and those for which $[Nb] > [Y]$ (B,C,H and F). The former group required only one model. For $Ce_aY_bNb_cO_n$ where $a+b+c=1$ and $n = 2a+3/2b+5/2c-x$, the stoichiometry, n , for a given temperature and pressure, was calculated by equating Ce_aO_{2a-x} with CeO_n where $n = 2-y$ from Bevan and Kordis, giving $x = ay$.

For samples where $[Nb] > [Y]$ the concentration of niobium above the limit $[Nb] = [Y]$ and given by $[Nb]^* = [Nb] - [Y]$ can be compensated in two ways; either by the formation of oxygen interstitials or by reduction of the cerium ion. In the former case the stoichiometry was calculated as above. In the latter case, it was necessary to distinguish between initial $CeCe^x$ and $CeCe'$ ions. Here $Ce_{(a-c+b)}O_{2(a-c+b)-x}$ from

$\text{Ce}_{(a-c+b)}\text{Ce}'_{(c-b)}\text{YbNb}_c\text{O}_{2(a-c+b)+4c-x}$ where $a+b+c = 1$ and $2(a-c+b)+4c = 2$ is equated to the Bevan and Kordis data giving $x = (a-c+b)y$ and $n = 2(a-c+b)+4c-x$.

Since the Nb^{5+} ion is capable of reduction to Nb^{4+} , a model in which $[\text{Nb}]^*$ was compensated by reduction of Nb, and where both Nb and Ce were reduced with decreasing $p\text{O}_2$ was produced. Thermogravimetric data for Nb_2O_5 was taken from Kofstad and Anderson (175) and extrapolated to give data at the temperatures and oxygen pressures of the Bevan and Kordis data for pure ceria. In this case, for $\text{Ce}_a\text{YbNb}'_{(c-b)}\text{Nb}_b\text{O}_{2a+2(c-b)+3/2b+5/2b-x-z}$, $\text{Ce}_a\text{O}_{2a-x}$ is equated with the Bevan and Kordis data as before, giving $x = ay$, and $\text{Nb}_b\text{O}_{5/2b-z}$ is equated with the extrapolated data of Kofstad and Anderson for $\text{Nb}_2\text{O}_{5-y}$, where $z = yb/2$ and $n = 2a+2(c-b)+3/2b+5/2b-x-z$.

A graph comparing the models for sample B is given in fig.5.3.2.5e. Codes 1a, 1b, and 11 in the legend refer to cerium reduction, niobium reduction and oxygen interstitial models respectively.

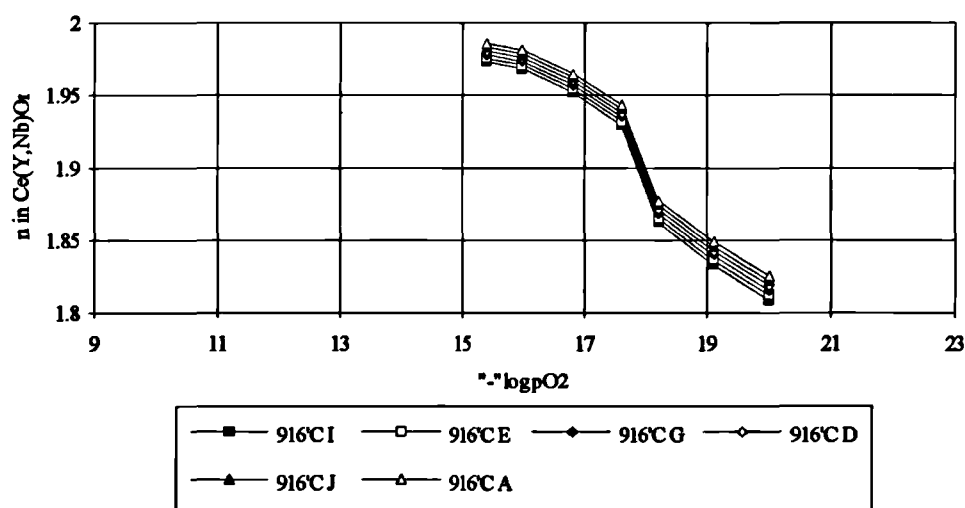


FIG. 5.3.2.5a MODEL FOR SAMPLES WITH $[\text{Y}] > [\text{Nb}]$ AT 916°C
(COMPOSITIONS GIVEN BY I-A (SECTION 4.1))

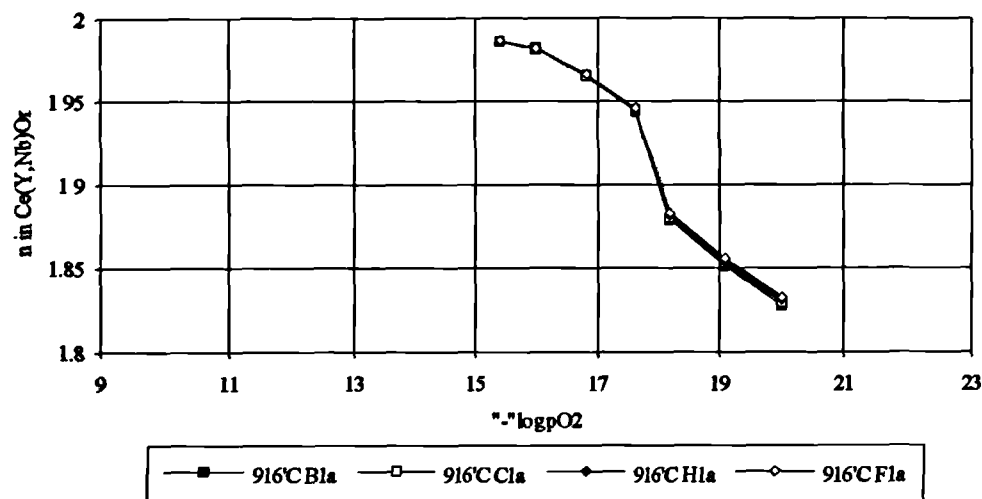


FIG. 5.3.2.5b CE REDUCTION MODEL FOR SAMPLES WITH $[Nb] > [Y]$ AT 916°C
(COMPOSITIONS GIVEN BY B - F)

It is unlikely that the niobium ions would behave as those in the pure oxide; the levels of Nb doping were relatively low, and the crystal structure was not that of niobium oxide. Low levels of lower valent dopant affect the defect behaviour of ceria, particularly at high pO_2 (section 3.2.1). In section 5.3.4 it will be shown that dopants influence the activation energy of oxygen diffusion. The model does not account for any defect interaction. It is probably because of defect interactions, that the slopes of the $\log x$ graphs in the experimental data are not consistent with those predicted by the models discussed in section 3.4; at 900°C for sample C between $-1/6$ and $-1/7$, and between $-1/7$ and $-1/8$. Sample B is a better fit at between $-1/5$ and $-1/6$.

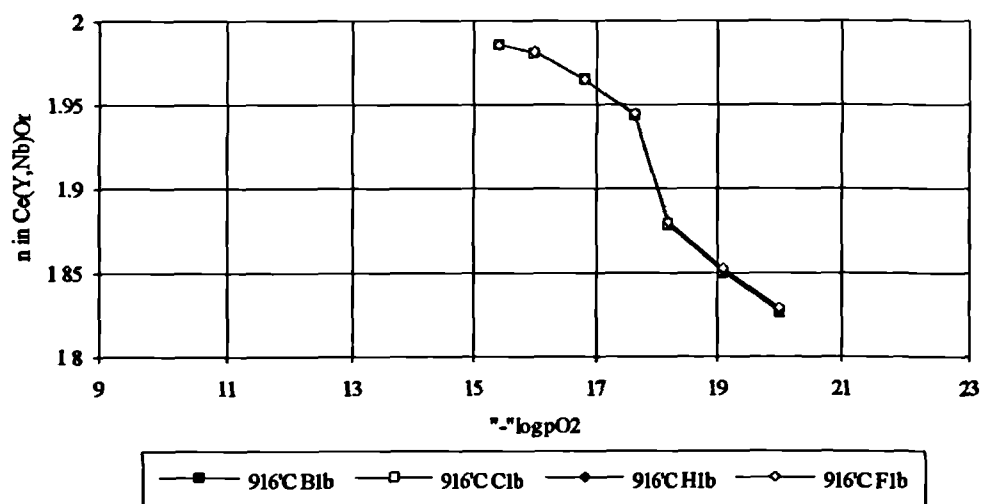


FIG. 5.3.2.5c NB REDUCTION MODEL FOR SAMPLES WITH $[Nb] > [Y]$ AT 916°C
(COMPOSITIONS GIVEN BY B-F)

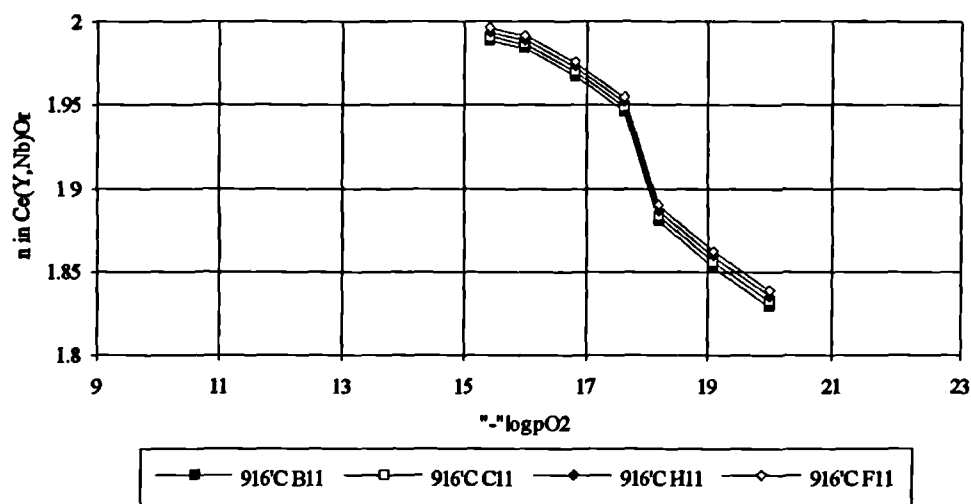


FIG. 5.3.2.5d OXYGEN INTERSTITIAL MODEL FOR SAMPLES WITH [Nb] > [Y] AT 916°C
(COMPOSITIONS GIVEN BY B-F)

Comparison of the model with the experimental data shows the change of n with $p\text{O}_2$ for all the samples is not as steep as had been predicted, but is rather spread out over a wider range of $p\text{O}_2$. The compositions at $p\text{O}_2 \cdot 10^{-19}$ are close to the predicted compositions. The effect of the dopant in changing the thermodynamic behaviour of the oxide could cause this. Fig 5.3.2.5f shows that temperature change also affects the slope. Change in temperature seems to be more important in a study of stoichiometry than the particular model. Literature and experimental data also show that the slope is steeper but covers a smaller range of $p\text{O}_2$ at lower temperature. During the TG experiment the temperature could only be maintained to $\pm 3^\circ\text{C}$.

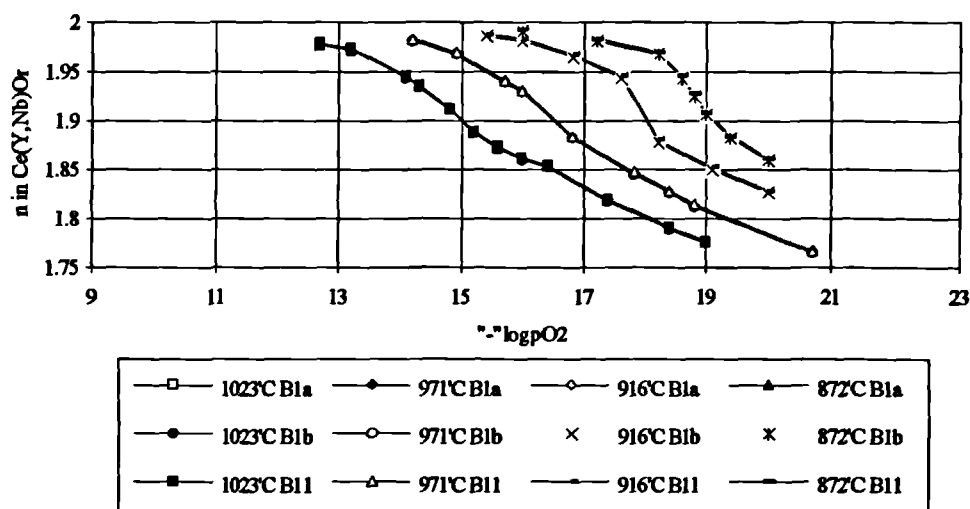


FIG. 5.3.2.5e COMPARISON OF MODELS FOR COMPOSITION B
AT 872, 916, 971 AND 1023°C

Comparison of the experimental data for samples B and C with the models 1a,b (cf. 1) and 11 (cf. 2) shows a closeness in the data for the two samples, though not as close as that for 1a or b. Thus it would appear that interstitial oxygen ions are present in the material at higher pO_2 .

5.3.3 CONDUCTIVITY DATA

The data were measured within $\pm 5^\circ\text{C}$ of 890°C , $\pm 10^\circ\text{C}$ of 975°C , and $\pm 5^\circ\text{C}$ of 830°C . The temperature is the average, taken from the difference in temperature across the sample. This was sometimes as large as 40°C . The accuracy of the conductivity with respect to composition cannot be determined as the experiments were carried out on only one sample of each composition. A good correlation was noted for data measured in oxidising and reducing directions. Sample breakage prevented data from being measured in both directions for some specimens. The literature data were measured at 800°C , 900°C and 1000°C by most of the researchers (79,104,108,130). The Naik and Tien data (120,123) were measured at 805°C , 905°C and 1029°C . Section and figure headings are given to the nearest 100°C for simplicity.

In the literature at 1000°C , the lower valent doped sample (300ppm Ca) has a higher conductivity than the pure ceria single crystal. Naik and Tien's polycrystal (120) also had a higher conductivity than the single crystal. This is probably because their sample is at a higher temperature. All materials reach a point where conductivity levels out, seen to then decrease for the single crystal. The range over which the niobium doped material maintains a constant conductivity (10^{-15} - 10^{-18}) is encouraging, as this is the range over which the fuel cell is expected to operate.

The sudden drop in conductivity shown in fig. 5.3.3a for sample B is a result of the sample cracking during the experiment. It can be seen however that the curve of the data is unaffected. The estimated σ_{max} for sample A is 1.6-1.8S/cm, and for sample B 5S/cm. The data shows a more or less constant conductivity from 10^{-15} . These values are little better than those in the literature for yttria doped and pure ceria at the temperature.

At 900°C the data for sample A is marginally better than that for yttria doped ceria in the literature, and the maximum conductivity was reached at a slightly higher oxygen pressure. The data for B and C is little better than that for pure ceria in the literature, as was found at 1000°C .

In the following graphs pO_2 is measured in atmospheres, and conductivity in S/cm.

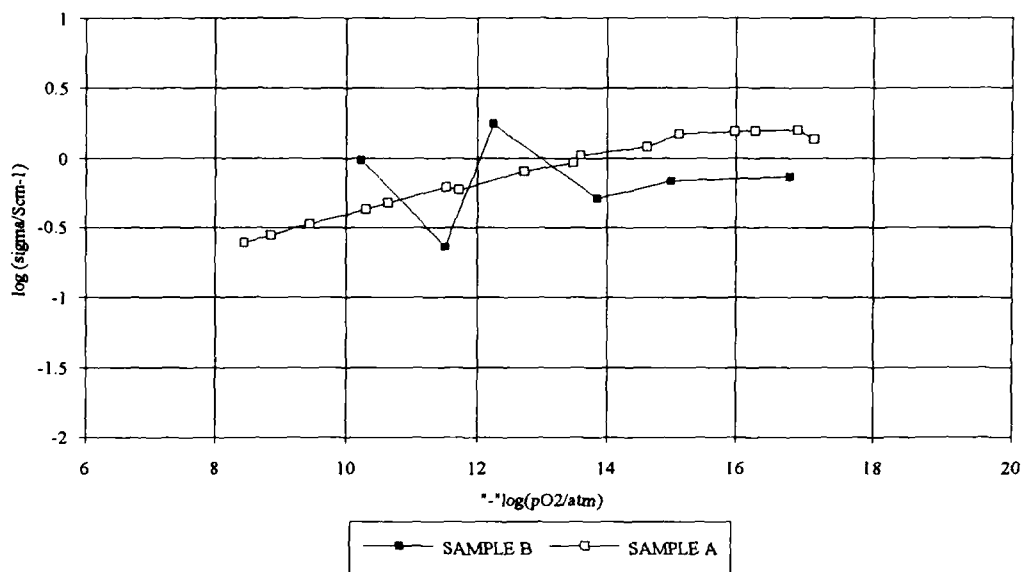


FIG. 5.3.3a 1000°C CONDUCTIVITY v. OXYGEN PRESSURE

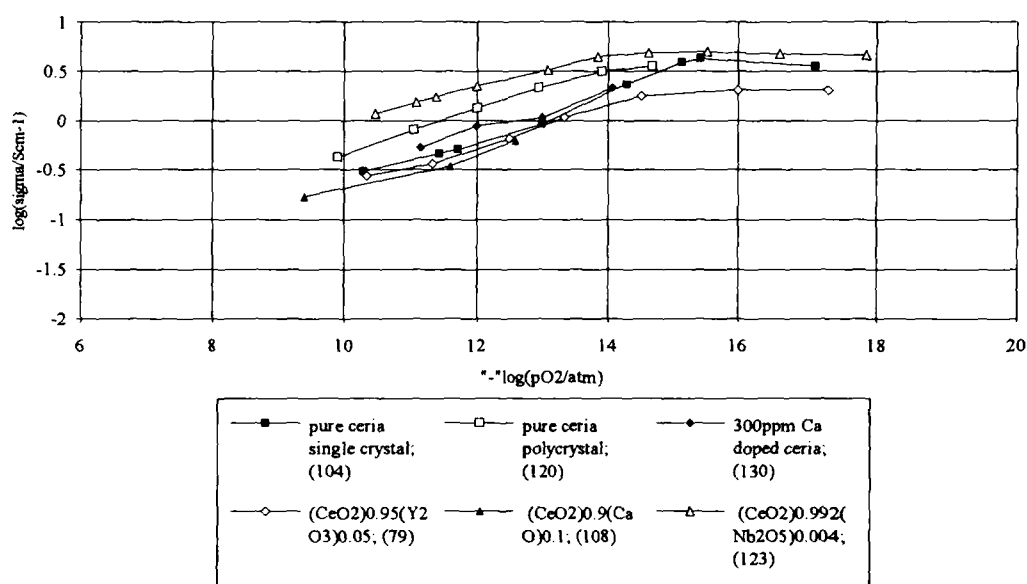


FIG. 5.3.3b 1000°C CONDUCTIVITY v. OXYGEN PRESSURE (REF. IN LEGEND)

At 800°C it can be seen in the literature that the difference between conductivity of the niobium doped sample and the rest, particularly at high $p\text{O}_2$ is much larger than at higher temperature. It corresponds well with the value for sample B at 830°C. Thus niobium doping appears to be a particular advantage if good conductivity is required

at lower temperatures. Greater ease of reduction at these temperatures (section 5.3.2.3) in addition to the reduction introduced by the dopant could contribute to this.

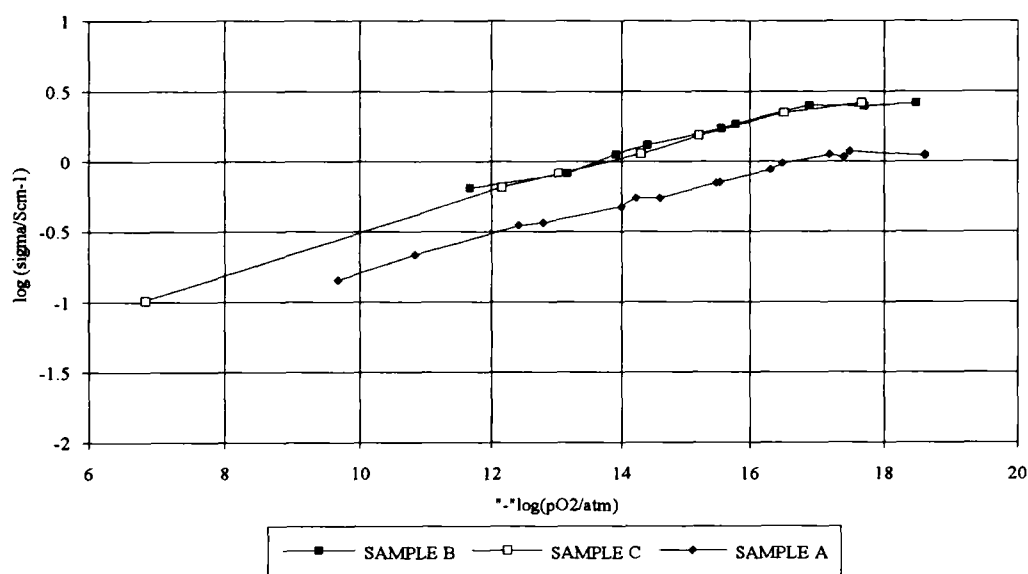


FIG. 5.3.3c 900°C CONDUCTIVITY v. OXYGEN PRESSURE

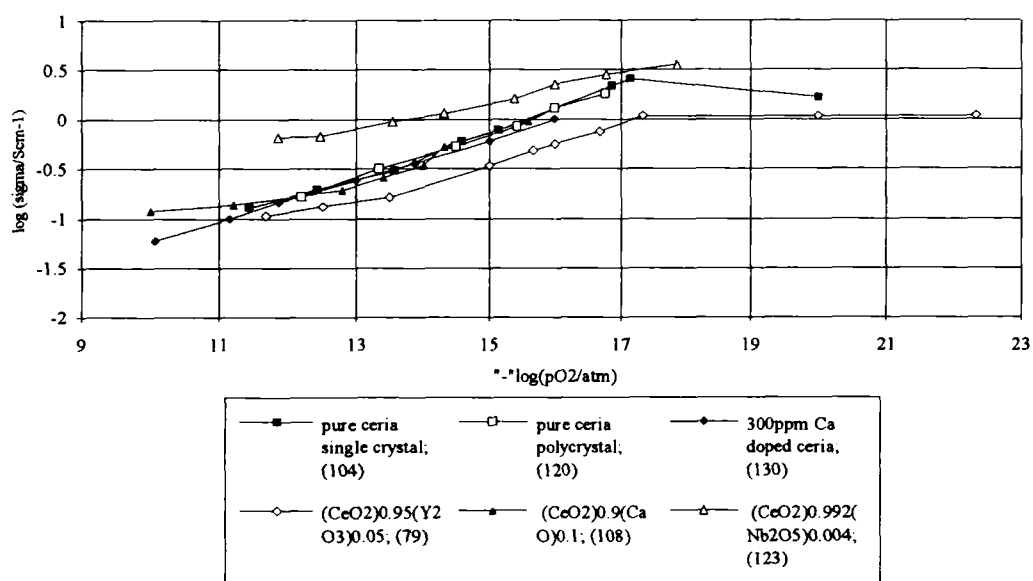


FIG. 5.3.3d 900°C CONDUCTIVITY v. OXYGEN PRESSURE (REF. IN LEGEND)

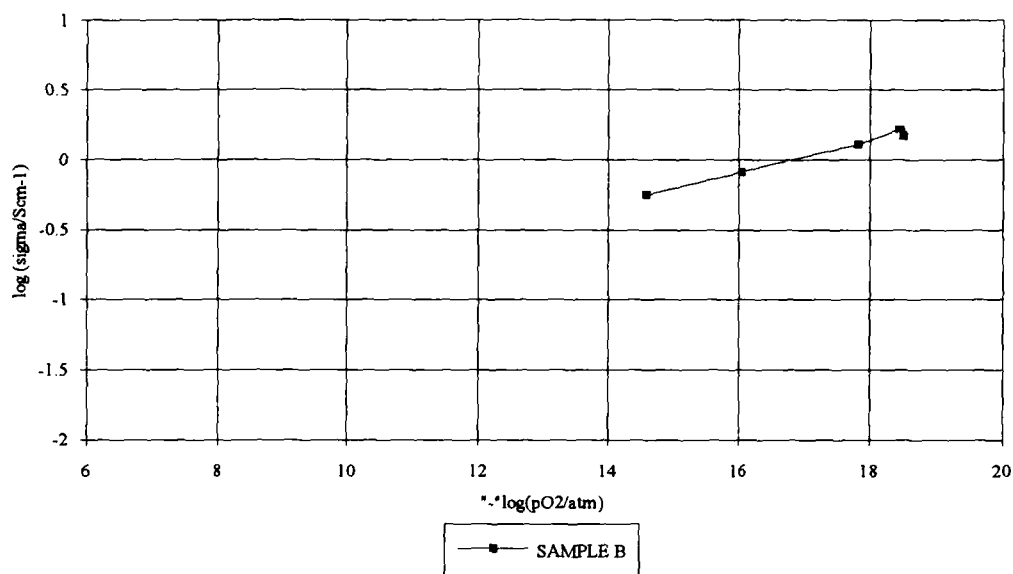


FIG. 5.3.3e 830°C CONDUCTIVITY v. OXYGEN PRESSURE

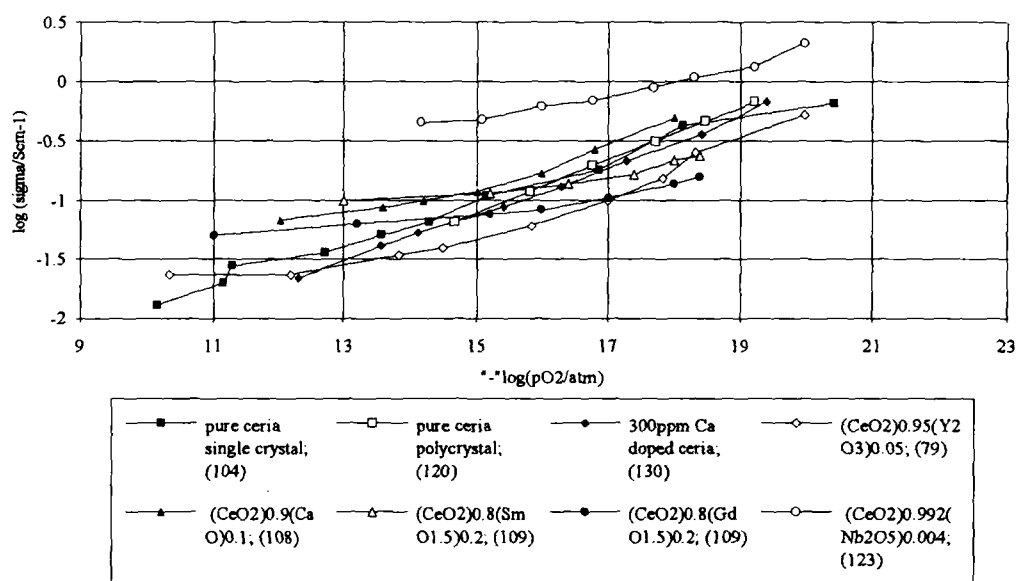


FIG. 5.3.3f 800°C CONDUCTIVITY v. OXYGEN PRESSURE (REF. IN LEGEND)

Examination of the results for conductivity indicates that higher conductivities are achieved for niobia doped ceria that does not contain yttria, rather than for the doubly doped material. This may indicate that a second phase is present in my samples, since the trend in conductivity appears to be in opposition to the measured compositional data, where the difference in [Y] and [Nb] was larger than anticipated. The

conductivities measured for sample A were similar to those for yttria doped ceria, which is lower than anticipated, and in opposition to the composition as analysed. There was no significant difference found in the results for samples B and C, although the amount of niobium in the two samples differs. Though the conductivities measured were higher than for sample A, they were not as high as the literature values for Nb doped ceria.

It would appear that double doping has no beneficial effect on the conductivity of doped cerias, and may reduce the effectiveness of niobium in promoting electronic conductivity over and above what would be expected given the amount of Y present. It is possible that Nb and Y form a defect pair in the material, and this is supported by the composition of the second phase in sample Y55, given in section 4.4.4. Additionally, the matrix of this material contained more yttrium than niobium. The defects may interact at a distance, as those found by Wang et al (111). Alternatively, the ICP analysis of the samples could be incorrect, and the actual composition of the samples closer to that which was anticipated. In this case, the result for sample A would be near to that expected. However that would not explain the similarity in results for B and C, or why the data are lower than those for the singly doped material. Formation of a defect pair, which may also nucleate a second phase, would reduce the electrostatic stresses in the material, and as was discussed in section 3.2 yttrium ions have formed pairs with other positive defects (vacancies).

The data given in figs 5.3.3g,h were measured at Imperial college. The conductivity of the samples in forming gas is much higher than in air, and has a shallower slope, indicating a low activation energy of conduction. The maximum conductivity here for sample Y1 in forming gas is rather higher than those obtained for higher Nb doped samples discussed in this section. The activation energy is calculated at 0.41eV for I5 at higher temperature and 0.26eV at lower temperature. For sample Y1(FG) the activation energy was calculated as 0.43eV. The similarity in activation energy between I5 in air and Y1 in forming gas suggests that conduction occurs by the same mechanism in the two materials; small polaron hopping. The values are similar to those found in the literature ((fig.3.3),119-120). Shingler observed a change in activation energy with temperature at high pO_2 in his samples (60). In samples containing a second phase he found that the activation energy increased sharply at lower temperature. The reverse was found here.

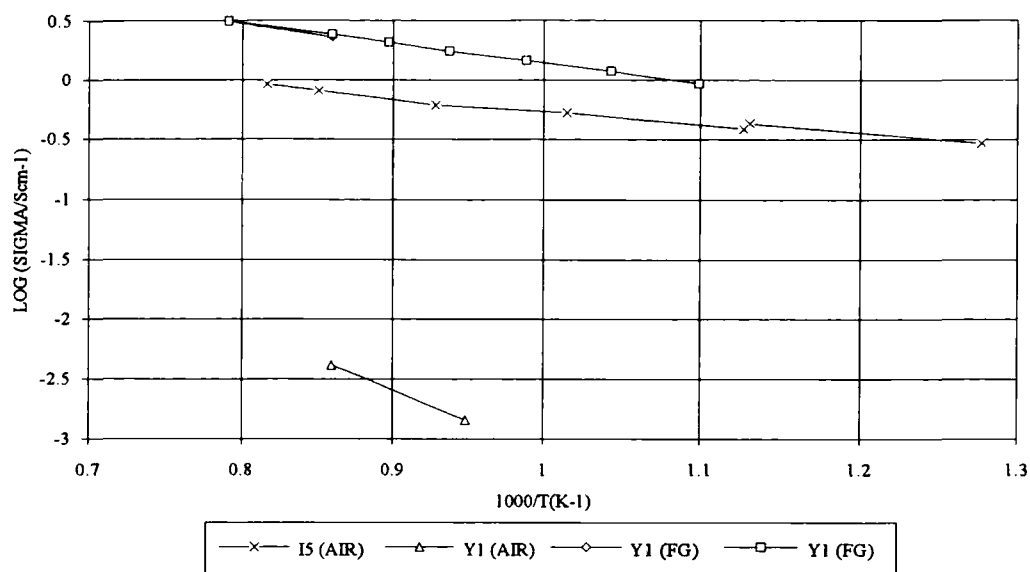


FIG. 5.3.3g LOG(CONDUCTIVITY) v. 1000/T

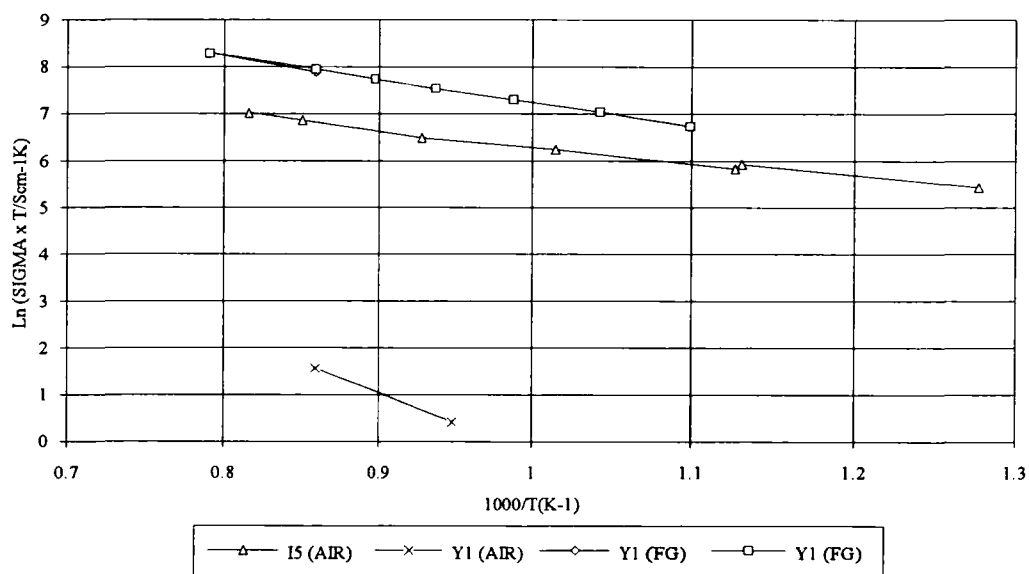


FIG. 5.3.3h LOG (CONDUCTIVITY x T) v. 1000/T

All the data show that Ce^{3+} ions are also present in the higher doped material at high pO_2 , since the conductivity of the doped material in this region is higher than the nondoped material. Thus the compensation mechanism must include both incorporation of oxygen interstitial ions and reduction of cerium ions. This was found to be the case by Naik and Tien (123).

5.3.4 OXYGEN DIFFUSION

The results are given in tables 5.3.4a-c. The data of two samples of Dr. P.H.Middleton (CL and CN) are included here for comparison. All the results below were submitted to the 1st International Symposium on Ionic and Mixed conducting Ceramics 1991 (173).

TABLE 5.3.4a DIFFUSION AND SURFACE EXCHANGE COEFFICIENTS

SAMPLE	TEMP. (°C)	D* (cm ² /s)	k (cm/s)	E _a (kJ/mol)
Y0	900	4.00E-08	9.00E-07	
Y05	900	1.00E-07	3.00E-07	
Y55	900	3.00E-08	1.00E-06	
	800	1.00E-08	1.00E-07	60 (+/-20)
	700	8.00E-09	2.00E-07	
Y6	900	3.00E-08	1.00E-06	
	800	2.00E-08	7.00E-07	57(+/-3)
	700	9.00E-09	7.00E-08	

D* is the self diffusion coefficient, and k is the surface exchange coefficient. Doping with niobium reduces the diffusion coefficient, by reducing the number of available oxygen vacancies. The data for samples CL (Ce_{0.997}La_{0.003}O_{2-x}) and CN (Ce_{0.985}Nb_{0.015}O_{2-x}) is shown below.

TABLE 5.3.4b DIFFUSION DATA FOR P.H.M. SAMPLES

SAMPLE	TEMP. (°C)	D* (cm ² /s)	k (cm/s)	E _a (kJ/mol)
CL	960	8.00E-09	1.00E-06	
	900	4.00E-09	2.00E-06	127 (+/-6)
	800	1.00E-09	5.00E-08	
CN	960	4.00E-11	7.00E-07	
	900	3.00E-11	2.00E-07	50 (+/-8)
	800	2.00E-11	5.00E-08	

When compared to the nominally doped CL, doping with higher or lower valent dopants can be seen to have reduced the activation energy of diffusion quite considerably. The diffusion mechanism in sample CN is clearly different to that for the remaining samples, and is believed to be an interstitial mechanism (124). Matzke (103) gives the following equation for diffusion.

$$D = D_0^v[V_O]\exp\{-E_a^v/RT\} + 2D_0^i[O_i]\exp\{-E_a^i/RT\} \quad [2]$$

where the superscripts v and i represent vacancy and interstitial mechanisms. For a material in which diffusion occurs by a vacancy mechanism, the latter part of the equation can be ignored, and for an interstitial mechanism the former. Where graphs

of $\ln D$ v. $1/T$ are plotted, the activation energy E_a can be calculated, as can the preexponential factor. The preexponential factors are given below.

TABLE 5 3 4c PREEXPONENTIAL FACTORS	
SAMPLE	PREEXPONENTIAL FACTOR (CM ² /S)
Y55	1.2 (+/-0.3) x 10 ⁻⁵
Y6	1.1 (+/-0.1) x 10 ⁻⁵
CL	1.8 (+/-1.8) x 10 ⁻³
CN	5.3 (+/-0.2) x 10 ⁻⁹

The data for the samples here may be compared with that for $UO_{2\pm x}$ as given by Matzke (103). E_a^V and E_a^i for urania were reported to be 264kJ/mol and 99kJ/mol respectively, whilst the energy for the formation of frenkel defects required for diffusion in the stoichiometric material was given as 293kJ/mol. Similarly D_O^V and D_O^i were given as 1.44cm²/s and 0.013cm²/s respectively. Whilst the activation energies are higher than those found for the doped cerias reported here, the same pattern is observed. The near stoichiometric material CL has the highest activation energy, whilst that for CN is lower than the activation energies of samples Y55 and Y6. The preexponential factor of CN incorporating D_O^A is also very much smaller than those for samples Y55 and Y6. This would seem to suggest that diffusion in this sample does indeed occur by an interstitial mechanism.

At 900°C the highest exchange coefficients are found in samples CL, Y55 and Y6. The coefficients are a measure of gas-solid exchange at the interface, and are therefore important when characterising a material for use in a fuel cell. Work on this has recently been carried out at Imperial College (174). Steele indicates that the exchange current density can be measured by isotopic oxygen exchange measurements according to the equation:

$$i_o = k V_m z F \quad [3]$$

where i_o is the exchange current density, k the surface exchange coefficient, z the ionic charge, and F the Faraday constant. V_m is the molar volume of oxygen in the solid. A high exchange current density is required in a cell, if polarisation is to be low.

Samples Y55 and Y6 additionally have a higher diffusion coefficient than sample CL at 900°C. Examination of the matrix composition of these samples given in section 3.1 indicates that there is more yttrium than niobium. Sample Y05 has a higher diffusion coefficient, but lower surface exchange coefficient than Y55 and Y6. That Y0 has a diffusion coefficient lower than Y05 can be explained by remembering that the

intended composition is such that the yttria content for Y0 is lower than for Y05 even after the concentration of niobium has been subtracted.

It would seem that the surface exchange coefficient is not as dependent on the oxygen vacancy content as the diffusion coefficient, but that other factors also influence this. The exact mechanisms are not clear. Steele (174) wrote that good k values were found for surfaces that he describes as catalytically active. Therefore, the ease of $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$ may be important in providing electrons at the surface of the material. Steele also found that the values for yttria doped ceria were higher than those for Pt coated YSZ. It would seem, that as in the mechanism for oxidation of methane as proposed by Mogensen (71), both charge transfer and oxygen transport are more efficient when they can occur on the same site.

Simultaneous doping with Y and Nb does not appear to adversely affect the properties of the ceria, though as far as diffusion and surface exchange coefficients are concerned, there is no apparent benefit either. Since all measurements were carried out at a high $p\text{O}_2$, the behaviour of the material at low oxygen pressures is not known, but it is unlikely that an interstitial mechanism would operate.

5.3.5 CATALYSIS

Catalysis experiments were carried out on sample I and on sample C. Graphs of conversion and selectivity are compared here. The conversion graphs show the proportions of unreacted CH_4 and O_2 gases with respect to the total as a function of temperature. Selectivity refers to the proportion of the carbon based products compared to the total carbon in products again as a function of temperature. The hysteresis for sample I may be attributed to a nonequilibrium state. Alternatively, the difference in lattice oxygen between the two samples may be significant on initial reduction; sample C would be expected to lose oxygen more readily than I (section 5.3.2). For the experiment on sample I and the constant temperature experiments, readings were taken as far as possible every 20 minutes during the heating and cooling cycle. Twenty minutes is the time taken by the chromatograph to make one analysis. The experiment on sample C was carried out by Dr. Middleton, and the time between readings was variable, as he allowed the material to reach equilibrium at each temperature.

CO_2 was found to be the primary product on both samples up to 750°C. Above this temperature CO was formed, and the amount of CO_2 decreased. Examination of the graphs for selectivity shows that CO_2 was the primary product from about 100°C,

below which, C_2 's are more predominant. At these low temperatures however, the volume of product is negligible when compared to the unreacted gases. The proportion of products does not increase significantly until 400°C, when the CO_2 level begins to increase.

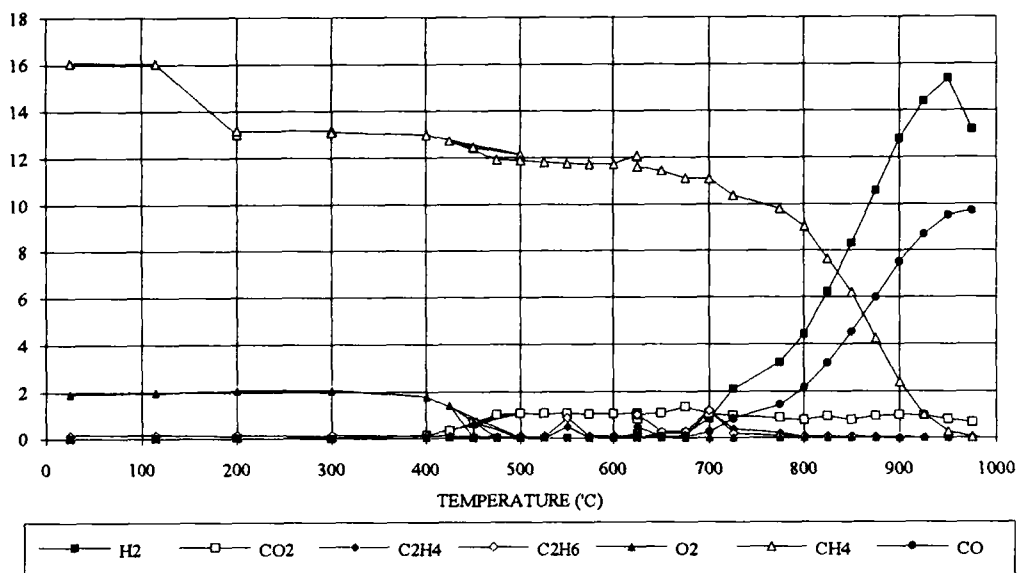


FIG. 5.3.5a SAMPLE C, RAW DATA

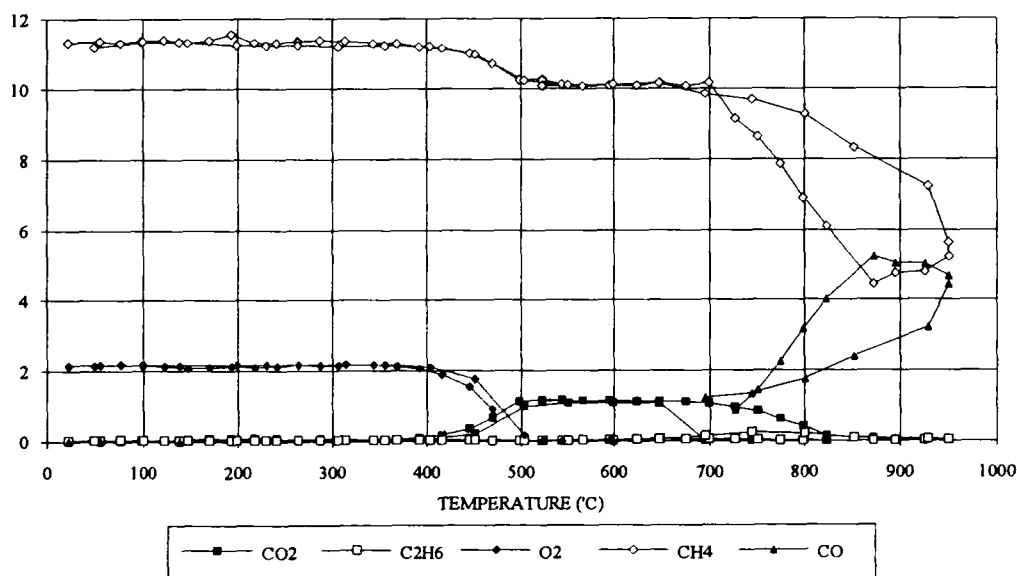


FIG. 5.3.5b SAMPLE I, RAW DATA

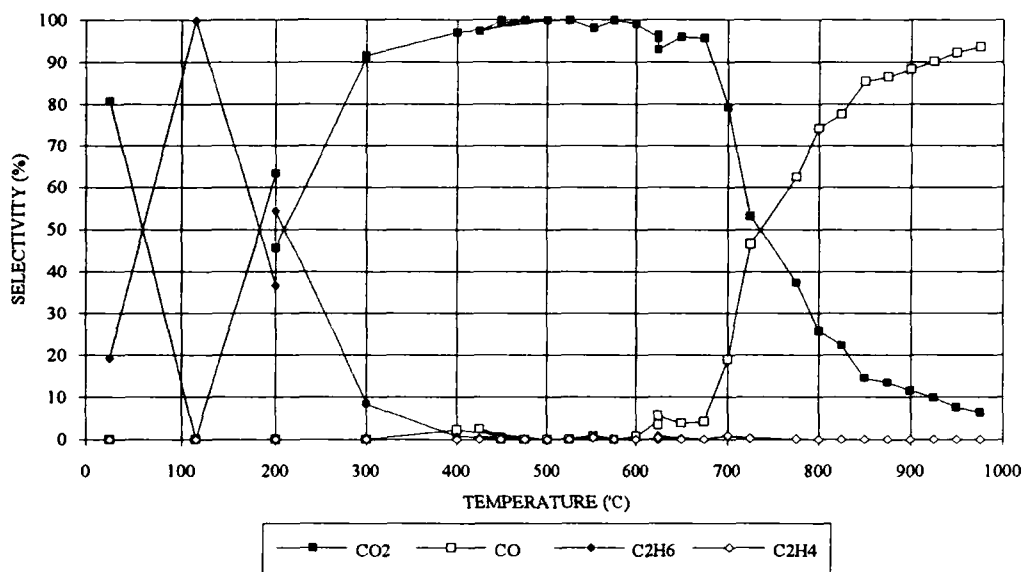


FIG. 5.3.5c SELECTIVITY, SAMPLE C

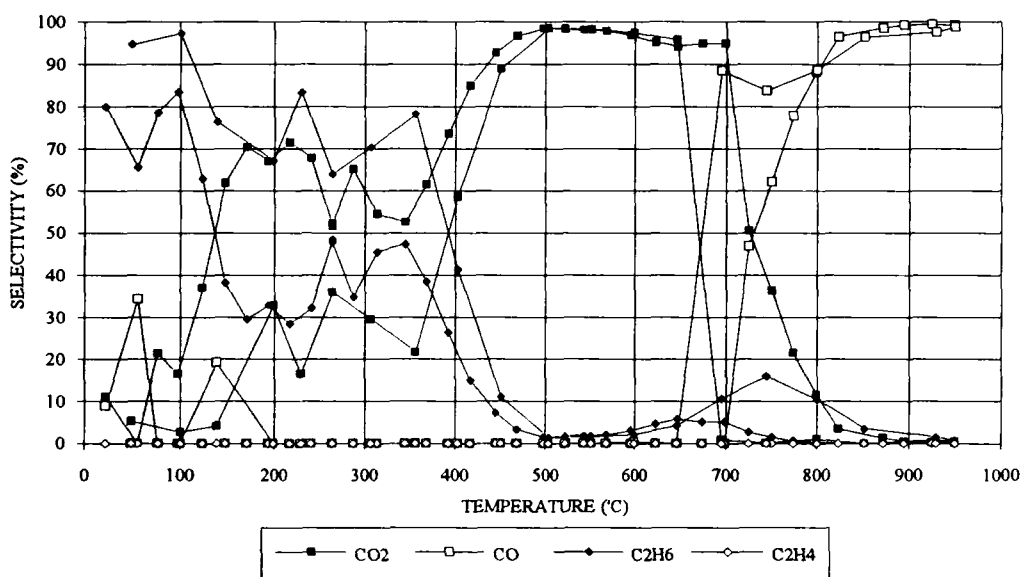


FIG. 5.3.5d SELECTIVITY, SAMPLE I

By 500°C all oxygen supplied in the gas mixture has reacted. The CO₂ level continues to increase with temperature, so that further oxygen must be supplied by the lattice oxygen of the powder. As can be seen, the decrease in CH₄ remaining is very shallow between 500°C and 750°C, and is a lot steeper by 800°C when the level of CO is higher.

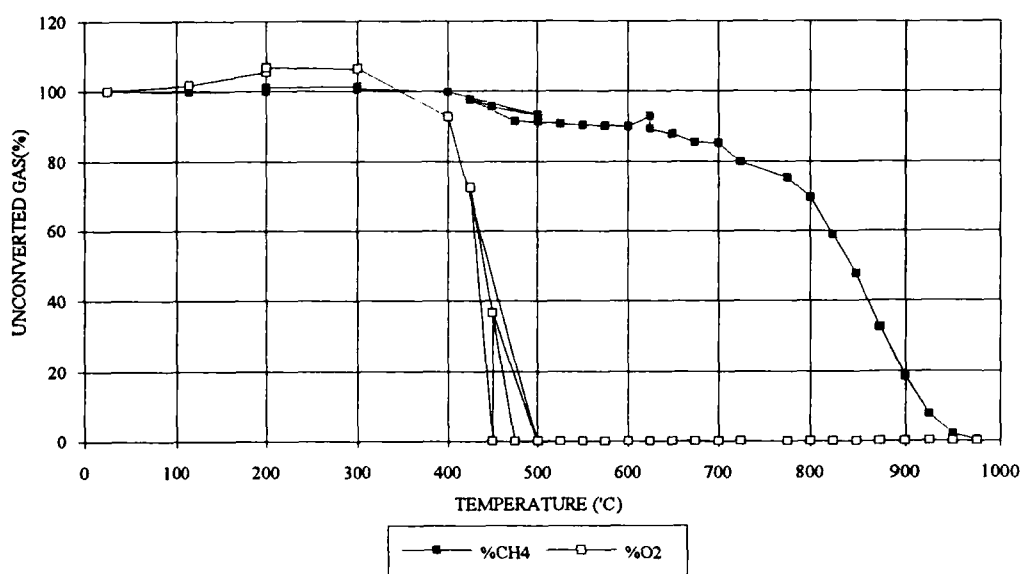


FIG. 5.3.5e CONVERSION, SAMPLE C

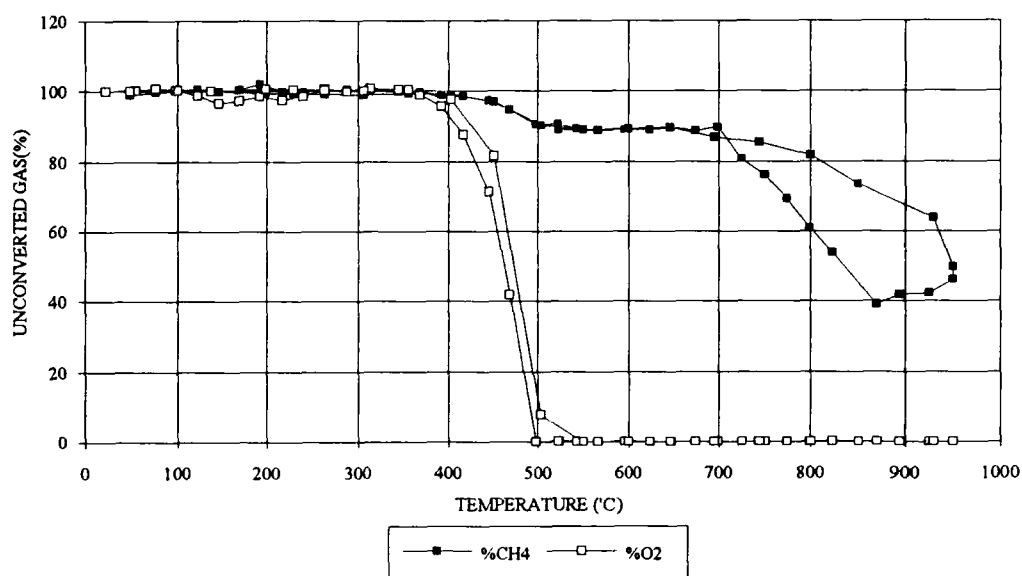


FIG. 5.3.5f CONVERSION, SAMPLE I

Analysis of the hydrogen present in the product gases is only available for the experiment on sample C. The levels of hydrogen start to increase at the same time as CO, but the slope is steeper. This would indicate that the CH₄ is decomposing at temperatures above 750°C and accounts for the large drop in the unreacted gas. Lattice oxygen reacting with the carbon can prevent carbon deposition. Carbon deposition will be discussed later in this section.

A series of constant temperature experiments was carried out. Graphs are included plotting exhaust composition against time at two temperatures for each sample. At 469°C for C the CH₄ level decreases from 100% to 85%, whereas for I at 469°C the level is 85% throughout. Both samples show an accompanying 12% O₂ and 3%CO₂. At 522°C for sample C and I, there is 90%CH₄ and 10%CO₂, all oxygen having reacted. The proportions were the same, both with and without helium making up the balance of the gas

Experiments were also carried out at higher and lower temperatures, both with and without helium, and in each case the results follow the pattern shown here. During this experiment, the flow rates of the methane and oxygen were not altered when the helium was shut down.

The discrepancy in the centre of fig. 5.3.5k is a result of a drop in the flow of oxygen. The discrepancy towards the end of fig. 5.3.5l is a result of the furnace cooling during the experiment, and that in the middle of fig. 5.3.5l a result of a cessation in the flow of methane. It can be seen that when methane and oxygen were reintroduced the former values are quickly recovered.

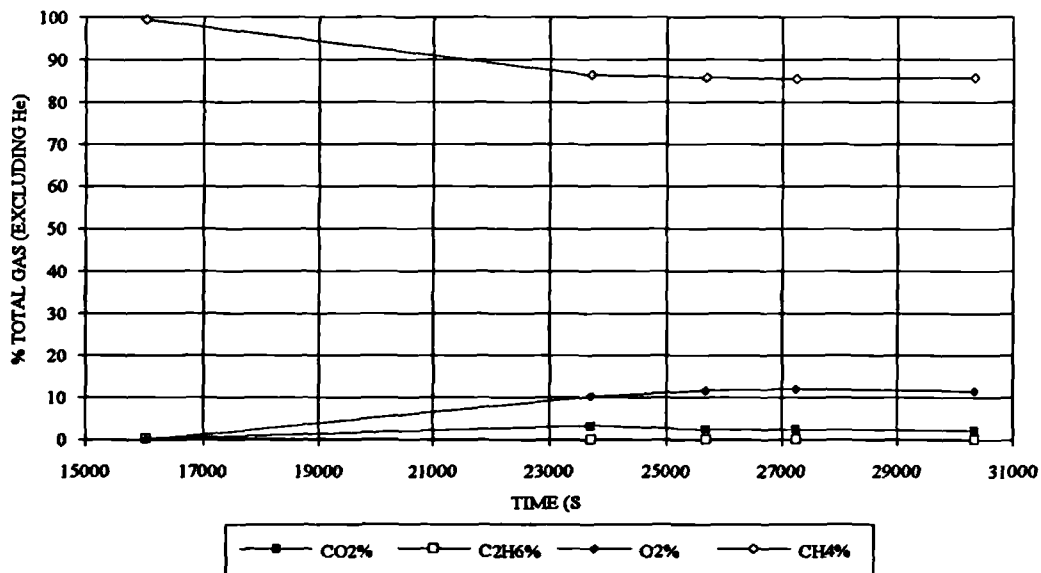


FIG. 5.3.5g 469 C, SAMPLE C (WITH He)

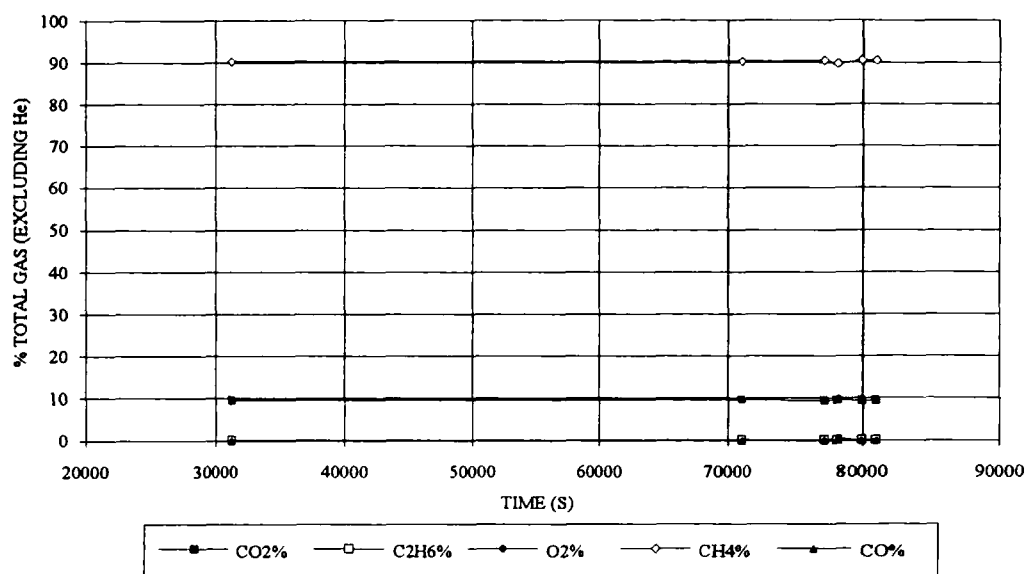


FIG. 5.3.5h 522°C SAMPLE C (WITH He)

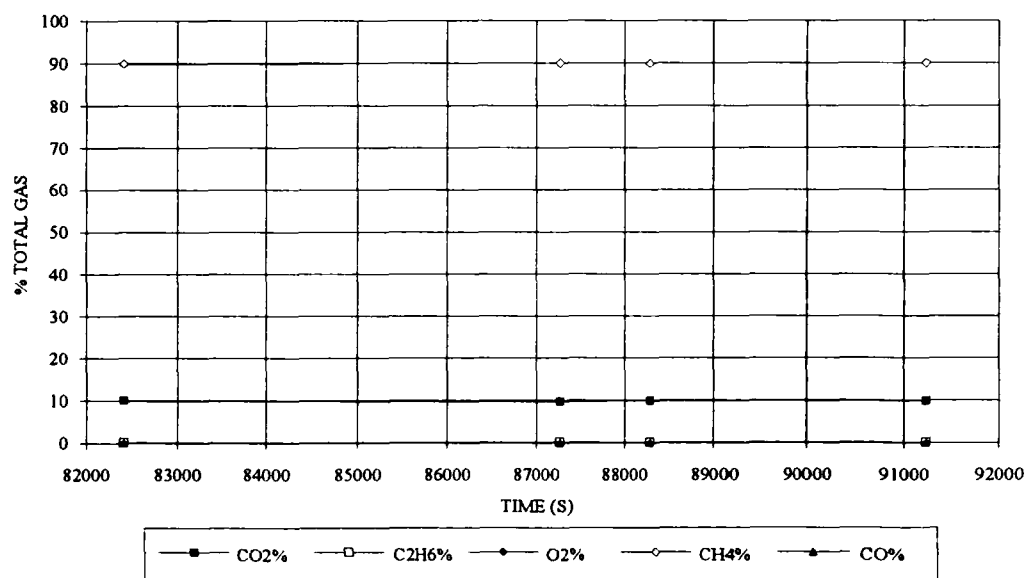


FIG. 5.3.5i 522°C, SAMPLE C (NO He)

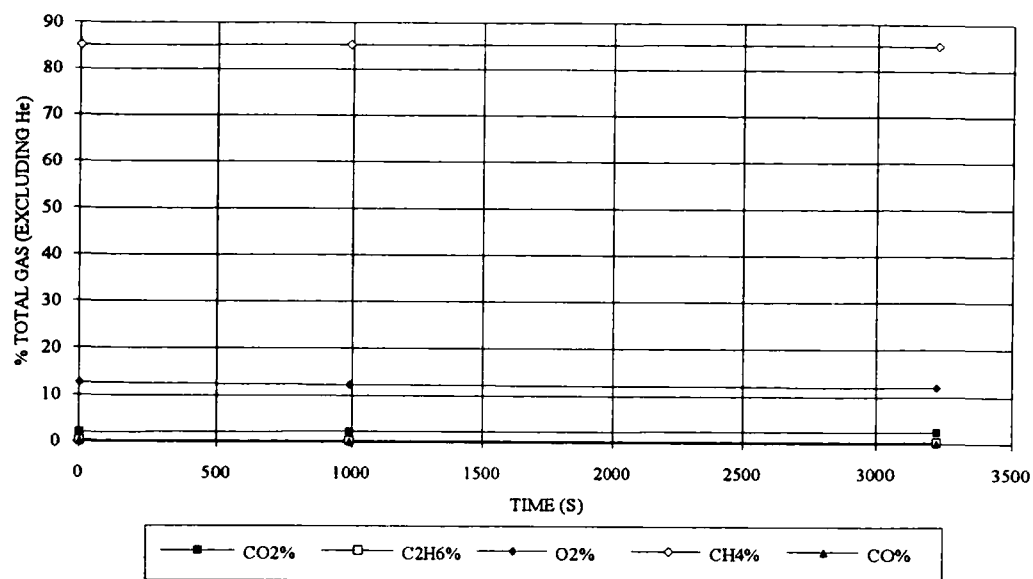


FIG. 5.3.5j 469°C, SAMPLE I (WITH He)

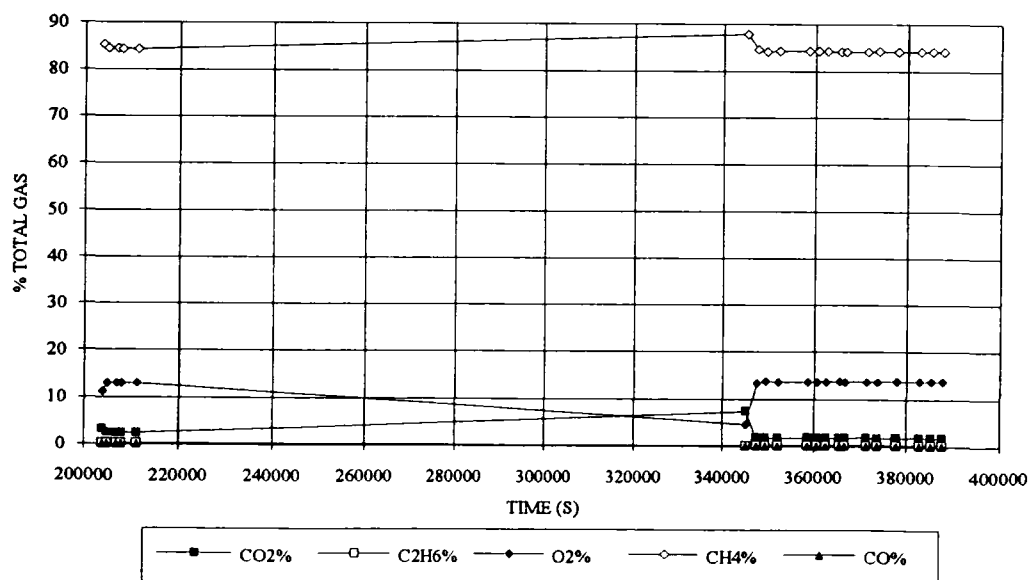


FIG. 5.3.5k 496°C, SAMPLE I (NO He)

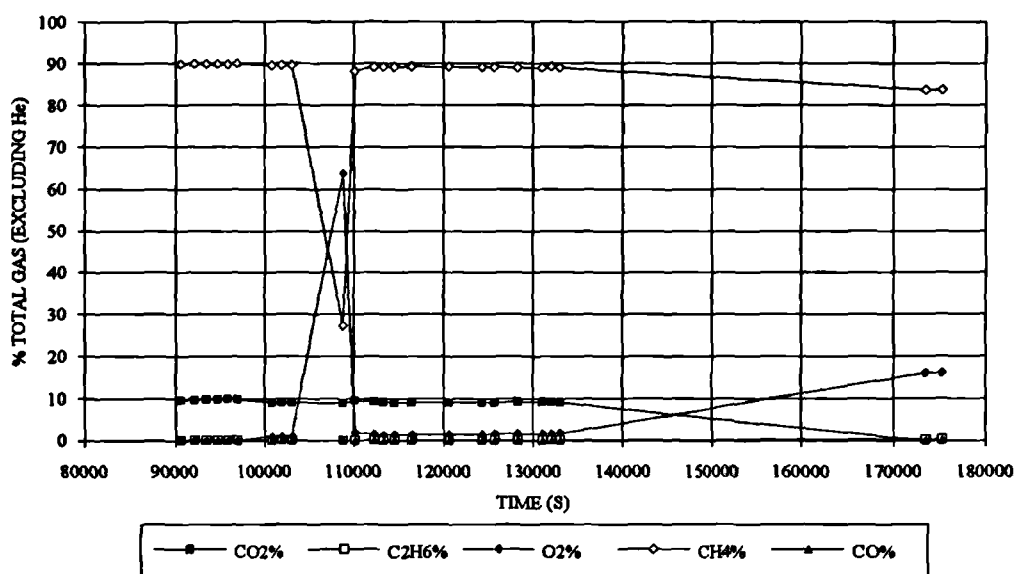


FIG. 5.3.51 522°C, SAMPLE I (WITH He)

At high temperature it is difficult to examine the sample and furnace tube for signs of carbon deposition, and also, since there is only a limited amount of lattice oxygen available, it was felt that were the sample left long enough at any temperature above 750°C, carbon deposition may occur. The experiments were carried out on sample I. The results of the carbon deposition experiments indicate that the process depends on the temperature, and the quantity of methane present. There are two processes that can result in deposition of carbon.



The proportions of gases used in the deposition experiments are well within the range at which thermal cracking of methane would be expected to occur at temperatures as low as 227°C (176). The reacting gases were considerably more dilute in the catalysis experiments. It would seem that deposition becomes a problem only when the levels of CO increase. The formation of CO is, in any case, an indication of the lack of oxygen. The carbon deposition on the post catalyst region of the reaction tube, can be explained by considering the heating of the gas as it flows through the reaction tube. It would appear that carbon deposition can only be avoided in a fuel cell where

sufficient oxygen is supplied, and that a ceria anode cannot be left in a methane environment at temperatures higher than 700°C when not in use.

TABLE. 5.3.5 RESULTS OF CARBON DEPOSITION EXPERIMENT		
TEMP.(°C)	CH ₄ :He	DESCRIPTION
700	75:25	slight greying of sample surface, some carbon on postcatalyst region of reaction tube
800	75:25	darker grey, more carbon on postcatalyst region
900	75:25	dense carbon deposits throughout sample, postcatalyst region darker
800	100:0	carbon deposits exceed sample area on both sides, dark carbon on postcatalyst region, light carbon on precatalyst region

5.4 MULTILAYER EXPERIMENTS

The experiments will be discussed according to the slurry type that was used, in a discussion of the sintering

5.4.1 TAPECASTING SLURRY (TC)

The following recipe was obtained from R. Rudkin, shown here scaled down.

1g	ceramic
0.0167g	fish oil
0.15g	polyvinylbutyral
0.0375g	ethylene glycol
0.0375g	dibutylphthalate
0.6g	ethanol

This type of slurry is best suited to larger batches of powder than given here.

TABLE 5.4.1 RESULTS WITH TAPECASTING SLURRY

SAMPLE	SLURRY BATCH	CONSISTENCY	SUBSTRATE	SINTERING		DESCRIPTION
				T(°C)	t(hrs)	
i	1(C)	added ethanol, paintlike	ZrO ₂ sheet etched in HF	1400	6	dispersed, easily removed
ii	""	""	""	""	2	""
iii	""	""	""	1300	""	""
iv	""	aged, gumlike	green ZrO ₂ pellet	1450	8	good adherence
v	""	""	"" with rough surface	""	""	""
vi	2(C)	paintlike	green ZrO ₂ pellet	1300	1	dispersed, good adherence
vii	""	""	""	""	""	""
viii	""	""	""	""	""	""
ix	3(H)	paintlike	green ZrO ₂ pellet	1450	6	good, cracks in surface
x	""	""	""	1300 (F.G)	5	grey appearance of substrate, no adherence
xi	""	""	Ce-Gd	1600	4	unsuccessful

F.G. is forming gas

For this type of slurry, sintering was most successful on samples iv and v, where the slurry had aged to a chewing gum consistency. This had to be pressed rather than painted onto the substrate. It did not prove possible to reproduce this ageing in subsequent batches of the slurry. Because of the small quantities being dealt with, the exact ratios of the different components were difficult to obtain.

Sample x was sintered in a reducing atmosphere, as suggested both by Mogensen (72), and by Dr. Middleton and Professor Steele during discussions in the department. On removal from the furnace, the zirconia substrate had a greyish appearance, and is presumed to have been reduced. The ceria coating also appeared grey, and was not connected to the zirconia. The zirconia surface just below the coating was cracked. It is believed that the failure to adhere can be attributed to the organics in the slurry forming carbon, as they were unable to oxidise in the reducing atmosphere. It is possible that this technique may be more successful if the organics can be burnt off before sintering. However, the stresses involved in sintering multilayer samples should be considered. Virkar (67) discussed the stresses arising between different layers in multilayer samples. The following equation may be used to calculate the stresses in such samples being cooled or heated from a nonstress situation.

$$s = (\alpha_1 - \alpha_2) (T_a - T_b) E / (1 - \nu) \quad [9]$$

where α_1 and α_2 are the coefficients of expansion, T_a and T_b are temperature. E is the young's modulus, and ν the poissons ratio of the thin layer. The layer is very much thinner than the substrate. The coefficient of expansion of doped ceria in forming gas has been discussed in section 5.3.1. For this calculation several assumptions have been made. 1) The reducing atmosphere causes little change in the expansion coefficient of the zirconia. 2) The coefficient of expansion of the sample measured is similar to that for the coating here. 3) The value of the coefficient expansion is the same from 800°C to 1300°C. 4) The contraction on cooling is the exact reversal of the expansion process. 5) The young's modulus and poissons ratio of ceria are close to those for zirconia, given as $E = 200\text{GPa}$ and $\nu = 0.25$ (67). 6) The expansion coefficient of zirconia was taken to be $10 \times 10^{-6} \text{ K}^{-1}$ (67).

At the sintering temperature there are no stresses between the substrate and the coating. However, as the sample cools the ceria coating contracts faster than the zirconia substrate. Because the coating is thin, and the substrate thick, this results in a large tensile stress in the coating, whilst the compressive stress in the substrate can be taken to be negligible. On cooling from 1300 to 800°C, the resulting stress in the coating has been calculated:

$$s = (64.7 \times 10^{-6} - 10 \times 10^{-6})(1300 - 800)200 \times 10^9 / 0.75 = 7290 \text{ MPa} \quad [10]$$

with further stresses on cooling to room temperature This stress is enormous, and it is extremely unlikely that any coating would be able to withstand it. Virkar states that a stress of 580MPa is much larger than the fracture strength of zirconia coatings.

Such calculations can also be made for samples cooled in air, and the stresses may well account for the cracks visible in the surface of sample ix. In this case:

$$s = (12.26 \times 10^{-6} - 10 \times 10^{-6})(1450-25)200 \times 10^9 0.75 = 859 \text{MPa} \quad [11]$$

It seems that one of the problems is the high sintering temperatures required for ceramics. At lower temperatures the stresses would obviously be lower. It is not clear why the coating of sample xi failed to adhere to a ceria based substrate.

5.4.2 ETHYL CELLULOSE - DIBUTYLPHTHALATE SLURRY (ED)

This slurry is made by heating a 1:14 ratio of ethyl cellulose and dibutylphthalate until the ethyl cellulose has all dissolved. This is then mixed 50:50 with the ceramic powder, resulting in a paste. This paste was painted onto the substrate, and had to be dried by placing the sample on a hotplate before sintering. This created problems with the boiling of the paste causing excess porosity in the coating, and the temperature had to be carefully controlled to prevent this. The paste showed a tendency to age once the organics and powders had been mixed. The powder particles slowly formed gritty agglomerates.

TABLE 5.4.2 RESULTS FOR ETHYL CELLULOSE - DIBUTYLPHTHALATE SLURRY

SAMPLE	SLURRY BATCH	CONSISTENCY	SUBSTRATE	SINTERING T(°C)	t(hrs)	DESCRIPTION
i	1(H)	thick paste	green Ce-Gd	1600	6	poor
ii	""	""	""	""	""	""
iii	""	""	presintered Ce-Gd	""	""	""
iv	""	""	green ZrO2	""	""	""
v	2(ZrO2)	""	Ce-Gd	""	""	""
vi	3(H)	""	presintered Ce-Gd	1450	""	good, no sign of stress in layer
vii	""	""	presintered ZrO2	""	""	good, feint cracks in surface
viii	2	""	presintered Ce-Gd	""	""	poor, ZrO2 does not adhere

Samples vi and vii were both successful. Although there were signs of fine cracks in the coating on the zirconia substrate, adherence was still good Zirconia did not stick to a ceria gadolinia substrate, the reasons for this were unclear. The coating itself was in one piece, and appeared to have delaminated. This can occur if the compressive

stresses in the coating on cooling are too great. Virkar (67) has indicated that delamination can occur where:

$$|\Delta\alpha\Delta T| \geq (2\gamma_{fm}(1-\nu^2)/hE)^{1/2} \quad [12]$$

where γ_{fm} represents the interfacial energy of debonding, and h is the thickness of the film. The thinner the film, the lower the likelihood of delamination. The interfacial debonding energy may vary from sample to sample.

5.4.3 ETHYL CELLULOSE - TERPINIOL SLURRY (ET)

This slurry is made by mixing the ethyl cellulose and terpinol until a thick gel-like consistency is reached. This is mixed with the ceramic powder at 50:50 by weight. They are mixed together with ethanol to a liquid consistency that can be painted onto the sample. Such a slurry is suitable for screen printing techniques (168). Because this slurry is more volatile than the last, the samples may be dried under an infra-red lamp before sintering.

The coatings applied with this slurry were very much thinner than those from previous coatings, and appeared to be even throughout. Coatings were applied to both sides of the samples in this case.

TABLE 5.4 3 RESULTS FOR ETHYL CELLULOSE - TERPINIOL SLURRY

SAMPLE	SLURRY BATCH	CONSISTENCY	SUBSTRATE	SINTERING		DESCRIPTION
				T(°C)	t(hrs)	
i	1(H)	paintlike	presintered Ce-Gd	1450	6	adheres well, barely visible
ii	"	"	"	"	"	adheres well, thicker

5.4.4 REDUCTION EXPERIMENTS

The samples were reduced in an atmosphere of flowing CO₂/H₂. It had been intended that the ED samples be reduced under the same conditions as the TC samples, but the CO₂ gas flow ceased during the experiment. Both samples were found in pieces, presumably as a result of the severe reduction that would have occurred in a pure hydrogen atmosphere. Sample TCiv was examined by optical and electron microscopy, and compared to the nonreduced sample TCv. It was found that an interfacial layer had formed between the substrate and the coating. When the sample was reduced, the coating broke away, leaving the substrate and interfacial layer. Linescan analyses were carried out across the interface of both samples, and the results are given in table 5.4.4.

TABLE 5.4.4 RESULTS FOR REDUCTION EXPERIMENTS			
SAMPLE	TEMP. (°C)	pO ₂	DESCRIPTION
TCiv	900	1.00E-17	change in colour of surface from green to yellow
TCvii	""	""	complete removal of coat- ing from ZrO ₂
ED vi, vii	""	4.00E-20	both samples broken, and coatings removed

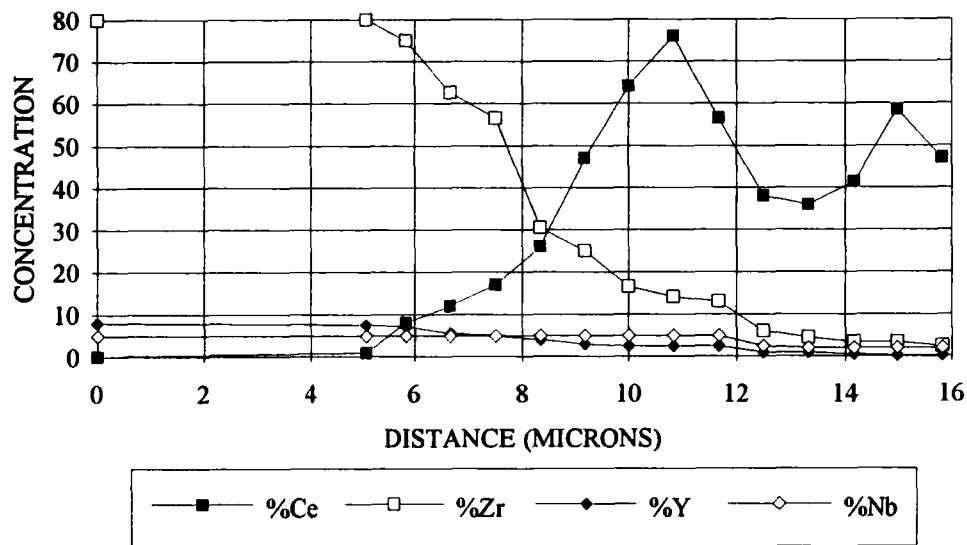


FIG. 5.4.4a INTERFACIAL REGION FOR SAMPLE TCiv.

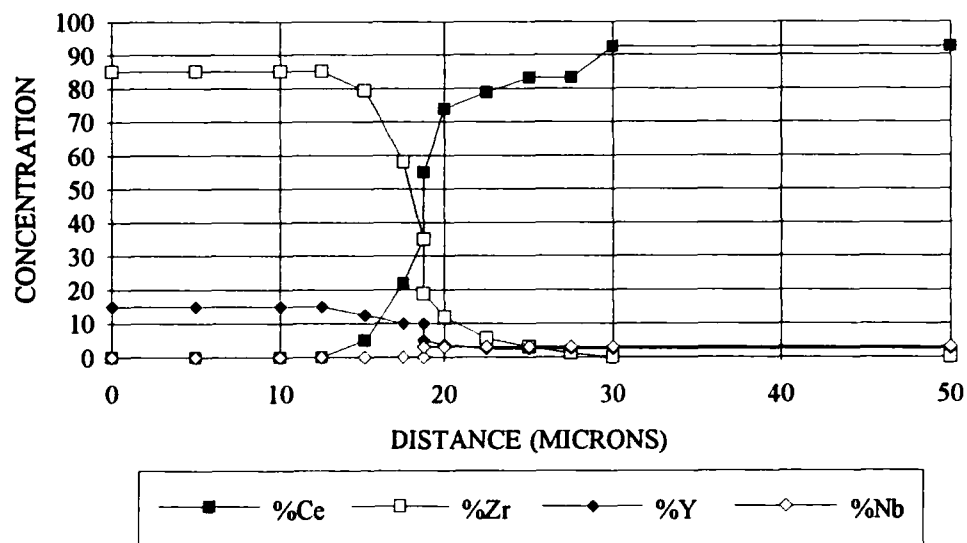


FIG. 5.4.4b INTERFACIAL REGION FOR SAMPLE TCv.

It is not possible to present an accurate quantity for each element in the figures (5.4 4a-b). The vertical axis merely represents the distribution of the individual elements across the interface, and is only a rough guide to the relative proportions of the elements. The distance scale is approximate in both graphs. Fig. 5.4.4b covers a larger distance scale than fig. 5.4.5a. In sample iv it is mainly the interfacial region that is being examined. This region can be seen clearly in fig. 5.4.5a. The interfacial region is about the same size in both samples. Photographs of both the polished and fracture surfaces across the interface can be seen in figs. 5.4.4c-f.

5.4.5 CERIA - SILVER PAINT COATINGS

Several samples were prepared mixing varying amounts of ceria powder (H) with silver paint. Those coatings on green zirconia were unsuccessful because the sintering temperature was limited by the melting point of the silver. The pellets showed much less shrinkage than that seen in pellets sintered at higher temperature. Furthermore, the pellets were red-pink in appearance, because of the diffusion or soaking of the silver paint into the green pellet.

Coatings applied to presintered zirconia were also unsuccessful. There was a tendency for the powder and paint to separate. Where they mixed well before application this resulted in a grey powder which was easily removed from the substrate surface, and had clearly failed to sinter.

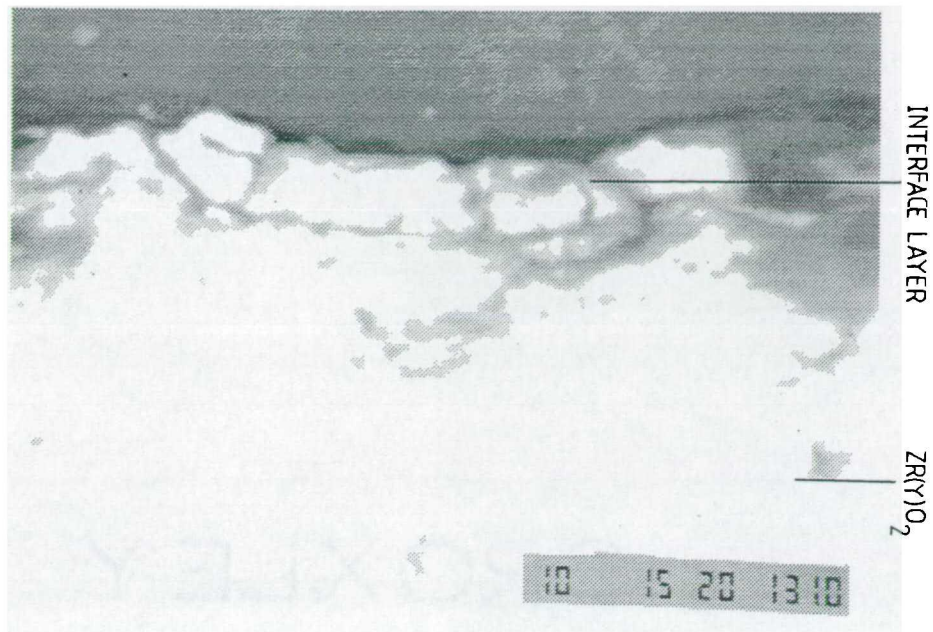


FIG.5.4.4c SEM BACKSCATTERED MICROGRAPH TCiv CROSSECTION X2000

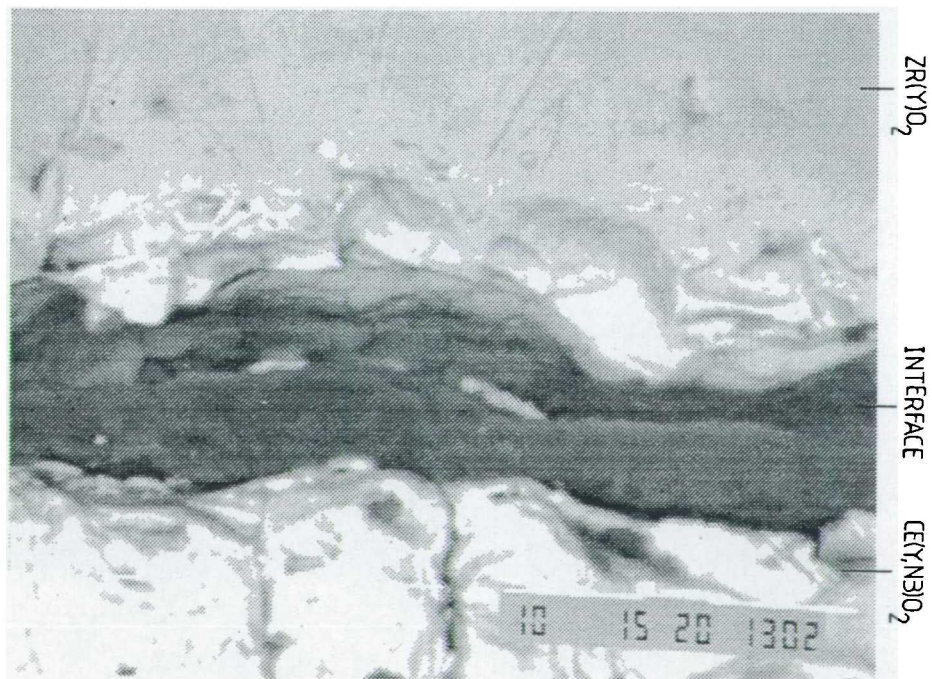


FIG 5 4.4d SEM BACKSCATTERED MICROGRAPH TCv CROSSECTION X1500

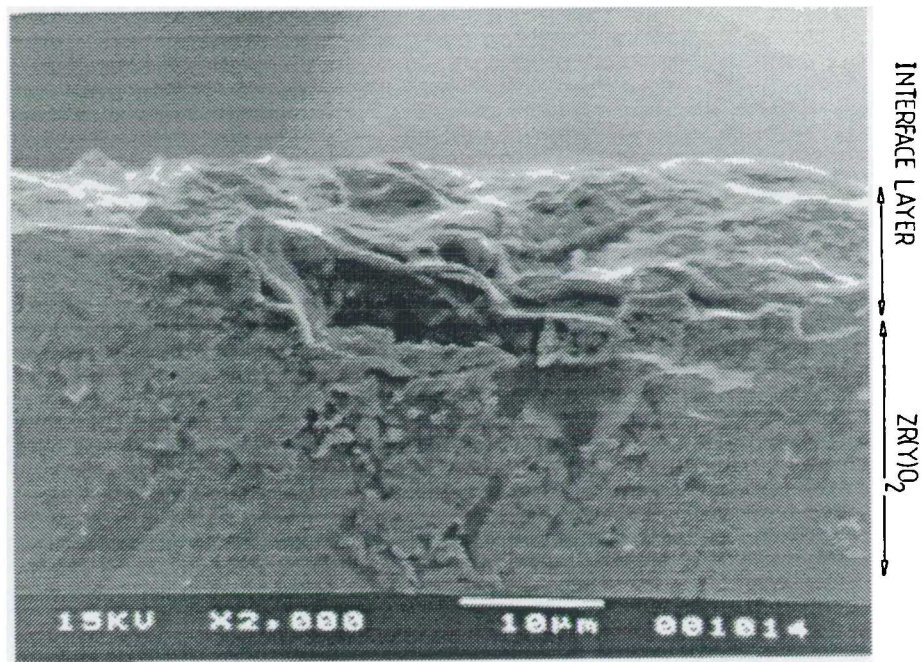


FIG.5.4.4e SEM MICROGRAPH TCiv FRACTURE SURFACE AT CROSSECTION

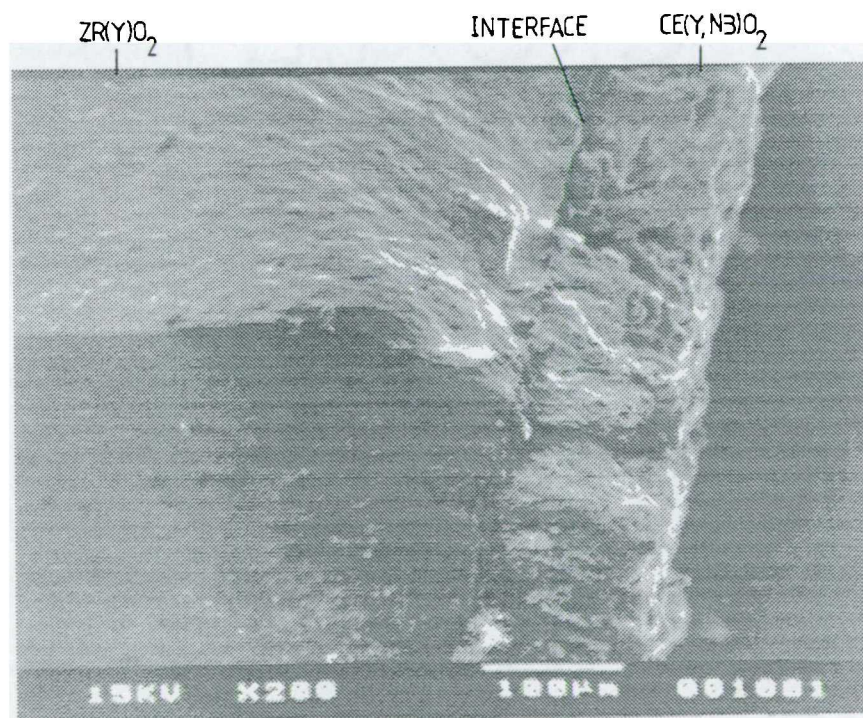


FIG 5 4 4f SEM MICROGRAPH TCv FRACTURE SURFACE AT CROSSECTION

5.5 SUMMARY

There is no direct x-ray or SEM evidence to suggest that there may be a second phase in the higher purity samples. However, both the conductivity results and examination of the variation in lattice parameter seem to suggest that a second phase may be nucleating in the higher Nb doped materials, between samples A and B (3 and 3.5% intended Nb content). The conductivities of samples B and C were found to be very similar, whilst that of A was lower. A discontinuity in the curve of fig. 5.2.1 in that composition region could be attributed to a second phase. The lattice parameter decreases until 2-2.5%Nb as plotted (intended composition), and then increases as $[\text{Nb}] > [\text{Y}]$ (actual composition). This increase would be anticipated. Nucleation of a second phase could then be altering the pattern of change in lattice parameter. This could indicate, that given the analysed compositions of A and B (table 5.2.2a), double doping does not necessarily have a detrimental effect on the solubility of Nb in ceria. It would not appear to necessarily improve it either. The difference $[\text{Nb}]-[\text{Y}]$ for samples B and C is 0.7 and 1.5 cation% respectively, and the limit estimated for Nb doped ceria between 1.2 and 1.28% (section 3.3.1). It is unfortunate that the difference in actual $[\text{Nb}]$ between samples was not as close as had been intended. Double doping does appear to adversely affect the conductivity of the material however, and this may be attributed to defect interactions, possibly at a distance.

The coefficient of thermal expansion was not reduced by higher valent doping, but was rather increased. The coefficient of expansion for the doubly doped materials having a lattice parameter smaller than that of pure ceria may be expected to be decreased. There was no observable reduction in oxygen loss when comparing the doubly and singly doped materials (section 5.3.2). Thus the expansion at low oxygen pressure will not have been significantly decreased. High fabrication temperatures of cosintered components exacerbate problems of thermal mismatch between cosintered components; the sintering temperature is very much higher than the operating temperature. This is particularly true of ceria which must be sintered at 1550-1600°C compared to zirconia at 1300-1400°C. Other methods of depositing both porous and impervious ceramic layers on top of each other need to be explored. Preferably, techniques that can be carried out at the cell operating conditions should be developed. This would eliminate mismatch stresses during operation (66); they would only be encountered during heating and cooling. For high temperature SOFC's it is hoped that such heating and cooling cycles would be kept to a minimum.

Higher valent doped ceria has a lower oxygen diffusion coefficient at high pO_2 , and diffusion is believed to occur via an interstitial mechanism in this material. The value at low pO_2 is not known. In the unlikely event that diffusion is not hindered by defect interaction, diffusion in this material would be expected to change from an interstitial to a vacancy mechanism. Vacancies lead to lattice expansion. At 800°C, the electronic conductivity of the higher valent doped ceria is considerably higher than that of the pure and lower valent doped materials. The catalytic properties of both the lower and higher valent doped materials are similar under reducing conditions. This is to be expected since the electronic properties of cerias under these conditions are similar. Both the electronic and catalytic properties depend on transfer of electrons between Ce^{3+} and Ce^{4+} ions. The ease of reduction of the higher valent doped sample may have been beneficial above 750°C. Good oxygen diffusion and electronic conductivity are competing mechanisms, except where ionic conduction occurs by an interstitial mechanism. The low solubility of the higher valent dopants, and the greater ease for oxygen loss from interstitial sites mean that it is unlikely that a ceria can be produced with an interstitial oxygen diffusion mechanism under anodic conditions. The solubility of the higher valent dopants in ceria cannot be beneficially improved because of the large mismatch in ionic radius. Whilst double doping has improved the overall solubility, the material behaves as predicted by Kroger (section 3.4.2, (125)), but causing a decrease in lattice parameter. In the higher valent doped material, both oxygen interstitial and cerium ion reduction mechanisms are believed to compensate for the additional charge.

A choice needs to be made between oxygen diffusion and electronic conduction, particularly at lower temperatures. As the temperature is increased, the difference in conductivity between the samples is smaller. However, at these higher temperatures, lattice expansion is a problem. The conductivity of the higher valent doped ceria is in any case, probably too low to act as a current collector in the anode. It is therefore, probably better to use the lower valent doped material as part of a cermet as did Eguchi et al (section 2.3.3, (40-41)). Doped ceria is a good catalyst for the oxidation of methane from temperatures of 450°C upwards with CO_2 being the primary product until about 750°C after which CO predominates. At these high temperatures, above 700°C, carbon deposition may occur if oxygen transport through the electrolyte and anode is too slow.

6. CONCLUSIONS

1. Double doping did improve the overall solubility of niobium in cerium oxide ((4.5-5 cation% for 3.7/3.8%Y).
2. Double doping did not beneficially improve the solubility of niobium in cerium oxide. The revised solubility limit, after accounting for the yttrium concentration, was found to be close to that for the singly doped material (0.7-1.5 cation%).
3. Double doping adversely affected the maximum conductivity of the material when compared to the singly doped material; possibly due to increased defect interactions.
4. Double doping reduced the lattice parameter of the material, whereas singly doping with either ion had been found to increase it.
5. Whilst the reduced lattice parameter may have reduced the coefficient of thermal expansion, there was no apparent benefit during cosintering experiments.
6. Expansion during reduction is considerably larger than expansion due to temperature change. Attempts at firing in a reducing atmosphere are unlikely to be successful.
7. Oxygen ion conduction in higher valent doped samples at high pO_2 occurs via an interstitial mechanism.
8. Electron conduction in higher valent doped samples occurs via small polaron hopping.
9. Initial reduction with decreasing pO_2 occurs more readily on higher valent doped samples than pure ceria or lower valent doped samples, because loss of interstitial oxygen is energetically more favourable than loss of lattice oxygen.
10. Charge compensation in higher valent doped samples is by both oxygen interstitial formation and reduction of the cerium ion.
11. Doped ceria is a good catalyst for the oxidation of methane above 450°C. Lower and higher valent doped samples behave similarly in the reducing atmosphere.
12. Carbon deposition may occur on ceria anodes above 700°C if oxygen transport through the electrolyte and anode is too slow.

7. SUGGESTIONS FOR FURTHER WORK

Further thermogravimetric and conductivity studies carried out at a greater range of temperatures, as had originally been intended here, would yield information about the defect structure of the material, and its variation with composition. Changes in activation energies at different compositions and temperatures could be compared.

The solubility of niobium in the doubly-doped material needs to be more clearly defined.

Other deposition techniques for ceramic layers need to be examined, that do not require such high treatment temperatures, in order to minimise thermal stresses.

Experiments using the cell as a prototype anode could also be carried out, to determine whether the low conductivity of the material is good enough for use in a cell, since the catalytic properties are desirable.

REFERENCES

1. B.C.H.Steele *Materials Technology on Fuel Cell Development* Materials and Design 11(1) 1990 p.4-10
2. A.J.McEvoy, K.R.Thampi, J.Van herle *Interface Microstructure and Electrocatalysis in SOFC's* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.623-31.
3. A.J. Appleby, F.R.Foulkes *Fuel Cell Handbook* Van Nostrand Rheinhold 1989 p.3-31, 579-611.
4. M.Mogensen, B.Kindl, B.Malmgren-Hansen *On the Prospects of Operating an SOFC on Dry Natural Gas* Fuel Cell Seminar Programs and Abstracts 1990.
5. A.McDougall *Fuel Cells* Energy Alternative Series MacMillan 1976 p.22-30.
6. D.P.Gregory *Fuel Cells* M&B Monographs 1972 p.11.
7. C.Mantell *Batteries and Energy Systems* McGraw Hill 1983 p.8-11.
8. B.C.H.Steele *Oxygen Ion Conductors and their Technological Applications* Solid State Ionics Symposium, E-MRS Conference on Advanced Materials, Strasbourg, France 27-31 May 1991.
9. B.C.H.Steele *Fuel Cells and High Energy Batteries* Proc. of Symposium on Energy and the Environment Exxon Corporate Research Lab, Annandale,N.J. 18 May 1990.
10. B.C.H.Steele *Oxygen Ion Conductors* Solid Ionic Conductors ed. T.Takahashi World Scientific Publications 1989 p.402.
11. Ed. S.S.Penner *Assessment of Research Needs for Advanced Fuel Cells* Energy 11 1986 p.1-229.
12. T.E.Swarr, S.Karavolis, D.L.Maricle *Enhanced Ceria-A Low Temperature SOFC Electrolyte* International Fuel Cells Internal Report HP249 p.1-6.
13. N.Q.Minh *Ceramic Fuel Cells* J.Am.Ceram.Soc. 76(3) 1993 p.563-88.
14. P.Van den Berghe, H.Tannenberger US Patent no.4130693 Dec.19 1978 appl.801392 May 27 1977.
15. S.C.Singhal *Zirconia Based Fuel Cells for Power Generation* Abstracts International Forum on Fine Ceramics Nagoya 1992 p.159-67.
16. T.Yazawa *Present State of SOFC in Japan* Proceedings 1st First International Symposium on Solid Oxide Fuel Cells ed. S.C. Singhal Electrochemical Society 1989 p.387-93.
17. H.Tagawa *Status of SOFC Development in Japan* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H Iwahara Electrochemical Society 1993 p.6-15.
18. M.Ipponmatsu *Manufacturing Technology of Solid Oxide Electrolyte Fuel Cell* Abstracts International Forum on Fine Ceramics Nagoya 1992 p.154-8.

19. K.Kendall *Novel Ceramic Designs for Fuel Cells* Abstracts International Forum on Fine Ceramics Nagoya 1992 p.143-8
20. D.T.Hooie *Status of SOFC Development in USA* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.3-5.
21. P.Zegers *Status of SOFC Development in Europe* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H Iwahara Electrochemical Society 1993 p.16-20.
22. S.P.S.Badwall, K.Foger *Status of SOFC Development in Australia* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.21-7.
23. G.C.Bond *Heterogeneous Catalysis: Principles and Applications* Oxford Science Publications Clarendon Press 1987 p.12-29,38-59,115-129.
24. G.Maggio, I.Ielo, V.Antonucci, N.Giordano *Morphological Optimisation of a SOFC Anode Based on Theoretical Considerations: A Preliminary Approach* Proceedings 2nd International Symposium on Solid Oxide Fuel Cells ed. F.Grosz, P.Zegers, S.C.Singhal, O.Yamamoto Commission of the European Communities 1991 p.611-20.
25. T.Kawada, N.Sakai, H.Yokokawa, M.Dokiya, M.Mori, T.Iwata *Characteristics of Slurry Coated ZrO_2 Cermet Anodes for SOFC* J.Electrochem.Soc. 137(10) 1990 p.3042-7.
26. S.Murakami, Y.Akiyama, N.Ishida, T.Yasuo, T.Saito, N.Furukawa *Development of Solid Oxide Fuel Cell with Composite Anodes* Proceedings 2nd International Symposium on Solid Oxide Fuel Cells ed. F.Grosz, P.Zegers, S.C.Singhal, O.Yamamoto Commission of the European Communities 1991 p.561-8.
27. T.Kawada, N.Sakai, H.Yokokawa, M.Dokiya, M.Mori, T.Iwata *Structure and Polarisation Characteristics of SOFC Anodes* Solid State Ionics 40/41 1990 p.402-6.
28. K.C.Chou, S.Yuan, U.Pal *Deposition, Electrical Property and Direct Porosity Measurement of Ni-ZrO₂ Cermet Electrodes* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.431-43.
29. T.Norby, O.J.Velle, H.Leth-Olsen, R.Tunold *Reaction Resistance in Relation to Three-Phase Boundary Length of Ni/YSZ Electrodes* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.473-83.
30. J Mizusaki, H Tagawa, T.Saito, K.Kamitani, T Yamaura, K Hirano, S Ehara, T.Takagi, T. Hikita, M.Ipponmatsu, S.Nakagawa, K Hashimoto *The Preparation of*

- Nickel Pattern Electrodes on YSZ and their Electrochemical Properties in H_2/H_2O Atmospheres* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.533-41.
31. M.Mogensen, T.Lindegard *The Kinetics of Hydrogen Oxidation on a Ni-YSZ SOFC Electrode at 1000°C* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.484-93.
32. C.Perego, L.Zanibelli, M.Catrullo, G.Piro *Temperature Programmed Reduction (TPR) Characterisation of Ni/YSZ for Solid Oxide Fuel Cell* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.454-63.
33. T.Shirakawa, S.Matsuda, A.Fukushima *Characterisation of NiO/YSZ Electrode by Temperature Programmed Reduction* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.464-72.
34. J.Guindet, C.Roux, A.Hammou *Hydrogen Oxidation at the Ni/ZrO₂ Electrode* Proceedings 2nd International Symposium on Solid Oxide Fuel Cells ed. F.Grosz, P.Zegers, S.C.Singhal, O.Yamamoto Commission of the European Communities 1991 p.553-9.
35. M.E.Seiersten, P.H.Middleton *Redox Behaviour of Plasma Sprayed Nickel Anodes* Proceedings 2nd International Symposium on Solid Oxide Fuel Cells ed. F.Grosz, P.Zegers, S.C.Singhal, O.Yamamoto Commission of the European Communities 1991 p.569-76.
36. P.H.Middleton, M.E.Seiersten, B.C.H.Steele *Morphology and Electrochemistry of Porous Nickel/Zirconia Cermets* draft 1991.
37. K.Okumura, Y.Yamamoto, T.Fukui, S.Hanyu, Y.Kubo, Y.Esaki, M.Hattori, A.Kusunoki, S.Takeuchi Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.444-53.
38. H.Miyamoto, M.Sumii, K.Mori, I.Koshiro, F.Nanjo, M.Funatsu *Improvement of Anode Performance by YSZ Surface Modification* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.504-11.
39. L.S.Wang, S.A.Barnett *Role of Electrode Interfacial Resistances in the Characteristics of Sputter Deposited Medium Temperature SOFC's* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p 649-655
40. T.Setoguchi, K.Okamoto, K.Eguchi, H Arai *Effects of Anode Material and Fuel on Anodic Reaction of SOFC* J Electrochem.Soc 139(10) 1992 p.2875-80

41. K.Eguchi, T.Setoguchi, K.Okamoto, H.Arai, *An Investigation of Anode Material and Anodic Reaction for Solid Oxide Fuel Cell* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.494-503.
42. K.Eguchi, T.Setoguchi, M.Sawano, S.Tamura, H.Arai *A Study on Anode and Interconnector Materials for Solid Oxide Fuel Cells* Proceedings 2nd International Symposium on Solid Oxide Fuel Cells ed. F.Grosz, P.Zegers, S.C.Singhal, O.Yamamoto Commission of the European Communities 1991 p.603-10.
43. B.C.H.Steele, I.Kelly, P.H.Middleton, R.Rudkin *Oxidation of Methane in Solid State Electrochemical Reactors* Solid State Ionics 28-30 1988 p.1547-52.
44. P.H.Middleton, H.J.Steiner, G.M.Christie, R.Baker, I.S.Metcalf, B.C.H.Steele *Evaluation of Novel Oxide Anodes for Methane Conversion in SOFC Systems* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells (as 41) 1993 p313-9.
45. B.C.H.Steele, P.H.Middleton, R.A.Rudkin *Material Science Aspects of SOFC Technology with Special Reference to Anode Development* Solid State Ionics 40/41 1990 p.388-93.
46. H.U. Anderson, J.H.Huo, D.M. Sparling *Review of Defect Chemistry of LaMnO_3 and LaCrO_3* Proceedings 1st First International Symposium on Solid Oxide Fuel Cells ed. S.C. Singhal Electrochemical Society 1989 p.111-28.
47. H.Tagawa, J.Mizusaki, M.Katou, K.Hirano, A.Sawata, K.Tsuneyoshi *On the Solid State Reaction between Stabilised Zirconia and some Perovskite-Type Oxides* Proceedings 2nd International Symposium on Solid Oxide Fuel Cells ed. F.Grosz, P.Zegers, S.C.Singhal, O.Yamamoto Commission of the European Communities 1991 p.681-8.
48. H.Yokokawa, N.Sakai, T.Kawada, M.Dokiya *Chemical Thermodynamic Compatibility of Solid Oxide Fuel Cell Materials* Proceedings 2nd International Symposium on Solid Oxide Fuel Cells ed. F.Grosz, P.Zegers, S.C.Singhal, O.Yamamoto Commission of the European Communities 1991 p.663-70.
49. D.P.Sutija, T.Norby, P.A.Osburg, P.Kofstad *AC Van Der Pauw Measurements of the Electrical Conductivity of Iron-Doped Calcium Titanate* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.552-61.
50. A.Holt, E.Ahlgren, P.W.Poulsen *Synthesis, Electrical Properties and Defect Chemistry of Ti-Doped NdCrO_3* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H Iwahara Electrochemical Society 1993 p.562-71.

51. M.Huang, P.H.Middleton, M.Priestnall, R.Rudkin, A.Selcuk, B.C.H.Steele, X.Turrillas *Oxide Electrodes for Ceramic Electrochemical Reactors* Centre for Technical Ceramics, Imperial College, London August 1990.
52. R.M.C.Marques, J.R.Frade, F.M B.Marques *Ceramic Materials for SOFC Anode Cermets* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.513-22.
53. M.T.Colomer, J.R.Jurado, R.M C.Marques, F.M B Marques *Evaluation of Titania-Doped YSZ for SOFC Anodes* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.523-32.
54. S.S.Liou, W.L.Worrell *Mixed-Conducting Oxide Electrodes for Solid Oxide Fuel Cells* Proceedings 1st First International Symposium on Solid Oxide Fuel Cells ed. S.C. Singhal Electrochemical Society 1989 p.81-9.
55. J.J.Bentzen, H.Schwartzbach *Electrical Conductivity, Structure, and Thermal Expansion Behaviour of ZrO_2 - CeO_2 - Gd_2O_3 - Y_2O_3 Solid Solutions* Solid State Ionics 40/41 1990 p.942-6.
56. M.Gouet, S.Lo, H.Delebarre, M.Guillou *Thermodynamics of CeO_{2-x} Based Solid Solutions* High Temperatures-High Pressures 13 1981 p.51-6.
57. M.Gouet, J.Carriat, B.Chappey, M.Guillou *Doping of Cerium-Based Solid Solutions by CaO , Y_2O_3 , Sm_2O_3 , Ta_2O_5 and Nb_2O_5* High Temperatures-High Pressures 13 1981 p.43-9.
58. B.Cales, J.F.Baumard *Mixed Conduction and Defect Structure of ZrO_2 - CeO_2 - Y_2O_3 Solid Solutions* J.Electrochem.Soc. 131 1984 p.2407-13.
59. T.Ishihara, K.Sato, Y.Mizuhara, Y.Takita *Oxygen Ion Conductivity of Yttria-Niobia Mixed Oxide with Fluorite Related Structure* prepublication copy 1991.
60. M.J.Shingler *Electrical Conductivity and Phase Equilibria of Niobium-Doped Cerium (IV) Oxide* PhD Thesis Case Western Reserve University US May 1989.
61. J.M.Floyd *Oxygen Transport in Oxides of the Fluorite Structure* PhD University of London November 1969.
62. H.Yahiro, Y.Baba, K.Eguchi, H.Arai *High Temperature Fuel Cell with CeO_2 - Y_2O_3 Solid Electrolyte* J.Electrochem.Soc. 135(8) 1988 p 2077-80.
63. J.A.Kilner *Fast Ion Transport in Solids* Solid State Ionics 8(3) 1983 p.201-7.
64. T.Kudo, H.Obayashi *Oxygen Ion Conduction of the Fluorite-Type $Ce_{1-x}Ln_xO_{2-x/2}$ (Ln - Lanthanoid Element)* J.Electrochem.Soc. 122(1) 1975 p.142-7.
65. H.Arai, K.Eguchi, T.Setoguchi, H.Itoh, T.Inoue *Thin Film Solid Oxide Fuel Cells with ZrO_2 and CeO_2 -based Electrolytes* Proceedings 1st First International Symposium on Solid Oxide Fuel Cells ed S C. Singhal Electrochemical Society 1989 p.288-92.

66. K.Mehta, S.J.Hong, J.F.Jue, A.V.Virkar *Fabrication and Characterisation of YSZ Coated Ceria Electrolytes* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.92-103.
67. A.V.Virkar *Theoretical Analysis of SOFC's with Two Layer Composite Electrolytes: Electrolyte Stability* J.Electrochem.Soc. 138(5) 1991 p.1481-7.
68. A.V.Virkar, J.Nachlas, A.V.Joshi, J.Diamond *Internal Precipitation of Molecular Oxygen and Electromechanical Failure of Zirconia Solid Electrolytes* J.Am.Ceram.Soc. 73(11) 1990 p.3382-90.
69. B.C.H.Steele verbal communication.
70. H Iwahara, T.Yajima, T.Hibino, H.Ushida *Performance of Solid Oxide Fuel Cell Using Proton and Oxide Ion Mixed Conductors Based on $\text{BaCe}_{1-x}\text{Sm}_x\text{O}_{3-\alpha}$* J.Electrochem.Soc. 140(6) 1993 p.1687-91.
71. M.Mogensen, J.J.Bentzen *Oxidation of Methane on Oxide Electrodes at 800-1000°C* Proceedings 1st International Symposium on Solid Oxide Fuel Cells ed. Subhash C.Singhal Electrochemical Society 1989 p.99-110.
72. M.Mogensen *Properties of CeO_2 Based SOFC Anode Materials* Proceedings 2nd International Symposium on Solid Oxide Fuel Cells ed. F.Grosz, P.Zegers, S.C.Singhal, O.Yamamoto Commission of the European Communities 1991 p.577-84.
73. M.Mogensen, C.Bagger, B.Kindl, F.W.Poulsen, P.Knudsen *Results from the Danish SOFC Programme* Fuel Cell Meeting Tuscon, Arizona November 1992.
74. B.Zachau-Christiansen, T.Jacobsen, K.West, S.Skaarup *Electrochemical Determination of the Oxygen Stoichiometry in Doped Ceria* Proceedings 3rd International Symposium on Solid Oxide Fuel Cells ed.S.C.Singhal, H.Iwahara Electrochemical Society 1993 p.104-11.
75. H H.Mobius, B.Rohland US Patent 3377203 Apr. 9 1968.
76. T.Takahashi, H.Iwahara, Y.Suzuki Proceedings 3rd International Symposium on Fuel Cells Bruxelles 16-20-VI 1969 Presses Academiques Europeennes p.113-9.
77. I.S.Metcalf, P.H.Middleton, P.Petrolekas, B.C.H.Steele *Hydrocarbon Activation in Solid State Electrochemical Cells* draft 1991.
78. R.D.Shannon, C.T.Prewitt *Effective Ionic Radii Oxides and Fluorides* Acta.Cryst. B25 1969 p.925-946.
- 79.H.L.Tuller, A.S.Nowick *Doped Ceria as a Solid Electrolyte* J.Electrochem.Soc 122(2) 1975 p.255-59
80. I.K.Naik, T.Y.Tien *Electrical Conduction in Nb_2O_5 Doped Cerium Dioxide* J.Electrochem.Soc. 126(4) 1979 p.562-6.

81. H.L.Tuller *Mixed Conduction in Nonstoichiometric Oxides* Nonstoichiometric Oxides ed. O.T.Sorensen Academic Press 1981 p.271-335.
82. P.Kofstad, A.Z.Hed *Defect Structure for Nonstoichiometric CeO₂* J.Am.Ceram.Soc. Discussion and Notes 50(12) 1967 p.681-2.
83. R.N.Blumenthal, R.J.Panlener, J.D.Balser 58B69 *Thermodynamic Study of Nonstoichiometric Cerium Dioxide* Am Ceram.Soc.Bull. 48 1969 p.409.
84. F.S.Brugner, R.N.Blumenthal *Electrical Conductivity of Single Crystal CeO₂* J.Am.Ceram.Soc 54(1) 1971 p 57.
85. B.C.H.Steele, J.M.Floyd *The Oxygen Self-Diffusion and Electrical Transport Properties of Nonstoichiometric Ceria and Ceria Solid Solutions* Proc.Brit.Ceram.Soc. 19 1971 p.55.
86. J.Faber, M.A.Seitz, M.H.Mueller *Defect Characterisation in CeO_{2-x} at Elevated Temperatures I: Xray Diffraction* J.Phys.Chem.Solids 37(10)B 1976 p.903-7.
87. J.Faber, M.A.Seitz, M.H.Mueller *Defect Characterisation in CeO_{2-x} at Elevated Temperatures II: Neutron Diffraction* J.Phys.Chem.Solids 37(10)B 1976 p.909-15.
88. J.R.Sims, R.N.Blumenthal *A Defect Structure Investigation of Nonstoichiometric Cerium Dioxide: I High Temperature X-ray Lattice Parameter Measurements* High Temperature Science 8 1976 p.99-110.
89. J.R.Sims, R.N.Blumenthal *A Defect Structure Investigation of Nonstoichiometric Cerium Dioxide: II High Temperature Macroscopic Length Measurements* High Temperature Science 8 1976 p.111-9.
90. J.R.Sims, R.N.Blumenthal *A Defect Structure Investigation of Nonstoichiometric Cerium Dioxide: III Defect Structure Analysis* High Temperature Science 8 1976 p.121-8.
91. D.J.M.Bevan, J.Kordis *Mixed Oxides of the Type MO₂ (fluorite)-M₂O₃-I. Oxygen Dissociation Pressures and Phase Relationships in the System CeO₂-Ce₂O₃ at High Temperatures* J.Inorganic and Nuclear Chemistry 26 1964 p.1509-23.
92. O.T.Sorensen *Thermodynamic Studies of the Phase Relationships of Nonstoichiometric Cerium Oxides at Higher Temperatures* J.Solid State Chem. 18 1976 p.217-33.
93. S.P.Ray, A.S.Nowick, D.E.Cox *Xray and Neutron Diffraction Study of Intermediate Phases in Nonstoichiometric Cerium Dioxide* J.Solid State Chem. 15 1975 p.344-51.
94. S.P.Ray, D.E.Cox *Neutron Diffraction Determination of the Crystal Structure of Ce₇O₁₂* J.Solid State Chem. 15 1975 p.333-43.
95. B.Iwasaki, T.Katsura Bull.Chem.Soc.Japan 44 1971 p.1297- .

96. R.N.Blumenthal, R.L. Hofmaier *Temperature and Composition Dependence of the Electrical Conductivity of Nonstoichiometric CeO_{2-x}* J.Electrochem.Soc. 121(1) 1974 p.126-131.
97. H.L.Tuller, A.S.Nowick *Doped Ceria as a Solid Electrolyte* J.Electrochem.Soc 122(2) 1975 p.225-59., H.L.Tuller, A.S.Nowick
98. R.Korner, M.Ricken, J.Nolting, I.Reiss *Phase Transformations in Reduced Ceria: Determination by Thermal Expansion Measurements* J.Solid State Chem. 78 1989 p.136-47.
99. A.S.Nowick *Defects in Ceramic Oxides* MRS Bulletin November 1991 p.38-41.
100. A.S.Nowick *Atom Transport in Oxides of the Fluorite Structure* Diffusion in Crystalline Solids ed. A.S.Nowick, G.E.Murch Academic Press 1984 p.143-88.
101. J.A.Kilner, B.C.H.Steele *Mass Transport in Anion-Deficient Fluorite Oxides* Nonstoichiometric Oxides ed. Sorensen Academic Press 1981 p.233-68.
102. M.Gouet, S.Lo, H.Delebarre, M.Guillou *Thermodynamics of CeO_{2-x} Based Solid Solutions* High Temperatures-High Pressures 13 1981 p.51-6.
103. H.J.Matzke *Diffusion in Nonstoichiometric Oxides* Nonstoichiometric Oxides ed. Sorensen Academic Press 1981 p.178-99.
104. H.L.Tuller, A.S.Nowick *Defect Structure and Electrical Properties of Nonstoichiometric CeO₂ Single Crystals* J.Electrochem.Soc. 126(2) 1979 p.209-17.
105. J.E.Garnier, R.N.Blumenthal, R.J.Panlener, R.K.Sharma *A Thermodynamic Study on CaO-Doped Nonstoichiometric Cerium Dioxide* J.Phys.Chem.Solids 37 1976 p.369-78.
106. R.Gerhardt, A.S.Nowick *Grain Boundary Effect in Ceria Doped with Trivalent Cations I. Electrical Measurements* J.Am.Ceram.Soc. 69(9) 1986 p.641-6.
107. R.Gerhardt, A.S.Nowick, M.E.Mochel, I.Dumler *Grain Boundary Effect in Ceria Doped with Trivalent Cations II Microstructure and Microanalysis* J.Am.Ceram.Soc. 69(9) 1986 p.647-51.
108. H.Arai, T.Kunisaki, Y.Shimizu, T.Seiyama *Electrical Properties of Calcia-Doped Ceria with Oxygen Ion Conduction* Solid State Ionics 20(4) 1986 p.241-8.
109. H.Yahiro, T.Ohuchi, K.Eguchi, H.Arai *Electrical Properties and Microstructure in the System Ceria-Alkaline Earth Oxide* J.Mat.Sci. 23 1988 p.1036-41.
110. K.Eguchi, T.Kunisaki, H.Arai *Effect of Microstructure on the Ionic Conductivity of Ceria-Calcia Oxides* J.Am.Ceram Soc. 69(11) 1986 p C282-5.
111. R.Wang, J.A.Gardner, W.E.Evenson, J.A.Sommers *Oxygen Vacancy Complexes in Cerium Oxide Studied by In PAC Spectroscopy* (1992) to be publ.; R.Wang, J.A.Gardner, W.E.Evenson, J.A.Sommers *Indium Dopant/Defect Complexes in*

Lightly-Doped Ceria Ceramic Transactions 24: Point Defects and Related Properties of Ceramics 1991 p.71-8.

112. R.T.Dirstine, R.N.Blumenthal, T.F.Kuech *Ionic Conductivity of Calcia,Yttria and Rare-Earth Doped Cerium Dioxide* J.Electrochem Soc. 126(2) 1979 p.264-.

113. T.Kudo, H.Obayashi *Oxygen Ion Conduction of the Fluorite-Type $Ce_{1-x}Ln_xO_{2-x/2}$ (Ln Lanthanoid Element)* J.Electrochem Soc. 122(1) 1975 p.142-7.

114. R. Gerhardt-Anderson, A.S.Nowick *Ionic Conductivity of CeO_2 with Trivalent Dopants of Different Ionic Radii* Solid State Ionics 5 1981 p.547-50.

115. V.Butler, C.R.A.Catlow, B.E.F.Fender *Defect Structure of Anion-Deficient ZrO_2* Solid State Ionics 5 1981 p.539-42.

116. V.Butler, C.R.A.Catlow, B.E.F.Fender, J.H.Harding *Dopant Ion Radius and Ionic Conductivity in Cerium Dioxide* Solid State Ionics 8 1983 p.109-13.

117. M.Yashima, N.Ishizawa, M.Yoshimura *Application of an Ion-Packing Model Based on Defect Clusters to Zirconia Solid Solutions: I.Modelling and Local Structure of Solid Solutions* J,Am.Ceram.Soc. 75(6) 1992 p.1541-9.; M.Yashima, N.Ishizawa, M.Yoshimura *Application of an Ion-Packing Model Based on Defect Clusters to Zirconia Solid Solutions: II.Applicability of Vergards Law* J,Am.Ceram.Soc. 75(6) 1992 p.1550-7.

118. J.A.Kilner, R.J.Brook *A Study of Oxygen Ion Conductivity in Doped Nonstoichiometric Oxides* Solid State Ionics 6 1982 p.237-52.

119. H.Tuller, A.S.Nowick *Small Polaron Electron Transport in Reduced CeO_2 Single Crystal* J.Phys.Chem.Solids 1977 p.859-67.

120. I.K.Naik, T.Y.Tien *Small Polaron Mobility in Nonstoichiometric Cerium Dioxide* J.Phys.Chem.Solids 39 1978 p.311-5.

121. C.Kittel *Electron-Phonon Interaction: Polarons* Introduction to Solid State Physics Wiley&Sons 1986 p.281-3.

122. M.Gouet, J.Carriat, B.Chappey, M.Guillou *Doping of Cerium-Based Solid Solutions by CaO , Y_2O_3 , Sm_2O_3 , Ta_2O_5 and Nb_2O_5* High Temperatures-High Pressures 13 1981 p.43-9.

123. I.K.Naik, T.Y.Tien *Electrical Conduction in Nb_2O_5 Doped Cerium Dioxide* J.Electrochem.Soc. 126(4) 1979 p.562-6.

124. R.W. Vest *Defect Structure and Electronic Properties of Ceramics* Physics of Electronic Ceramics A Ed. L.L.Hench, D.B.Dove Marcel Dekker 1971 p.99-130.

125. F.A.Kroger *The Chemistry of Imperfect Crystals V.2* North Holland Publishing Company 1974.

126. G.Brouwer *A General Asymptotic Solution of Reaction Equations Common in Solid State Chemistry* Philips Res. Report 9 1954 p 1954

127. C.J.Kevane *Oxygen Vacancies and Electrical Conduction in Metal Oxides* Physical Review 133A(5) 1964 p.1431.
128. J.Patterson *Conduction Domains for Solid Mixed Conductors and Electrolytic Domain for Calcia Stabilised Zirconia* Physics of Electronic Ceramics A Ed. L.L.Hench, D.B.Dove Marcel Dekker 1971 p.131-54.
129. R.J.Panlener, R.N.Blumenthal, J.E.Garnier *A Thermodynamic Study of Nonstoichiometric Cerium Dioxide* J.Phys.Chem.Solids 36 1975 p.1213-22.
130. J.W.Dawicke, R.N Blumenthal *Oxygen Association Pressure Measurements on Cerium Oxide* J.Electrochem.Soc. 133(5) 1986 p.904-9.
131. M.Hillert, B.Jansson *Thermodynamic Model for Nonstoichiometric Ionic Phases-Application to CeO_{2-x}* J.Am.Ceram.Soc. 69(10) 1986 p.732-4.
132. I.Riess, H.Janczikowski, J.Nolting *O_2 Chemical Potential of Nonstoichiometric Ceria CeO_{2-x} Determined by a Solid Electrochemical Method* J.Appl.Phys. 61(10) 1987 p.4931-33.
133. J.Hattori, J.Inoko, Y.Murakami *Catalytic Activity of Lanthanide Oxides in Oxidation of Butane* J.Catalysis 42 1976 p.60-72.
134. L.Mendelovici, M.Steinberg *Reaction of Ethylene with Oxygen on a Pt/CeO₂ Catalyst* J.Catalysis 93 1985 p.353-9.
135. L.Mendelovici, M.Steinberg *Methanation and Water-Gas Shift Reactions Over Pt/CeO₂* J.Catalysis 96 1985 p.285-7.
136. J.S.Riek, A.T.Bell *Studies of Interactions of H₂ and Co with Pd/SiO₂ Promoted with La₂O₃, CeO₂, Pr₆O₁₁, Nd₂O₃, Sm₂O₃* J.Catalysis 99 1989 p.278-92.
137. H.C.Yao, Y.F.Yu.Yao *Ceria in Automotive Exhaust Catalysts 1.Oxygen Storage* J.Catalysis 86 1984 p.254-65.
138. C.Li, Y.Sakata, T.Arai, K.Domen, K.Maruya, T.Onishi *Adsorption of Carbon Monoxide and Carbon Dioxide on Cerium Oxide Studied by Fourier Transform IR Spectroscopy* J.Chem Soc. Faraday Transactions 85(6) 1989 p.929,1451-61.
139. W.C.Mackrodt, M.Fowles, M.A.Morris *Oxidation Catalysts Essentially Free from Group VIII Elements* European Patent Publ.0472307A1 (26.2.92) Appl.91307016.5 (31 07.91).
140. K.Otsuka, M.Hatano, A.Morikawa *Hydrogen from Water by Reduced Cerium Oxide* J.Catalysis 79 1983 p 493-6.
141. M.J.Readey, R.-R. Lee, J.W.Halloran, A.H.Heuer *Processing and Sintering of Ultrafine MgO-ZrO₂ and (MgO,Y₂O₃)-ZrO₂ Powders* J.Am Ceram.Soc. 73(6) 1990 p.1499-403.
142. J.G.Duh, J.U.Wan *Liquid Infiltration in ZrO₂ Ceramics* J.Mat.Sci. Letters 12 1993 p.473-5

143. J.U.Wan, J.G.Du *Effects of pH Value and Compact Pressure on Coppt. Y_2O_3 - CeO_2 - ZrO_2* J.Mat.Sci.Letters 12 1993 p 575-7.
144. C.Y.Shej, R.S Liu, C.T.Chang, P.T.Wu *Coprecipitation Process for the Precipitation of Superconductive Bi-Sr-Ca-Cu Oxides* Materials Letters 9(2/3) 1990 p.105-8.
145. B.S.Khurana, R.B.Tripathi, S M Kullar, R K.Kotnala, S.Singh, K.Jain, B.V.Reddi, R.C.Goel, B K.Das *Simultaneous Coprecipitation of the Hydroxides for Preparing $YBa_2Cu_3O_7$ Superconductors* J Mat Sci. Letters 8 1989 p.234-236.
146. P.A.Lessing *Mixed-Cation Oxide Powders via Polymeric Precursors* Ceramic Bulletin 68(5) 1989 p.1002-7.
147. M.Pourbaix *Atlas of Electrochemical Equilibria in Aqueous Solutions* Pergamon Press p.179-82,187-97,247-50,437-42.
148. H. Remy *Treatise on Inorganic Chemistry vol.1* Elsevier 1956 p.375-80.
149. M.S.Kaliszewski, A.H.Heuer *Alcohol Interaction with Zirconia Powders* J.Am.Ceram.Soc. 73(6) 1990 p.1504-9.
150. M.S.Huang *Preparation of Magnesium Doped Lanthanum Chromite for SOFC Applications* PhD University of London March 1991.
151. E.B.Slamovich, F.F.Lange *Densification of Large Pores:I Experiments* J.Am.Ceram.Soc. 75(9) 1992 p.2498-508
152. E.P.Butler, J.Drennan *Microstrucrural Analysis of Sintered High-Conductivity Zirconia with Al_2O_3 Additions* J.Am.Ceram.Soc. 65(10) 1982 p.474-8.
153. K.C.Radford, R.J.Bratton *Zirconia Electrolyte Cells Part1 Sintering Studies* J.Mater.Sci. 14 1979 p.59-65.
154. H-Y.Lu, S.-Y.Chen *Sintering and Compensation Effect of Donor- and Acceptor-codoped 3mol% Y_2O_3 - ZrO_2* J.Mat.Sci. 27 1992 p.4791-6.
155. J.Zheng, J.S.Reed *The Different Roles of Forming and Sintering on Densification of Powder Compacts* Am.Ceram Soc.Bull. 71(9) 1992 p.1410-6.
156. I.Fullarton Undergraduate final year project, Dept of Materials Imperial College 1990.
157. M.Cudworth *Investigation of Ceria Doped with Nb, Y, F* Summer Project Dept. Materials Imperial College 1990
158. A.J.Dyer, E.A D.White *A Study of Pentavalent Oxide Systems* Trans.Brit.Ceram.Soc. 63 1964 p.301-12
159. T.Negas, R.S Roth, C.L.McDaniel, H.S.Parker, C.D.Olson *Oxidation-Reduction Reactions of $CeMO_{4+x}$ ($M - Ta$ or Nb) Phases* Mater Res.Bull. 12 1977 p.1161-71.
160. A.Santoro, M.Marezio, R.S Roth, D Minor *Neutron Powder Diffraction Study of the Structures of $CeTaO_4$ and $NdTaO_4$* J.Solid State Chem. 35 1980 p.167-75.

161. G.G.Kasimov, N.D.Samsonova, M.F.Sorokina, L.D.Finkelstein *Study of the Electronic Configuration of Cerium Ions in Niobates* Izv.Akad.Nauk.SSSR Neorg.Mater. 14(2) 1978 p.301-4.
162. R.J.Cava, R.S.Roth, T.Negas, H.S.Parker, D.B.Minor *Crystal Chemistry, Modulated Structure and Electrical Conductivity in the Oxygen Excess Scheelite-Based Compounds $La_{1-x}Th_xNbO_{4+x/2}$ and $LaNb_{1-x}W_xO_{4+x/2}$* J.Solid State Chem. 40 1981 p.318-29.
163. D.Chatterji, R.W.Vest *Thermodynamic Properties of the System Indium-Oxygen* J.Am.Ceram.Soc. 55(11) 1972 p.575-8.
164. N.Fukatsu, S.Usuki, Z.Kozuka *On the Control of Oxygen Potential in Gas Atmosphere using the Stabilised Zirconia Galvanic Cell as an Oxygen Pump* J.Japan Inst.Metals (Nippon Kinzoku Gakkaishi) 40(12) 1976 p.1263-70.
165. Y.Saito, T.Maruyama *Oxygen Pump of Stabilised Zirconia and its Application to Thermal Analysis of Oxides* Report of the Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 8 1983 p.17-26.
166. J.Nowotny, I.Sikora, M.Rekas *Defect Structure and Electrical Properties of Undoped and Cr-Doped CoO* J.Electrochem.Soc. 131(1) 1984 p.94-100.
167. G.H.Jonker *The Application of Combined Conductivity and Seebeck Effect Plots for the Analysis of Semiconductor Properties* Philips Res.Reports 23 1968 p.131-8.
168. Dr. P.H.Middleton - private communication.
169. M. Hansen *Constitution of Binary Alloys* McGraw Hill 1958 p.41-2.
170. P.M.Hemenger *Measurement of High Resistivity Semiconductors Using the Van der Pauw Method* Rev.Sci.Instrum. 44(6) 1973 p.698-700.
171. Kagaku Binran Kisohe II Nihon Kagakukai
172. Ceramic Characterisation Techniques Japan Ceramic Assn.
173. S.Carter, R.J.Chater, J.Kajda, K.M.Liddicott, J.A.Kilner, B.C.H.Steele *Oxygen Self Diffusion (D^*) and Surface Exchange (k) Coefficients of CeO₂-Based Solid Solutions* Proceedings 1st International Symposium on Ionic and Mixed Conductors ed. T.A.Ramanarayanan, H.Tuller HTDM, Electrochem. Soc. 1991 p. 84-91.
174. B.C.H.Steele *Oxygen Transport and Exchange in Oxide Ceramics* 3rd Grove Fuel Cell Symposium 1993 to be published in J.Power Sources.
175. P.Kofstad, P.B.Anderson *Gravimetric Studies of the Defect Structure of α -Nb₂O₅* J.Phys.Chem.Solids 21 (3/4) 1961 p.280-6.
176. K.R.Williams *Hydrocarbon Fuels* An Introduction to Fuel Cells Chap 9 Elsevier 1966 p.214-27.