Technical Progress Report
LOW TEMPERATURE CATHODE SUPPORTED ELECTROLYTES

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Report for the period of
October 1, 2000 to March 31, 2001

Submitted by

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Executive Summary

October 2000 – March 2001

This project has three main goals: Thin Films Studies, Preparation of Graded Porous Substrates and Basic Electrical Characterization and testing of Planar Single Cells.

Substantial progress has been made on both characterizing thin films as well as developing methods to produce films on nanoporous substrates.

The results of electrical conductivity measurements on $\text{ZrO}_2\text{:16\%Sc}$ nanocrystalline thin films under controlled oxygen partial pressure and temperature are presented. The experimental data have been interpreted using a defect model, which describes the interaction between Sc and oxygen vacancies resulting in the formation of donor – $(Sc_{Zr}' - V_o^{\cdot\cdot} - e)^x$ and acceptor – $(Sc_{Zr}' - h)^x$ levels. From this the electronic and ionic contribution to the electrical transport has been determined and correlated with the band structure. These results suggest that $\text{ZrO}_2\text{:16\%Sc}$ possesses higher electronic conductivity than $\text{ZrO}_2\text{:16\%Y}$, which dominates the total conductivity in reducing atmospheres.

This is an important result since it indicates that Sc-YSZ maybe useful in the anode regions of the cell.

We have made important breakthroughs on depositing dense Ceria films on to porous LSM substrates.

In previous studies we have found that in order to produce a surface which is smooth enough to coat with dense polymer precursor derived films, the required thickness of the colloidal film layer is determined by the maximum surface roughness. That is, if we wish to make 2 micron thick colloidal oxide layers, the roughness of the LSM surface can not exceed 2 microns.

Currently, we are producing the composite $\text{CeO}_2\text{/LSM}$ structures that can be coated with polymer precursor to produce 0.5 to 1.5 micron thickness dense YSZ films. In the next quarter, we will be testing SOFC's using these structures.

YSZ/ $\text{CeO}_2\text{/LSM}$ composites have been formed by annealing at 800°C . Our studies show that the YSZ films are very dense with a 20 nm grain size.

SOFC's using these composites are being fabricated and we expect to obtain cell data during the next quarter. As we reported in November 2000, we have had difficulties in making pore free films with larger areas that about 0.2cm^2 which is due to problems in our clean room. Modifications have now been completed on the clean room and we should be approaching a class 100 in the film making area. This level of cleanliness is sufficient to obtain films without pores over areas up to 100cm^2 .

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1.0: Abstract

This project has three main goals or tasks:

Task 2.1: Thin Film Studies: Nanocrystalline Electrolyte

- 87% complete
- on schedule

Task 2.2: Preparation of Graded Porous Substrates

- 66% complete
- on schedule

Task 2.3: Basic Electrical Characterization And Testing of Planar Single Cells

- 50% complete
- behind schedule

2.0: Future Research

Research Planned for FY 2000-2001:

Continue Optimization of the Cathode Substrate. Evaluate:

- a) The influence of porous CeO₂ layer on SOFC performance.
- b) The influence of the addition of LSCF into CeO₂ layer on SOFC performance.
- c) The influence of the conductivity of the CeO₂ layer on SOFC performance.

Make Single Cell Fuel Cell Measurements

- a) Cell performance as a function of electrolyte thickness and temperature.
 - YSZ electrolyte
 - CeO₂ electrolyte
- b) Cell performance as a function of electrode composition.
 - Anode
 - Cathode

Improve Clean Room (*in order to make electrolyte of areas larger than 0.2 cm² our existing clean room must be improved*)

- a) Double size.
- b) More filters and air flow.
- c) This was completed March 1, 2001.

Begin Stack Design and Economic Modeling

Continue Studies Related to Placing Thin Electrolyte Films onto Porous Substrates

- a) Polymer precursor onto a graded substrate.
- b) Transfer of dense films to a porous substrate.

3.0: Individual Task Reports

Task 2.1: Thin Film Studies: Nanocrystalline Electrolyte

2.1.1: ZrO₂/Sc CHARACTERIZATION

*T. Suzuki, I. Kosacki, W. Huebner and H.U. Anderson, “**Microstructure Controlled Electrical Conductivity in Acceptor-doped ZrO₂ Thin Films**”, submitted to the 7th International Symposium on SOFC, Tsukuba 2001.*

*Paper submitted for 7th International Symposium
on SOFC, Tsukuba 2001.*

MICROSTRUCTURE CONTROLLED ELECTRICAL CONDUCTIVITY IN ACCEPTOR-DOPED ZrO₂ THIN FILMS

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ABSTRACT

The results of electrical conductivity measurements on ZrO₂:16%Sc nanocrystalline thin films under controlled oxygen partial pressure and temperature are presented. The experimental data have been interpreted using a defect model, which describes the interaction between Sc and oxygen vacancies resulting in the formation of donor $-(Sc_{Zr}' - V_o'' - e)^x$ and acceptor $-(Sc_{Zr}' - h)^x$ levels. From this the electronic and ionic contribution to the electrical transport has been determined and correlated with the band structure. These results suggest that ZrO₂:16%Sc possesses higher electronic conductivity than ZrO₂:16%Y, which dominates the total conductivity in reducing atmospheres.

INTRODUCTION

The enhancement of electrical conductivity and reaction kinetics is an important aspect in the study of oxygen conductors and success in this effort influences the development of fuel cells, gas sensors and ionic membranes. ZrO₂:16%Y (YSZ) is an exceptional material for such applications (1). Its electrical properties are strongly related to the oxygen non-stoichiometry, which is controlled by dopants and ambient atmosphere. A number of recent studies have shown that the microstructure can also influence electrical properties. These phenomena are attributed to grain boundary and size dependent defect equilibria, which becomes dominant when the grain size is less than 100nm. Such effects have been recently reported for nanocrystalline CeO₂ (2-4) and YSZ (3,4), where for both systems an enhancement in the conductivity was observed. Another important aspect of solid electrolytes application is the possibility of the fabrication of devices using the thin film structures, which can reduce the overall device resistance and finally the operating temperature.

Sc-doped ZrO₂ (ScSZ) has been recently considered as an alternative to YSZ solid electrolyte due to its higher electrical conductivity and improved mechanical properties (5-7). For the application of ScSZ in fuel cells it is important to evaluate the relationship between electronic and ionic conductivities under different oxygen partial pressure. However, there is a lack of data related to such characterization. Only one investigation has been published where the electronic conductivity for ScSZ was determined from a coulometric titration study (8). The results showed a significant contribution of electronic conductivity at low oxygen activity ($<10^{-25}$ atm) and high temperatures, over 900°C.

In the present work, the results obtained in a study of electrical transport of nanocrystalline ScSZ thin films are reported. The objective of this study was to determine the electrical conductivity as a function of temperature and oxygen activity. These measurements can provide information about the contribution of electronic and ionic conductivities to the electrical transport. The correlation of the data with a proposed defect model also provides an opportunity to determine the ionization energy of the created defect centers.

EXPERIMENTAL

Dense nanocrystalline ScSZ thin films have been obtained by a polymer precursor spin coating process. The preparation procedure has been reported in details elsewhere (3,4,9). For this study, ScSZ films (0.4 μ m thick) have been deposited on polycrystalline Al₂O₃-substrate. The sintering was carried out at 900°C for 4hrs in air, which yield a grain size of about 20nm. The crystallographic structure of the films was checked by x-ray diffraction. Obtained results shown that XRD pattern correlates well with standard indication the successful preparation of material with single fluorite structure

Electrical conductivity was studied using Solartron 1260 Frequency Response Analyzer with a 1296 Interface operating over the frequency range of 1-10⁷Hz and impedance up to 10¹⁰ Ω . Measurements were performed in the temperature range of 600-900°C and P_{O₂} range of 10⁻³⁰-1atm using O₂/N₂, CO/CO₂ and H₂/N₂ gas mixtures.

The impedance spectra were analyzed to yield the high-frequency semicircle related conductivity, which for nanocrystalline materials is attributed to the superposition of the bulk and grain boundary contributions (4,10,11). Such determined conductivity for nanocrystalline ScSZ was compared with similar data for nano- and microcrystalline YSZ specimens.

EXPERIMENTAL RESULTS

The electrical conductivity of 20nm grain sized ScSZ films as a function of oxygen partial pressure at different temperatures is shown in Fig.1. The conductivity exhibits a P_{O₂}-independent region at high oxygen activity and anomalous decrease at intermediate P_{O₂}. Those two regions are probably attributed to extrinsic ionic conductivity while at low P_{O₂} electrical conductivity follows the P_{O₂}^{-1/4} relationship and is related to extrinsic electronic conductivity. The decreased electrical conductivity in intermediate P_{O₂} is quite unique and suggests a different mechanism of the charge carrier compensation, which causes the decrease of the concentration of ionic carriers. This behavior has been also observed for nanocrystalline YSZ (3,4,10,11).

Fig.2 presents the comparison between conductivities of ScSZ and YSZ determined for at 900°C. In this figure the electronic conductivity estimated from data reported for microcrystalline YSZ (12) and ScSZ (8) are also presented. As can be seen, the nanocrystalline ScSZ certainly has a higher conductivity than either 20nm or 2400nm YSZ, however the electronic conductivity dominates electrical transport at oxygen activities below 10⁻¹⁵atm. Whereas for YSZ, electronic conductivity only becomes

significant at oxygen partial pressure less than 10^{-25} atm. The electronic conductivity of nanocrystalline ScSZ determined in this study is about 3 orders of magnitude higher than that reported for bulk specimens (8). Such enhancement is probably related to the grain size dependent defect equilibria, which can reduce the enthalpy of oxygen vacancy formation and finally change the non-stoichiometry of nanocrystalline material. The ionic conductivity of YSZ and ScSZ specimens, which dominates at high P_{O_2} is also influenced by microstructure. As can be seen in Fig.2, the ionic conductivity in nanocrystalline YSZ and ScSZ is about one order of magnitude higher than determined for microcrystalline YSZ. An anomalous decrease of the conductivity at intermediate $10^{-20} < P_{O_2} < 10^{-16}$ atm has also been observed. Such behavior can be explained by different charge carrier compensation in nanocrystalline materials. This observation strongly suggested non-equivalent positions for oxygen vacancies distributed in ZrO_2 lattice when different acceptors are presented and support the conception about the interaction between the defects resulting from the formation of associations. In the case of heavily acceptor doped oxides, the use of the ionic conductivity model based on the assumption of fully ionized and "free" oxygen vacancies is limited. A model, which addresses the electrical transport in these oxides, must consider the interactions between the oxygen vacancies and the dopants.

Fig.1, The electrical conductivity of nanocrystalline $ZrO_2:16\%Sc$ thin films as a function of oxygen activity at different temperatures. Solid lines represent the results of fitting the experimental results to the model (Eq.6).

Fig.2, The comparison between conductivities determined at 900°C for nanocrystalline thin films and microcrystalline bulk specimens of ZrO₂:16%Sc and ZrO₂:16%Y as a function of P_{O2}. Data for bulk YSZ exhibit the total conductivity, bulk + grain boundary contribution (10). Open symbols represent electronic conductivity data determined for bulk microcrystalline specimens (8,12).

DEFECT ASSOCIATIONS MODEL FOR ACCEPTOR DOPED OXIDES

In order to interpret the observed phenomena of the electrical conductivity in nanocrystalline YSZ and ScSZ (Figs.1 and 2) the defect pair model has been proposed (4,10,13). Here we briefly summarize the key required assumptions and equations. In this model an association between oxygen vacancies and acceptors has been considered, which results in the formation of a donor and acceptor centers:

$$(A_{Zr}' - V_o^{\bullet\bullet} - e)^x = (A_{Zr}' - V_o^{\bullet\bullet})' + e \quad [1]$$

$$(A_{Zr}' - h)^x = A_{Zr}' + h \quad [2]$$

where $A = Y$ or Sc . In this case, acceptor doped ZrO₂ can be considered being a compensated semiconductor with donor [1] and acceptor [2] levels whose concentration in

ionized and unionized states can be described by Fermi statistics. Based on this model and assuming that the total concentration of dopants is related to the sum of acceptors and donors, an expression for the concentration of ionized donors and acceptors can be obtained:

$$[A_{Zr'} - V_o^{''}] = [A_{Zr'}] = \frac{[A]}{2 + \frac{1}{2} \left[(r P_{O_2}^{-1/2})^{-1/2} + (r P_{O_2}^{-1/2})^{1/2} \right] \exp\left(\frac{E_A - E_D}{2kT}\right)} \quad [3]$$

From this expression, the concentration of ionized donors, which is related to ionic species, depends upon the oxygen activity as well as the difference between the ionization energy for the acceptor and donor level, $\Delta E = E_A - E_D$. Note that r is temperature dependent equilibrium constant between donors and acceptors (13).

This model predicts a decrease of ionic species concentration at both low and high P_{O_2} due to an increase in the number of unionized donors. Previous models do not predict such behavior. The obtained relationship is equivalent to extrinsic charge carrier compensation. When ΔE increases, the preexponential factor in Eq.3 tends to zero and the concentration of ionic species approaches $[A]/2$ which is consistent with the acceptor compensation by fully ionized oxygen vacancies (13).

Finally based on the Eq.3, which describes the relationship between the concentration of ionic species and oxygen activity, the expression for ionic conductivity can be obtained (13):

$$\sigma_i = 2 \cdot e \cdot [A_{Zr'} - V_o^{''}] \cdot \mu_i = \frac{2 \cdot e \cdot [A] \cdot \mu_i}{2 + \frac{1}{2} \left[(r P_{O_2}^{-1/2})^{-1/2} + (r P_{O_2}^{-1/2})^{1/2} \right] \exp\left(\frac{E_A - E_D}{2kT}\right)} \quad [4]$$

At low P_{O_2} the contribution of electronic conductivity should be also considered (13):

$$\sigma_e = e \cdot \mu_e \cdot N_C (r P_{O_2}^{-1/2})^{1/2} \exp\left(\frac{E_A + E_D - 2E_C}{kT}\right) \quad [5]$$

where μ_i and μ_e are the mobility of oxygen ions and electrons respectively. The obtained expressions for ionic and electronic conductivities (Eqs.4 and 5) have been used for the interpretation of relationships between the electrical conductivity and oxygen activity observed for nanocrystalline YSZ and ScSZ (Figs.1 and 2).

DISCUSSION

The isothermal conductivity curves reported in Figs.1 and 2 have been interpreted in terms of the above model in which electronic and ionic conductivities can be identified and separated. The total conductivity as a function of temperature and oxygen activity can be described at low P_{O_2} as:

$$\sigma = \sigma_i + \sigma_e = \frac{\alpha}{1 + \beta \cdot P_{O_2}^{-1/4}} + \gamma \cdot P_{O_2}^{-1/4} \quad [6]$$

where α and β are temperature dependent factors related to ionic conductivity while parameter γ describes the electronic conductivity.

Fig.3, Temperature dependence of ionic and electronic conductivities of nanocrystalline ZrO₂:16%Sc thin films under P_{O₂} = 1atm. Open symbols represent data determined for bulk microcrystalline specimens (5,8).

The solid curves in Figs.1 and 2 represent the result of the fitting of experimental results to the model (Eq.6). As can be seen, the proposed model correlates well with experimental results. The three conductivity parameters of α , β and γ were used to calculate partial conductivities for nanocrystalline ScSZ. Fig.3 shows the temperature dependence of ionic and electronic conductivity at fixed P_{O₂} = 1atm. The open symbols in this figure are the conductivities reported for bulk microcrystalline specimens. The electronic conductivity estimated from coulometric titration data (8) is about three orders of magnitude lowered than that reported in this study while the ionic conductivity is slightly higher compared with the data for bulk microcrystalline specimens (5). The differences in ionic conductivity observed for nano- and microcrystalline ScSZ can be attributed to the grain boundary effects. It is expected that the increased fraction of grain boundary volume in nanocrystalline materials should tend to enhance the electrical conductivity due to a

lowering of the impurity concentration and higher diffusion in the grain boundary compared to the bulk area. This behavior was observed for CaF_2 (14), CeO_2 (2-4) and $\text{SrCeO}_3\text{:Yb}$ (4,11) systems.

Note that the electronic conductivity activation energy is decreased from 2.64 to 1.6eV for micro- and nanocrystalline ScSZ respectively (Fig.3). This value is much lower than the 3.88eV reported for microcrystalline YSZ (12) and these differences can explain why the electronic conductivity is higher in ScSZ (Fig2). This observation correlates with a same effect observed for nano- and microcrystalline CeO_2 and is probably attributed to reduction of defect formation enthalpy in nanocrystalline materials (3,4,11). The effect of reduction in the electronic conductivity activation energy can be explain as the result of different in the ionization energy of donors in YSZ and ScSZ. It appears that Y can form a deeper level compared with Sc. The proposed model provides the ability to determine the energy of the donor level in ScSZ. This energy can be obtained from the temperature dependence of the minimum conductivity observed for P_{O_2} dependence (Fig.1). Assuming that in this point, $\sigma_i = \sigma_e$ and combining Eq.4 and Eq.5, the $\sigma_{\min}$ should be an exponential function of temperature:

$$\sigma_{\min} \sim \exp\left(\frac{-(E_C - E_D)}{kT}\right) \quad [7]$$

From a plot of the dependence of $\text{Log}(\sigma_{\min})$ as a function of $1/T$, the activation energy of donor level can be determined. Fig.4 presents such behavior determined for nanocrystalline ScSZ allows the determination of the activation energy, which is 0.9eV. This energy is much lower than the 2.2eV estimated for YSZ (15).

Fig.4, Temperature dependence of $\text{Log } \sigma_{\min}$ of nanocrystalline $\text{ZrO}_2\text{:16\%Sc}$ thin films.

Since the electronic conductivity of nanocrystalline ScSZ becomes significant in reducing atmosphere, its contribution to the total electrical transport should be considered. This can be discussed based on the dependence of the transference number. Fig.5 presents the ionic transference number, $t_i = \frac{\sigma_i}{\sigma_i + \sigma_e}$ which has been obtained based on the electronic and ionic conductivities as a function of temperature and oxygen activity. As can be seen, ScSZ is an excellent ionic conductor at $P_{O_2} > 10^{-12}$ atm. At the P_{O_2} region of 10^{-12} - 10^{-20} atm material is a mixed conductor with the ionic transference number varying from 1 to 0.1 while at $P_{O_2} < 10^{-20}$ atm ScSZ is good electronic conductor with electronic transference number higher than 0.99. These results on the electrical conductivity of nanocrystalline ScSZ strongly suggest some limitation for the use this material as a solid electrolyte in reducing atmosphere.

Fig.5, The ionic transference number as a function of oxygen activity determined for nanocrystalline $ZrO_2:16\%Sc$ thin films at different temperatures.

The observed enhancement of electronic conductivity in nanocrystalline ScSZ is strongly related to the microstructure controlled non-stoichiometry. The electrical conductivity measurements recently performed for bulk microcrystalline ($1.6\mu m$) specimens showed only very small changes with oxygen activity, which suggested ionic transport (16). This material has been also successfully used as an electrolyte in SOFC (17). The large increase in electronic conductivity observed for nanocrystalline ScSZ thin films

at $P_{O_2} < 10^{-15}$ atm suggests that it may find use as an anode in a SOFC with microcrystalline ScSZ as the electrolyte. Such compatibility between the electrode and electrolyte should reduce the internal resistance and finally improve the SOFC performance.

In order to improve the understanding of the role played by acceptors and the microstructure in non-stoichiometry of ScSZ, it is necessary to conduct the electrical conductivity measurements as a function of oxygen activity and correlate them with material grain size. This is presently under study.

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2.1.2: CeO₂ FILMS

T. Suzuki, I. Kosacki and H.U. Anderson, “Microstructural/Electrical Conductivity Relationships in Nanocrystalline Ceria Thin Films”, presented at the International Symposium on Soft Solution Processing, Tokyo 2000.

Paper presented on International Symposium
on Soft Solution Processing, Tokyo 2000
Microstructural/Electrical Conductivity Relationships in

Nanocrystalline Ceria Thin films

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Keywords: ceria, nanocrystals, thin films, non-stoichiometry, impedance spectroscopy,
electrical conductivity, defect model

Abstract

A study of nanocrystalline oxide thin film processing and influence of microstructure on the electrical properties of nanocrystalline Gd-doped CeO_2 thin films are reported. Nanocrystalline films on sapphire substrate were prepared using a polymeric precursor spin coating technique. The grain size of these films depends upon the annealing temperatures and the dopant content, where higher content of dopant realized lower grain size. The electrical conductivity of nanocrystalline Gd-doped CeO_2 thin films was studied as a function of temperature and oxygen activity and correlated with the grain size. The results show that the electronic conductivity of CeO_2 increases, while the ionic conductivity increases in doped samples as the grain size decreases. From these results, the enthalpy of oxygen vacancy formation was determined as a function of grain size. For CeO_2 sample, an enhancement of electronic conductivity was observed with decreasing grain size below 100nm. In the case of Gd-doped CeO_2 , the electrical conductivity results show that an increase of the ionic conductivity was observed as the grain size decreased, which is related to a decrease in the activation energy for the ion mobility.

1. INTRODUCTION

Nanocrystalline oxides are displaying electrical properties which appear to be unique and may lead to applications that are not attainable by conventional microcrystalline oxides [1-3]. As a result it is very important to understand the relationships between microstructure and electrical properties as well as to be able to control the microstructure in the nanocrystalline range. New phenomena observed in nanocrystalline oxides are related to the increasing of grain boundary volume and the change of the non-stoichiometry which may lead to enhance the reaction kinetics and electrical conductivity [2,3].

The grain boundary regions are characterized by a reduced atomic density and interatomic spacings deviating from the ones in the perfect lattice. The physical reason for the reduced density and the non-lattice spacings between the atoms in the boundary region is the misfit between the crystal lattices of different orientation joined along common interfaces. Therefore, the nanocrystalline system preserves in the crystals, a structure of low energy at the expense of the boundary regions where all misfit is concentrated so that a structure far from equilibrium is formed. The misfit between the crystals not only reduces the atomic density in the interfacial region in comparison to the perfect lattice but also causes strain fields to extend from the boundary regions into crystallites. These strain fields remove the atoms from their ideal lattice site. The amount of atomic displacement depends primarily on the interatomic potential. Hence different materials are expected to exhibit different atomic structures in the nanocrystalline state. So far, the synthesis of nanocrystalline materials has been carried out most frequently by assembling pre-generated small clusters by mean of consolidation and sintering. A variety of cluster generation methods have been reported and these are mainly categories in vacuum, gas-phase and condensed-phase synthesis [4].

Other methods such as deposition methods and sol-gel technique have also been utilized to synthesize nanocrystalline materials. Comparing to consolidation and sintering of clusters, these methods are the low temperature of the methods, which can be a significant advantage. Among these methods, recent studies shows that a polymer precursor spin coating technique [5], which is the low temperature nanocrystalline thin film synthesis method, has turned out to be effective for these reason;

- very stable precursor
- low processing temperature $\geq 400^{\circ}\text{C}$
- yields very dense and optical quality films.

These features enable to control the grain size and to obtain stable microstructure, which is very important and makes it possible to do systematic study of microstructure-physical properties relationships, including electrical and optical properties. Application of nanocrystalline oxides is very wide and includes the electrochemical devices such as solid oxide fuel cell, ceramic oxygen generator and partial oxidation membranes which are considered to be key technologies in the 21st century.

CeO_2 based solid solutions, which are exhibiting high oxygen ion transport, have been one of candidates for the electrochemical devices and intensively studied. Applying nanocrystalline structure to CeO_2 based solid solutions can be one of big concerns because it has potential to enhance the physical properties and performance [6]. Recent studies show that nanocrystalline ZrO_2 displays about two orders higher electrical conductivity than microcrystalline ZrO_2 at 600°C [7] and nanocrystalline CeO_2 increases the electronic conductivity with reducing the enthalpy of oxygen vacancy formation [8].

The objective of this study is to understand the relation between microstructure and

synthesis conditions, and also to determine the influence of the microstructure on the material nonstoichiometry and defect thermodynamics in both undoped and doped cerium oxides. In this paper the results of a study of the electrical and dynamical properties of nanocrystalline CeO_2 and Gd-doped CeO_2 thin films by the impedance spectroscopy are investigated.

2. Experimental

Sample Preparation

Figure 1 shows the process of the polymer precursor spin coating technique. Thin films are being prepared by spin coating a polymer precursor solution onto a substrate. The solutions are prepared by quantitatively dissolving water soluble cation sources such as nitrate and carbonate into solutions which contain chelating and polymerizing agents such as ethylene glycol, water and nitric acid. With appropriate heating, the resulting solution can be converted into a viscous solution ($\sim 100\text{cps}$), which can be coated onto a substrate. This technique allows mixing of the cations on the molecular level so is very useful for the preparation of homogenous oxide films. With proper heating, the polymer film can be pyrolyzed to yield a dense oxide film on the substrate. Typical film thickness is $0.01\sim 0.1$ micron/ deposition. Multiple depositions allow the film thickness to be increased into the micron range. The grain size of the films can be controlled by the annealing temperature of the film.

CeO_2 and Gd-doped CeO_2 thin films are being prepared using cerium nitrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and gadolinium nitrate $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ for doped specimens. The appropriate concentrations of cations were added to ethylene glycol. After complete dissolution, the transparent solution was heated to about 80°C and stirred for up to 72hrs until it turned

to a gelatinous polymeric liquid. By controlling the solution viscosity, the spin rate and the annealing temperature, oxide films with variable thickness and microstructure can be prepared on dense substrate. For this study, 5 – 30 depositions of a 2wt% precursor with the spin speed of 3000r.p.m were performed on sapphire substrates to yield a film thickness of about 0.1-0.6 μ m. The annealing temperature varied in the range of 400 – 1400°C. The microstructure and the phase stability of the thin films were characterized by SEM and XRD.

Scanning Electron Microscopy Analysis

Films of nanocrystalline CeO₂ were analyzed using a Hitachi S4700 field emission gun (FEG) and a high-resolution SEM analysis using 10kV acceleration voltage on carbon (graphite) coated samples. Grain size distribution was estimated from these SEM images using a computer software, NIH image.

XRD Characterization

X-ray diffraction data for thin film samples were collected using a SINTAG 2000 x-ray diffractometer operating with Cu K α 1 radiation. A typical 2 θ scan range of 20-80° and a step size of 0.05° were employed. The XRD spectra have been recorded in the off-set configuration to reduce the signal from monocrystalline substrate.

Conductivity measurement

The electrical conductivity of films has been studied by impedance spectroscopy using a Solartron 1260 frequency response analyzer with 1296 Interface. The impedance spectra are being obtained using a 2-probe measurement over the frequency range 1 Hz to 5 MHz. Silver is being applied as electrodes for these measurements. Excess film is scratched off

to make a contact to the cross-section of the film, where silver is applied. Measurements are being conducted in oxygen, air, helium and CO/CO₂ mixtures for the oxygen partial pressure range of 10^{-26} – 1 atm over the temperature range of 600 – 900°C.

3. Structure of CeO₂ and Gd-doped CeO₂ thin films

Figure 2 shows the SEM surface and cross section images of CeO₂ thin films with annealing temperature of (a) (b) 600 and (c) (d) 1400°C for 4hrs. Film thickness is around 0.3μm. Very uniform texture is seen in 600°C annealed sample. On the other hand, a 1400°C sample in Fig. 2 (c) displays uneven grain distribution with neck growth. From cross section image, the necks seem to be the results of grain's pulling each other. It is observed the disappearance of smaller grains and grain's isolation at higher annealing temperature, where the grain size exceeds the film thickness. The relation between the thickness of film and the grain's isolation was well studied theoretically by Miller *et al.* [9]. The grain size distribution of CeO₂ at $T_a = 600^\circ\text{C}$ is shown in Fig. 3. As can be seen, more than 90% of grains are in $10\pm 4\text{nm}$, which shows high uniformity of grain distribution.

Figure 4 displays the effect of annealing temperature on the grain size. The results show that the grain size reaches to the stable grain size within 4hrs. Figure of the grain size as a function of film thickness is inserted of Fig. 4. It is observed little influence of film thickness on the grain size in the range of 100nm-1μm film thickness. These results indicate that stable microstructures can be obtained by the polymeric precursor spin coating technique.

Figure 5 shows the XRD patterns of CeO₂ and Gd-doped CeO₂ specimens (10%Gd, 20%Gd) annealed at different temperatures. All samples were annealed for 4hrs. As can be seen, (111) and (200) peak patterns show the same tendency that no preferential orientation

at lower temperatures and the (111) line, which is the most intense for the fluorite structure, begins to decrease while at the same time the (200) line increases. These observations show out-of-plane (perpendicular to the substrate) orientation of the film with (200) preferential orientation. Only difference is that this transition shifts higher temperature as the amount of dopant increases.

Analysis of the shape of XRD lines has been used to determine the grain size (d_g) and the strain ($\Delta d/d$) for each specimen [10]. As can be seen in Fig. 6, the grain size strongly depends upon the annealing temperature and the presence of Gd. The grain size of Gd-doped CeO_2 is substantially reduced compared to that of undoped specimens. Evidently Gd influenced the grain growth kinetics either by pinning grain boundaries or perhaps changing thermodynamic factors such as the surface and grain boundary energies, γ_s , γ_{gb} , respectively. Similar behavior was previously reported in MgO doped Al_2O_3 that it was observed the reduction in the spread of the dihedral angles which leads to homogeneous microstructure, because of the presence of dopant [11]. Since the dihedral angles are determined from the ratio of γ_s/γ_{gb} , this could be an explanation of our results.

As shown in Fig. 7, specimens with smaller grain size are characterized by the higher amount of strain and no influence of dopant. From the observation of X-ray measurement, it is seen that the dopant restricts the grain growth of the thin film samples.

4. Electrical Conductivity of CeO_2 and CeO_2 :20%Gd thin films

The impedance spectra were analyzed to yield the high-frequency semicircle related conductivity, which is attributed to bulk conductivity for microcrystalline materials [12] and is superposition of bulk and grain boundary conductivity for nanocrystalline specimens [2, 3].

The equivalent diagrams which are used for the analysis of the impedance spectra for

nano- and microcrystalline materials are presented in Fig. 8.

Figure 9 shows impedance spectra of nanocrystalline $\text{CeO}_2:20\%\text{Gd}$ thin film for difference thickness from 110nm to 630nm. The grain size of these samples is 20nm, whose annealing temperature is 1000°C. As expected, it is observed only one semicircle, which is probably from bulk and grain boundary resistance. As thickness of the film (d) increased, it is observed the shrinkage of semicircle, which is proportional to $1/d$. The inserted in Fig. 9 shows the conductivity of each different thickness sample. Since all samples shows the same conductivity with the activation energy of $1.3 \pm 0.05\text{eV}$, there is no surface or interfacial current flow. The effect of electrode seems not to be appeared, probably because electrode resistance is small compared to sample resistance, which is related to large geometrical factor of samples.

The measurements of electrical conductivity as a function of oxygen partial pressure and temperature provide the information about the type of conductivity and thermodynamic parameters of the defects. The results of this study are interpreted by the model as shown below. Assuming that only ionic and electronic conductivity (σ_i and σ_e) exist and that they are controlled by the oxygen vacancy and electron concentration, respectively, then the expression for total conductivity is given by

$$\sigma_t = \sigma_i + \sigma_e = a + bP_{\text{O}_2}^{-r} \quad (1)$$

where

$$a = \frac{\sigma_{i0}}{T} \exp\left(-\frac{E_i}{kT}\right) \quad (2)$$

and

$$b = \frac{\sigma_{e0}}{T} \exp\left(-\frac{E_a}{kT}\right). \quad (3)$$

P_{O_2} , E_i , E_a , are the oxygen partial pressure, the activation energy for ionic conductivity and the activation energy for electronic conductivity, respectively. σ_{i0} and σ_{e0} are temperature independent constants.

Ionic defects for Gd-doped ceria can be introduced by the reaction as follows,

where Eq. 4 and 5 show the intrinsic and extrinsic reactions for oxygen vacancy, respectively. The electroneutrality relation here is given by

$$2[V_O^{\cdot\cdot}] = n + [Gd'_{Ce}] \quad (6)$$

where $[Gd'_{Ce}]$ is concentration of Gd (acceptor dopant) at the position of Ce.

The stoichiometry is determined by Eqs. 4 and 5 and the temperature dependence of the equilibrium constant for Eq. 4 is given by

$$K_R(T) = K_R^0 \exp(-\Delta H/kT) = [V_O^{\cdot\cdot}] n^2 P_{O_2}^{1/2} \quad (7)$$

where ΔH is the enthalpy for oxygen vacancy formation.

Overall conclusion of this model is when the extrinsic region ($[Gd'_{Ce}] = 2[V_O^{\cdot\cdot}]$) is dominant, the conductivity vs. P_{O_2} exhibits platou at higer P_{O_2} region and the power relationship with the slope of $r = 1/4$ at reduced atmosphere and E_a can be given as

$$E_a = \frac{\Delta H}{2} + E_h, \quad (8)$$

where E_h is the hopping energy which is related to the mobility of electron [13].

When the intrinsic region ($n = 2[V_O^{\cdot\cdot}]$) is dominant, the $\log_{10} \sigma$ vs $\log_{10} P_{O_2}$ relationship should follow the slope of $r = 1/6$ and temperature dependence of the conductivity

gives an activation energy equal to

$$E_a = \frac{\Delta H}{3} + E_h, \quad (9)$$

Details about this model are discussed elsewhere [8].

Figure 10 shows the electrical conductivity of (a) CeO_2 ($d_g = 30\text{nm}$) [8] and (b) $\text{CeO}_2:20\%\text{Gd}$ ($d_g = 36\text{nm}$) thin films as a function of P_{O_2} and temperature. As can be seen in Fig. 10(a), the electrical conductivity of CeO_2 sample is independent with P_{O_2} at high P_{O_2} , follows $P_{\text{O}_2}^{-1/4}$ behavior at low P_{O_2} at lower temperature. This behavior is considered to be related to impurities which behave as acceptors. As increasing temperature, the transition from $P_{\text{O}_2}^{-1/4}$ to $P_{\text{O}_2}^{-1/6}$ behavior is observed. The $P_{\text{O}_2}^{-1/6}$ relationship corresponds to the intrinsic charge compensation, $n = 2[V_{\text{O}}^{\bullet}]$. In Fig. 10(b), on the other hand, it showed the electrical conductivity of $\text{CeO}_2:20\%\text{Gd}$ sample is independent with P_{O_2} at high P_{O_2} , follows $P_{\text{O}_2}^{-1/4}$ behavior at low P_{O_2} at all temperature.

The results in Fig. 10 were used to determine a and b in Eq. 1, which are the electronic and ionic conductivity at $P_{\text{O}_2} = 1\text{atm}$, for both undoped and doped ceria samples. Figure 11 shows the temperature dependence of the electronic conductivity of CeO_2 thin films determined for different grain size specimens at $P_{\text{O}_2}=1\text{atm}$ [8]. It is observed that the electronic conductivity increases and activation energy decreases as the grain size d_g decreases. The discontinuity observed for the 30nm grain size sample is related to the transition seen in Fig. 10(a).

Figure 12 shows the temperature dependence of the ionic conductivity of $\text{CeO}_2:20\%\text{Gd}$ thin films determined for different grain size specimens at $P_{\text{O}_2}=1\text{atm}$. It is observed that the ionic conductivity increased as grain size decreased with decreasing the activation energy. The activation energy in the ionic conductivity is equal to the one of the ionic mobility.

Therefore, the grain boundary region in nanocrystalline specimens becomes favorable for ionic conduction. This could be related to the segregation of impurities at the increased grain boundary area when the grain size decreased [14].

The enthalpy of oxygen vacancy formation ΔH for CeO_2 and $\text{CeO}_2\text{:20\%Gd}$ was also calculated using the relation shown in Eq. 8 and 9, assuming an electron hopping energy of $E_h = 0.4\text{eV}$ [13] for CeO_2 samples and $E_h = 0.52\text{eV}$ [15] for $\text{CeO}_2\text{:20\%Gd}$ samples. Figure 13 shows ΔH for CeO_2 and $\text{CeO}_2\text{:20\%Gd}$ as a function of grain size, including previous results reported by Hwang [16] (CeO_2 , $d_g=15\text{nm}$) and Lübke [17] ($\text{CeO}_2\text{:20\%Gd}$, $d_g \sim 3\mu\text{m}$). It is seen that ΔH of CeO_2 decreases for grain size less than 100nm, which implies greater deviation from stoichiometry, which in turn increases the electrical conductivity. The values of ΔH determined for greater than 100nm grain size specimens agree with the value reported for single crystal CeO_2 , which was reported as $\Delta H=4.67\text{eV}$ [18]. Unlike CeO_2 samples, $\text{CeO}_2\text{:20\%Gd}$ samples showed little change of ΔH with microstructure. This may be related to the fact that oxygen vacancies exist sufficiently because of dopant and this somehow affects the equilibrium reaction in Eq. 4.

5. Summary

The results of a study related to the formation and the microstructure of CeO_2 and Gd-doped CeO_2 thin films obtained by a polymeric precursor spin coating technique have been presented. The dopant effect is significant and shows restraining of grain growth and texture. The films show very uniform grain distribution and highly stable microstructure. The electrical conductivity of CeO_2 and $\text{CeO}_2\text{:20\%Gd}$ is influenced by materials microstructure. The transition from extrinsic to intrinsic type of conductivity is observed for 30nm grain size CeO_2 specimen at elevated temperature, while for $\text{CeO}_2\text{:20\%Gd}$ conductivity

has extrinsic character in all investigated grain size regions temperatures. The enthalpy of oxygen vacancy formation, ΔH , as a function of grain size has been determined. The reduction in ΔH has been observed for CeO_2 specimens from 4.67eV to 1.77eV, which leads to increase about 4 order of magnitude in the electronic conductivity. For $\text{CeO}_2\text{:20\%Gd}$ ΔH does not change with the grain size and equals to 3.9eV. The increase of ionic conductivity in $\text{CeO}_2\text{:20\%Gd}$ was observed as grain size decrease. This can be explained by the reduction of the activation energy, which is related to the ionic mobility.

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FIGURE CAPTION

Figure 1: The polymeric precursor spin coating technique.

Figure 2: SEM images of CeO_2 thin film on sapphire substrate. All samples are annealed for 4hrs. (a) annealed at 600°C (surface) (b) 600°C (cross section) (c) 1400°C (surface) (d) 1400°C (cross section).

Figure 3: Grain distribution of CeO_2 thin films ($T_a = 600^\circ\text{C}$.)

Figure 4: Grain size as a function of annealing time for $\text{CeO}_2\text{:Gd}$ thin films. Inserted figure shows the film thickness dependent of grain size.

Figure 5: X-ray diffraction patterns ((111) and (200) directions) of $\text{CeO}_2\text{:Gd}$ thin films deposited on sapphire substrate with different annealing temperature.

Figure 6: The relationship between grain size and annealing temperature.

Figure 7: The relationship between strain and grain size.

Figure 8: Example of impedance spectra for (a) microcrystalline (b) nanocrystalline materials.

Figure 9: Impedance spectra of nanocrystalline $\text{CeO}_2\text{:20\%Gd}$ thin film (grain size 20nm) for different film thickness. Inserted figure: the electrical conductivity as a function of temperature.

Figure 10: The electrical conductivity of (a) CeO_2 (grain size 30nm) and (b) $\text{CeO}_2\text{:20\%Gd}$ (grain size 36nm) thin films as a function of oxygen partial pressure and temperature.

Figure 11: Temperature dependence of the electronic conductivity determined for CeO_2 as function of grain size.

Figure 12: Temperature dependence of the ionic conductivity determined for $\text{CeO}_2\text{:20\%Gd}$ as function of grain size.

Figure 13: The enthalpy of oxygen vacancy formation of CeO_2 and $\text{CeO}_2\text{:20\%Gd}$ thin films [16, 17].

(a) surface $T_a=600^{\circ}\text{C}$

(c) surface $T_a=1400^{\circ}\text{C}$

(b) cross section $T_a=600^{\circ}\text{C}$

(d) cross section $T_a=1400^{\circ}\text{C}$

$\text{CeO}_2\text{:Gd}$

Thin film on sapphire substrate

X-ray Intensity

Microcrystalline materials

Nanocrystalline materials

Task 2.2: Preparation of Graded Porous Substrates

2.2.1: YSZ/CeO₂/LSM

A. B. Gorman, *“Preparation and Characterization of Colloidal CeO₂ Films Impregnated by (La, Sr)(Co, Fe)O₃----(LSCF) on Sapphire”*

Thin films of La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3- δ} (LSCF) were prepared using a polymeric precursor spin-coating technique. La₂(CO₃)₃ and SrCO₃ were dissolved in dilute nitric acid with distilled water, and Co(NO₃)₃ and Fe(NO₃)₃ were dissolved in distilled water, all of which were standardized thermogravimetrically in air to 1000°C in order to determine the actual cation contents in the solutions. In the cases of the Co and Fe transition metal solutions, XRD was used in order to determine which oxide was formed at the elevated temperature.

Cation source solutions were weighed out according to their stoichiometric ratios. A molar ratio of 0.05 cations to ethylene glycol was used, and the sources mixed with the corresponding amount of ethylene glycol (typically 40ml). 2mL of nitric acid was added per 20ml of ethylene glycol, in order to start the condensation polymerization reaction. The final solution of cations, ethylene glycol, and nitric acid was heated and stirred at 70°C for 40 hours, resulting in a dark red, precipitate free precursor with a viscosity of 160cps as determined using a Brookfield viscometer and a small sample adapter. Thermogravimetric analyses (Cahn TG-1) were carried out in order to determine the concentration of oxide in the precursor, the pyrolyzation temperature of the precursor, as well as any oxide phase changes at elevated temperatures.

Thin films of LSCF were spin-coated on clean, polished, (100) Si substrates at 4000rpm for 30 seconds. The wet films were dried at 70°C for about an hour and pyrolyzed at 350°C for about 15 minutes. Subsequent films could then be deposited on the oxide surface using the same deposition technique. XRD was utilized in order to determine the phase formation of the LSCF films as a function of annealing temperature.

CeO₂ / LSCF thin film composites were fabricated by spin coating the LSCF precursor on the CeO₂ films prepared previously at 800°C. It was found that the LSCF precursor viscosity of 160cps was too high to penetrate the full thickness of the CeO₂ films, as determined by conductivity, Auger electron spectroscopy and FESEM. Subsequently, the precursor solution was diluted using 20 volume% ethanol, which was added to the precursor and stirred for 4 hours at room temperature. Ethanol serves as a molecular weight inhibitor in polyethylene glycol based solutions if it is chemically bonded to the polymer chain. It also serves to decrease the precursor viscosity if it simply stays in solution as a solvent. In this study, the ethanol addition decreased the LSCF precursor viscosity to 50cps, which allowed the precursor to dissolve through the thickness of the CeO₂ film.

LSCF films were deposited from the diluted precursor onto the CeO₂ thin films at 3000rpm for 30 seconds. Before spinning the precursor, the solution was allowed to soak through the CeO₂ film for 1 minute. The wet films were dried at 70°C for 2 hours and pyrolyzed at 350°C for 1 hour, after which subsequent films could be deposited.

The LSCF / CeO₂ composite thin films were characterized according to their electrical properties both across the plane of the film, and well as through the thickness in order to give some insight as to the composite structure. Planar DC electrical conductivity measurements were done in a 4-probe configuration similar to that detailed by van der Paaw. Ag paste (Ferro, Inc.) was used for the 4 electrode contacts on the surface of each 1cm² thin film composite on the sapphire substrates. The contacts were painted on, attached to Pt wire leads, and annealed at 600°C for 1 hour. Current-voltage characteristics of each sample were taken on a Solartron 1260 impedance analyzer which was connected to a personal computer. All measurements reported were found to be in the ohmic regime.

Thickness mode DC measurements were taken from the composite films fabricated on platinized Si as described earlier in the CeO₂ film case. Following electrical characterization, the composite films on sapphire were characterized microstructurally by FESEM. As-deposited surfaces and fracture cross sections were mounted using double-sided carbon tape and coated with evaporated carbon in order to make the samples conductive. Auger electron spectroscopy along with sputter profiling was also done in order to determine the concentration of LSCF throughout the composite thickness.

RESULTS

- **LSCF Films**

Figure 1 is a set of TGA/DTA curves for the LSCF precursor using a ramp rate of 2°C/min. Ultimately, the concentration of oxide in the precursor is 12wt%, which is fairly constant above 200°C. There is only one burnout step in the TGA curve, which is consistent with the existence of only polyethylene glycol as the organic content in the precursor. At temperatures greater than 100°C, some weight loss is observed due to the presence of water in the precursor (used as the solvent in this system). In other precursor systems containing ethylene glycol as well as larger organic molecules such as citric or tartaric acid, two burnout steps are observed, corresponding to the PEG burnout followed by the larger organic molecules. The DTA curve correlating to the TGA curve shows a dramatic exothermic spike at the burnout temperature, which is related to the gaseous carbon compound formations.

Figure 1: LSCF precursor in EG - DTA

A ramp rate of 2°C/min may induce errors in this burnout temperature measurement due to thermal lag in the sample as well as due to the slow burnout of the organics. Thus, a ramp rate of 0.5°C/min, along with a more sensitive microbalance (Cahn TG-1) was used to find more exactly the burnout temperature of the precursor. A sample of the precursor was dried externally at 90°C for 12 hours in order to rid the sample of most of the solvent, and this solid polymer was used in this part of the investigation. As seen in figure 2, the actual burnout temperature of the precursor is 175°C, a difference of approximately 25°C compared with the full precursor solution at the higher ramp rate.

Figure 2: TGA – LSCF 2080 precursor dried out 90°C TGA – 0.5°C/min.

XRD studies of the LSCF films deposited on Si substrates showed that after annealing the films at 350°C, a mixture of phases is present, including La_2O_3 and a Co-Fe oxide. The peaks are very broad, corresponding to a very small grain size, which makes interpretation of the spectra difficult. Annealing the samples at 600°C facilitates the formation of the full perovskite phase. The spectra taken for the sample annealed at 800°C shows the formation of FeSiO_4 , a result of the interaction between the thin film and substrate at this elevated temperature.

FESEM examination of an LSCF film deposited on sapphire and heat treated at 600°C shows that a single deposition of LSCF results in a film of 0.3 μm thickness (figures 3&4). It is also qualitatively apparent that the film is highly dense. Surface images of the same sample also show that the film is highly dense, crack-free, and only a few small defects are present due to dust particles present in the air around the wet film.

4-point conductivity studies of the LSCF film on sapphire substrate is shown in figure 5. The conductivity of this film correlates well with values measured previously, with an activation energy of 0.18eV at low temperatures, and leveling off near 600°C.

DC conductivity measurements through the thickness of the composite films deposited on platinized Si substrates shows that the LSCF forms a continuous phase through the thickness of the film after only one deposition. Increases in the conductivity with subsequent depositions are related to the increase in LSCF concentration parallel to the film thickness (i.e. filling of the porosity in the film).

Figure 3

Figure 4

DC conductivity measurements measured parallel to the thickness of the composite films deposited on sapphire substrates are shown in figure 6. As expected, the conductivity of the films increases with concentration of LSCF. However, the literature suggests that the concentration of LSCF in these films should be below the percolation limit of 36% CGO in bulk LSCF. The increase in conductivity to near that of the percolation threshold can be related to the formation of a continuous LSCF film on the surface of the CeO₂ film, as evidenced by both FESEM and Auger depth profiling.

Figure 5: LSCF 2080 thin film on sapphire conductivity.

Figure 6: Conductivity parallel to surface vs. temperature – CeO_2 / LSCF thin film as a function of LSCF concentration.

FESEM studies of the film fracture cross sections are shown in figure 7. As can be seen, the film is continuous and no cracking of the film occurs as a result of the LSCF impregnation. Also visible in the micrograph is a small film of LSCF impregnation. Also visible in the micrograph is a small film of LSCF on the surface of the composite. The thickness of this film is observed to be approximately $0.05\mu\text{m}$. Accounting for this surface film in the optical data leads to a concentration in the film of 8% leading to a porosity of 17%.

Figure 7

The surface view of these composites illustrate that the film is continuous parallel to the film, thus leading to an increase in electronic conductivity in this dimension (see below), while still allowing gas to diffuse to the three-phase boundary, and thus further increasing the efficiency of these films as electrodes.

Figure 8 illustrates Auger electron spectroscopy depth profiling for the 4 deposition LSCF / CeO₂ composite films. As can be see, the LSCF forms a small surface thickness layer (similar to that seen in the FESEM images), and has fairly constant concentration through the thickness of the films. Correlating well with the results obtained through optical spectroscopy, the concentration of the LSCF increases with multiple depositions.

Figure 8: Auger electron spectroscopy depth profile of a 4 deposition LSCF / CeO₂ composite thin film.

The use of these composites as cathodes in solid oxide fuel cells are expected to exhibit low interfacial resistance due to an increase in three phase boundary (tpb) length as mentioned earlier. The presence of LSCF through the thickness of the composite should not only add to the tpb length due to the mixed conductivity of the material itself, but also due to the addition of electrons to the reaction at the CeO₂ surfaces, while preserving the porosity of the films.

In order for these films to be applicable as fuel cell electrodes, however, these composites must be able to be processed on porous substrates. Using a much lower spinning speed for colloidal CeO₂ films on porous lanthanum manganite, processing of these composites on highly porous substrates is possible (figure 9). Processing of these films on rough, tape-cast YSZ electrolytes is also possible using this technique, as seen in figure 10.

Figure 9

Figure 10

CONCLUSIONS

Over the course of the past year, several investigations into the processing and characterization of SOFC anodes and cathodes were conducted. The conductivity of high purity CeO_2 thin films with varying porosity and grain size in the nanocrystalline regime was studied. Results from conductivity and microstructural characterization show that the conductivity of porous thin films dominated more by porosity effects, and grain size effects typically seen in nanocrystalline CeO_2 were not observed.

CeO_2 / LSCF composite thin films were processed using a colloidal deposition of CeO_2 , followed by impregnation of the porous film with an LSCF polymeric precursor. The films have a high thickness-mode conductivity after only a single deposition of LSCF, leading to the fact

that the LSCF is penetrating the full thickness of the porous CeO_2 . The conductivity parallel to the surface of the films increases with the number of LSCF depositions, even with LSCF concentrations less than the percolation limit. This is attributed to the increasing formation of a porous LSCF surface film. Processing of these structures on both porous and rough surfaces of LSM and YSZ illustrates the applicability of these films as cathodes in fuel cells.

2.2.2: FILMS ON $(\text{La,Sr})\text{MnO}_3$ ---(LSCF) POROUS SUBSTRATE

A. *Colloidal CeO_2 /LSM*

In the proceeding reports, we are showing the development of the CeO_2 layer. In this section, we report some of our recent results that were obtained by spin coating colloidal CeO_2 onto very porous LSM substrates. Figure 1 shows the structure of typical LSM substrates that were used in these studies. The techniques that were used for forming the film on the LSM is the same as that already described in the report so will not be discussed here.

(a) Top View

(b) Cross Section View

Figure 1. The microstructure of LSM substrate made by agglomerate sintering method.

Figure 2 and 3 show SEM images of a spin coated colloidal CeO_2 films on LSM substrates similar to that shown in figure 1. As can be seen the films are continuous and smooth the rough LSM surface very well. In previous studies we have found that in order to produce a surface which is smooth enough to coat with dense polymer precursor derived films, the required thickness of the colloidal film layer is determined by the maximum surface roughness. That is, if we wish to make 2 micron thick colloidal oxide layers, the roughness of the LSM surface can not exceed 2 microns.

Figure 2: Colloidal ceria planarizing layer. Cross section, medium resolution. Sintered at 600°C.

Figure 3: Colloidal CeO₂ porous (60% th. density) thin film on porous LSM substrate.

Currently, we are producing the composite CeO₂/LSM structures that can be coated with polymer precursor to produce 0.5 to 1.5 micron thickness dense YSZ films. In the next quarter, we will be testing SOFC's using these structures.

B. *YSZ/CeO₂/LSM*

Figure 1 shows a SEM image of the cross-section of a YSZ/CeO₂/LSM composite which has been annealed at 800°C. Our studies show that the YSZ films are very dense with a 20 nm grain size.

Figure 1: Field-emission SEM micrograph of a YSZ/Colloidal CeO₂/spray-pyrolized LSM composite. CeO₂ = 5μm, YSZ = 0.5μm.

SOFC's using these composites are being fabricated and we expect to obtain cell data during the next quarter. As we reported in November 2000, we have had difficulties in making pore free films with larger areas that about 0.2cm² which is due to problems in our clean room. Modifications have now been completed on the clean room and we should be approaching a class 100 in the film making area. This level of cleanliness is sufficient to obtain films without pores over areas up to 100cm².

Task 2.3: Basic Electrical Characterization and Testing of Planar Single Cells

INTRODUCTION

This report includes a brief summary of past results, and the current areas we are working in. Solid oxide fuel cells (SOFC) offer several advantages over current electrical power generation technology. They are more efficient, give off less pollution, and have the potential to be more reliable and less expensive. Currently fuel cells operate at 1000°C. Decreasing the temperature to 800°C or below should allow metals to be used to for the interconnect, thereby reducing cost, increasing durability, and extending service life.

As the operating temperature of fuel cells is reduced the kinetics of the reactions at the electrodes become an important source of energy losses. In this research SOFC electrodes are studied under different temperatures and gases.

EXPERIMENTAL PROCEDURE

ELECTROLYTE

Tape casting was used to create a 40µm thick, self-supporting, electrolyte. The electrodes were applied by screen printed onto the dense electrolyte. Commercially available 8 mole percent YSZ (Zirconia Sales of America), with a primary particle size of 0.25µm and a BET surface area of 8.0 m²/g, was used to fabricate the electrolyte. The YSZ powder was dried at 150°C for at least 24 hours to remove any absorbed water. It was then mixed with a tapecast binder and solvent system from Ferro Corp, B73210, and ball milled for 24 hours. The slurry was then slow rolled for at least 24 hours to remove any trapped air. Next, the slurry was tapecast onto a glass surface with a doctor blade height of 130µm and a casting speed of 1cm/s. After the tape dried, a platinum reference electrode was screen printed on the tape while it was still on the glass. Another layer of YSZ was then cast at the same speed on top of the first with a doctor blade height of 140µm. The tape was then removed from the glass and punched out into 4.44cm circles. Next, it was sintered at 1450°C for one hour with $\approx 0.16\text{g/cm}^2$ weight on top of it to prevent warping. All electrolytes used in this study were 40 µm thick after firing.

CATHODE

LSCF and LSM powders were synthesized by the glycine nitrate technique. Thermogravimetrically standardized cation sources were dissolved in water and nitric acid. The amino acid glycine is added to the solution to complex with the metal ions to prevent precipitation, and act as a fuel during charring. When the solution is heated about to 180°C the glycine will auto-ignite. Temperatures reach 1100 to 1450°C and the mixture is converted into fine, unagglomerated powder. The powders were then mixed with Ferro Corp's BX018-16 resin to make a screen printable paste. The paste was then screen printed on the electrolyte and fired at temperatures ranging from 800 to 1200°C forming the cathode.

ANODE FABRICATION

CuO and NiO powders were synthesized by the glycine nitrate technique, as described above. These powders were then mixed with $\text{CeO}_2\cdot 20\%\text{Gd}$. Again the powders are mixed with Ferro's resin to make a paste, which is then screen printed on the opposite side of the electrolyte, and fired at temperatures ranging from 700 to 1300°C. The oxide powders will be reduced insitu. Next, platinum or silver current collectors are screen-printed to form a grid pattern on each electrode. A SEM image of a cross section of a fuel cell is shown in figure 1.

Figure 1

SUPPORTS

To provide structural integrity 350 μ m supports were tape cast and fired at 1450°C. Platinum pads, which will be used to make electrical connections, were painted on the supports using Platinum paste (Ferro Corp). The paste was then used to bond platinum wires to the pads. The supports were then fired to 1250°C to sinter the platinum. The supports and wires were then connected to the electrolyte using silver paste (Ferro Corp), which was then fired to 700°C, see figure 2.

Figure 2

SAMPLE MOUNTING

Mullite rings were superglued to the supports, and then cemented to the mullite tubes using Aremco cement #503, see figure 2 and 3. Platinum wire, inside an alumina thermocouple tube, was used to make electrical contact to the platinum pads on the cathode side. Nickel wire was used on the anode side. The mullite tubes were then mounted inside a silica tube furnace, see figure 4.

Figure 3

Figure 4

TESTING

The furnace is heated at a rate of $2^{\circ}\text{C}/\text{min}$ to the measurement temperature. Gas was then fed to the cell. The oxidant and fuel enter the mullite tube opposite the fuel cell. The gas travels down to the cell, and then out through a thermocouple tube. N_2 is used as the sweep gas, to remove any oxidant or fuel leaking out the inner tubes. Gas flow is controlled by four mass flow controllers, and monitored by ball flow meters. Air flowing at 200 sccm was used as the oxidant. Two different gases flowing at 200 sccm were used as the fuel. 97% forming gas (90% N_2 , 10% H_2) and 3% H_2O , and 97% methane (CH_4) 3% H_2O .

The fuel cell was equilibrated for at least one hour at the measurement temperature and atmosphere. Five point current-voltage measurements were then made at temperatures from 600 to 950°C . The reference electrode, inside the electrolyte, was used to separate the anode and cathode losses. An experimental diagram is shown in figure 5.

Figure 5

RESULTS

Cu-CGO Anode

The power density vs. current density for a Cu-CGO / YSZ / LSCF fuel cell using forming gas as a fuel is shown in figure 6. The $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ cathode was sintered at 1000°C , while the 40 v% Cu, $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ anode was sintered at 850°C for 4 hours. The fuel was 97% forming gas and 3% H_2O .

Figure 6 - Power density of a fuel cell using air as the oxidant and 97% FG 3% H₂O as the fuel. Cu - Ce_{0.8}Gd_{0.2}O₂ was used for the anode (40 vol. % Cu) and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ was used for the cathode.

The power density for the same cell, but now using 97% Methane 3% water as the fuel is shown in figure 7.

Figure 7 - Power density of a fuel cell using air as the oxidant and methane bubbled through water as the fuel. Cu - Ce_{0.8}Gd_{0.2}O₂ was used for the anode (40 vol. % Cu) and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ was used for the cathode.

The maximum power density vs. temperature for each fuel is shown in figure 8. The extra energy required to oxidize the methane reduced the maximum power density. However this reduction seems to be temperature insensitive. As the temperature was reduced the penalty for using methane didn't increase.

Figure 8 - Cu-CGO / YSZ / LSCF maximum power density vs. temperature for different fuels.

Using the reference electrode the losses for the anode at 800°C are shown in figure 9. The losses for methane were about 50mV higher than forming gas.

Figure 9 - Cu-CGO / YSZ / LSCF overpotentials at 800°C using methane and forming gas as fuels.

Ni-CGO Anode

The power density vs. current density for a Ni-CGO / YSZ / LSM fuel cell using forming gas as a fuel is shown in figure 10. The $\text{La}_{0.7}\text{Sr}_{0.2}\text{MnO}_3$ cathode was sintered at 1200°C, while the 40 v% Ni, $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ anode was sintered at 1300°C for 4 hours. The fuel was 97% forming gas and 3% H_2O .

Figure 10 - Power density of a fuel cell using air as the oxidant and 97% FG 3% H_2O as the fuel. Ni - $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ was used for the anode (40 vol. % Ni) and $\text{La}_{0.7}\text{Sr}_{0.2}\text{MnO}_3$ was used for the cathode.

The anode overpotentials of the nickel and copper anodes at 800 and 850°C are compared in figure 11, and 12. Initially the overpotentials are equal, while at higher currents the nickel overpotential is lower. This means that initially the Cu anode has enough reactive sites so that its losses don't dominate.

Figure 11 - Ni-CGO and Cu-CGO overpotential at 800°C using forming gas as the fuel gas.

Figure 12 - Ni-CGO and Cu-CGO overpotential at 850°C using forming gas as the fuel gas.

When Ni-YSZ anodes are exposed to methane carbon deposits form, causing the current density to decrease with time to zero. This didn't occur with this Ni-CGO anode. If the gas is switched to 97% methane the current decreases but doesn't decrease to zero, see figure 13.

Figure 13 - Ni-CGO / YSZ / LSM Cell Measurements at 800°C when switching from 97% FG to 97% Methane at $t=0$.

DISCUSSION

PRESENT WORK

IMPEDANCE OF ELECTRODE MATERIALS IN ONE ATMOSPHERE

In this research, different metal-ceramic composites are being studied as low temperature (500 to 800°C) SOFC anodes. Ni Cu, Mn, and Ag metals will be studied in combination with $\text{CeO}_2\text{:20\%Gd}$ or $\text{ZrO}_2\text{:16\%Y}$. Impedance spectroscopy will be performed on YSZ pellets using symmetric electrodes, and forming gas as a fuel.

IMPEDANCE OF ELECTRODE MATERIALS IN TWO ATMOSPHERES

One of the problems of the one atmosphere experiment is that accurate results are difficult to obtain in methane. Carbon deposits form at the reducing electrode. The reactions are no longer symmetric, and difficult to separate. Because of this we are also modifying the fuel cell testing system described above to allow us to measure the impedance of a fuel cell under operating conditions.

THIN FILM OVERPOTENTIALS

The five probe fuel cell with an internal reference electrode described above is excellent for temperatures above 800°C. However, as the temperature drops the electrolyte begins to dominate. To increase the accuracy of the low temperature measurements on YSZ electrolytes an electrode supported thin film electrolyte must be used.

Separating the electrode loses becomes more difficult in electrode supported cells. An external reference electrode can be included opposite the supporting electrode but including this electrode increases the difference in the area of the anode and cathode, see figure 14. This area mismatch increases the uncertainty of the true current density.

Figure 14

We are currently developing a new cell design shown in figures 15, and 16.

Figure 15

$$\eta_{\text{Anode}} = V_{\text{RA}} - V_{\text{A}}$$

$$\eta_{\text{Cathode}} = V_{\text{RC}} - V_{\text{C}}$$

$$\eta_{\text{Electrolyte}} = V_{\text{RA}} - V_{\text{A}}$$

Figure 16

Because the support for the cell is made of YSZ the reference electrode can be located on it. This design allows accurate overpotential measurements without increasing the mismatch of the electrodes.

Appendix

Papers Presented or Submitted for Publication

Appendix A

“Influence of Microstructure on the Nonstoichiometry in
Ceria and Zirconia Thin Films”

Harlan U. Anderson, Toshio Suzuki and Igor Kosacki
University of Missouri-Rolla

Invited Paper at The International Symposium on Defects, Transport
And Related Phenomena is held in conjunction of the
103rd American Ceramic Society Meeting
Indianapolis, IN
April 22-25, 2001

Invited Paper

The International Symposium on Defects, Transport and Related Phenomena is held in conjunction of the 103rd American Ceramic Society Meeting in Indianapolis, April 22-25, 2001.

INFLUENCE OF MICROSTRUCTURE ON THE NONSTOICHIOMETRY IN CERIA AND ZIRCONIA THIN FILMS

Authors: Harlan U. Anderson, Toshio Suzuki and Igor Kosacki

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Over the last several years the electrical properties of both ceria and zirconia have been widely studied in our research laboratory. The motivation of these studies has been to increase our understanding of these materials to hopefully enable us to operate solid oxide fuel cells within the 600 to 800 C range.

This presentation discusses several of these investigations related to the electrical and optical properties of thin films (0.3 to 2 micron thick) and bulk specimens of both pure and acceptor doped ceria and zirconia were studied as function to temperature, oxygen activity and microstructure. The results show that in addition to being sensitive to temperature and oxygen activity, the electrical conductivity and defect structure are influenced by the grain size of the particular oxide. Essentially what it shows is that the nonstoichiometry may be modified by either microstructure or dopant level, which in turn results in changes in either the electronic or ionic conductivity. For example, at 600 C, 16m%Y-ZrO₂, (YSZ) shows such a strong grain size dependence that the ionic conductivity of 20nm grain size is >an order of magnitude higher than that of the same composition with 2 micron grain size which is due to increased ionic mobility. Whereas the electronic conductivity of undoped ceria when the grain size decreases below 50 nm, due to reduction in the defect formation enthalpy.

An attempt will be made to correlate the results of a number of different experimental techniques such as XRD, SEM, EXAFS, Raman Spectroscopy, TEM and electrical conductivity to give a coherent picture of the relationships between microstructure, stoichiometry, optical and electrical properties.

Appendix B

“Raman Spectroscopy of Nanocrystalline Ceria and Zirconia Thin Films”

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University of Missouri-Rolla

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102nd Annual American Ceramic Society Meeting
St. Louis, MO
April/May, 2000

RAMAN SPECTROSCOPY OF NANOCRYSTALLINE CERIA AND ZIRCONIA THIN FILMS

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ABSTRACT

The results of Raman scattering studies of nanocrystalline CeO_2 and $\text{ZrO}_2:16\%\text{Y}$ (YSZ) thin films are presented. The relationship between the lattice disorder and the form of the Raman spectra is discussed and correlated with the microstructure. It has been shown that the Raman line shape results from phonon confinement and spatial correlation effects and yields the information about material non-stoichiometry and impurity level.

INTRODUCTION

One of the most important aspects of the study of nanocrystalline materials is the ability to enhance their properties by controlling the microstructure. A number of studies have shown that materials with the grain size less than 100nm exhibit optical, electrical, catalytic and mechanical properties that are different than those observed for conventional microcrystalline specimens [1-5]. Such effects have been recently reported for YSZ and CeO_2 specimens, which are important for their electrochemical properties with a variety of applications including gas sensors, fuel cells and ionic membranes. The study of those nanocrystalline oxides showed that their electrical transport is attributed to grain boundaries whose volume can be controlled by the grain size [3,4,6,7].

Direct comparison has been achieved between the electrical conductivity of single crystal, micro- and nanocrystalline YSZ [3,4,8]. The results show that nanocrystalline specimens typically have ionic conductivity (at 600°C) that is about two orders of magnitude higher than that observed for microcrystalline specimens of the same material and this enhancement is attributed to changes in

the ion mobility [6,8]. Nanocrystalline CeO_2 is an example of a material in which the microstructure can influence the electronic conductivity because as the grain size decreases in the nanocrystalline region, the enthalpy of oxygen vacancy formation decreases which implies greater non-stoichiometry consistent with the enhanced electronic conductivity observed for nanocrystalline specimens [7-9].

Since the defect formation in nanocrystalline materials is controlled by the microstructure, it can also influence the dynamical properties, which are sensitive to lattice disorder and are extremely important due to its influence on the ionic conductivity. From this point of view, Raman spectroscopy, which yields information about the interaction between the ions can be very helpful in the study of the microscopic nature of nanocrystalline materials.

In ideal crystals, due to the infinite spatial correlation length of the phonons, the first order Raman scattering spectrum is characterized by $q = 0$ for the momentum selection rule, which results in the presence of phonon modes from the center of Brillouin zone. However, since the crystalline perfection is influenced by impurities or lattice disorder, the phonon functions become spatially confined which may lead to changes in the shape and frequency of the Raman lines and also the presence of the symmetry forbidden modes [10].

In this paper the results of a study of the dynamical properties of CeO_2 and YSZ in the form of sintered disks and thin films by Raman spectroscopy are presented. These materials were selected as an example of systems, which show both intrinsic (CeO_2) and extrinsic (YSZ) type of the electrical conductivity. The objective of this study was to determine the influence of microstructure and crystalline quality of specimens by analysis of the Raman spectra. This analyze provides the ability to determine the lattice defect concentration which is related to the non-stoichiometry and/or impurity level of the specimens. The relationship between these measurements and oxygen vacancy concentration estimated from the electrical conductivity will be also discussed.

EXPERIMENTAL

Dense nanocrystalline CeO_2 and YSZ thin films were prepared on sapphire substrates using a polymeric precursor spin coating technique reported in detail elsewhere [3-5,8]. This process allows the preparation of the oxides from a precursor, which can be converted to dense oxide films by spin coating, drying and crystallizing at temperatures in the range of 300-1200°C. Such low temperatures compared to those typically required by normal powder processing techniques (1400-1800°C), allow the formation of dense nanocrystalline specimens. For this study CeO_2 and YSZ film with the thickness in the range of 0.4-0.7 μm have been deposited on sapphire single crystal substrates.

The crystallinity, integrity and phase purity obtained specimens were investigated by x-ray diffraction and electron microscopy. The microstructure of a

particular film is characterized by very uniform and narrow distribution of grain size whose average size ranges from 4 to 330nm depending upon the annealing temperature.

The Raman spectra were recorded at room temperature using a Lille XY spectrograph equipped with a Spex CCD detector (2000x800 pixels). Spectra were recorded in the micro-configuration with the laser beam impacting a region of about 1µm in diameter. The excitation source was the 514.5nm line of an argon laser at the power level of 5mW.

RESULTS AND DISCUSSION

Fig.1 shows the Raman spectra of nanocrystalline CeO₂ films compared with the spectrum for a bulk single crystal. The Raman-active mode corresponds to the frequency of $\omega_R = 466\text{cm}^{-1}$ and is attributed to a symmetrical stretching mode of the Ce-O8 octahedron vibrational unit. Therefore, this mode should be very sensitive to any disorder in the oxygen sublattice resulting from thermal, doping, or grain size induced effects. The influence of the microstructure of CeO₂ on the shape of Raman spectra was observed by the broadening of the line and increases in its asymmetry which are attributed to the reduction of the phonon life-time in the nanocrystalline regime [10,12,13]. The Raman line broadening of CeO₂ can be described by the dependence of the half width upon the inverse of grain size, which follows a linear behavior $-\Gamma(\text{cm}^{-1}) = 10 + 124.7/d_g(\text{nm})$ [4,11]. These data are in good correlation with results reported for nanocrystalline powder specimens [12].

Important information regarding the lattice disorder can be obtained from the analysis of the shape of the Raman line, which has been performed using a spatial correlation model [13,14]. This model was proposed to describe the crystalline quality by introducing a parameter called the coherence length, which is defined as the average size of the region of material homogeneity and was first applied to describe the Raman line shape for implanted GsAs [13]. According to this model, the Raman line intensity, $I(\omega)$ at the frequency, ω can be written as:

$$I(\omega) = \int_0^1 \exp\left(\frac{-q^2 L^2}{4}\right) \cdot \frac{d^3 q}{[\omega - \omega(q)]^2 + \left(\frac{\Gamma_0}{2}\right)^2} \quad (1)$$

where q is the wave vector expressed in units of $2\pi/a$ (a is the lattice constant). Γ_0 is the half width of the Raman line determined for an ordered specimen. The expression of $\exp(-q^2 L^2/4)$ represents a Gaussian spatial correlation function with parameter L as the coherence length, and $\omega(q)$ is the function of Raman phonon

dispersion. This function has been determined for CeO_2 based on a rigid-model calculation [12] and was used in the current analyze.

Fig.1 Raman spectra of single crystal and nanocrystalline CeO_2 together with the curve fit according to the spatial correlation model (Eq.1, solid lines).

Fig.1 shows the Raman spectra for different grain sized CeO_2 and the corresponding line-shape fit performed using the spatial correlation model, (Eq.1). As can be seen this model correlates well with the experimental data when the microstructure of CeO_2 is changed from single crystal to the nanometer range.

Note that this procedure used only one fitting parameter, which is the phonon coherence length. Therefore, the disorder induced by the microstructure could be well defined by the coherence length. Fig.2 presents the relationship between the so determined coherence length and the grain size of the CeO₂ specimens. As can be seen, the coherence length is not microstructural dependent when the grain size is larger than 100nm and equals 10.5nm (20 lattice constants). The observed behavior illustrates the limit above which line broadening and asymmetry are not detectable. Note that for the specimens with grain size larger 150nm, the Raman line is practically the same as that of a single crystal (Fig.1).

Fig.2 The coherence length as a function of the grain size of nanocrystalline CeO₂ thin films. Dashed line is the coherence length estimated from spherical model.

When the grain size is smaller than 100nm, the coherent length decreases rapidly and equals 1.1nm for a 4nm grain sized specimen (2 lattice constants). Such large changes can be attributed to the grain boundary phase whose volume increases with decreasing grain size. The observed behavior can be described by the model in which the fraction of atoms on the surface of each grain was considered [11,15]. Assuming spherical symmetry of the grains and molecules, the coherence length should depend upon the 1/3 power of the grain size - $d_g^{1/3}$. Fig.2 shows the results of such estimation [11]. As can be seen, the coherence length determined from the Raman spectra correlates well with model predictions for the grain size smaller than 100nm. This observation coincides with the changes of the fraction of grain boundary volume estimated from the model, which sharply increases from 1 to 30% when grain size is reduced from 100 to 5nm [15].

The Raman spectra observed for bulk YSZ specimens are different from those of CeO_2 because the Raman-active mode at frequency of 620cm^{-1} is asymmetrical and the spectra contain additional lines at 259 , 362 , 487 and 690cm^{-1} (Fig.3). This behavior is attributed to disorder in the system where both the spectra of for the phonon density and their integral intensity are determined by ionic defects in the oxygen sublattice. Strong disorder in YSZ is induced by acceptors, which result in the formation of oxygen vacancies on the level of 10^{21}cm^{-3} . Such high defect concentration can lead to a breakdown of the selection rules and allows the additional modes that are forbidden for the fluorite structure.

Fig.3 The comparison of Raman spectra of CeO_2 and YSZ bulk single crystals.

Fig.3 shows the comparison of Raman spectra obtained for CeO_2 and YSZ single crystals. The increase of the half width of the Raman line observed for YSZ, which is over 6 times that observed for nominally pure CeO_2 specimens, can be attributed to the lattice disorder related to the acceptor doping. Note the line broadening on the low frequency side which is typical for disordered systems and

is related to the influence of the spectra by the phonon state density function, which has maxima for the optical and acoustical modes at frequencies lower than 620cm^{-1} [16].

Fig.4 Raman spectra of micro- and nanocrystalline YSZ together with the curve fit according to the spatial correlation model (Eq.1, solid lines).

The amount of structural disorder observed in YSZ can be also be described by the ratio between the low and high-frequency side of the Raman line. For YSZ, this ratio is 2.1, while for nominally pure CeO_2 single crystal the line is fully symmetrical and its shape can be described by single Lorentzian form which strongly suggests that CeO_2 is an ordered system with the contribution of phonons only from the center of Brillouin zone.

The influence of the microstructure of YSZ on the Raman spectra has been examined for different grain sized specimens. As can be seen in Fig.4, the line asymmetry and its half width increase with decreasing grain size. This observation correlates with the previously discussed behavior for CeO_2 , however due to high level of acceptor doping, this effect is much less than that observed for nanocrystalline CeO_2 specimens (Fig.1). When the grain size of YSZ decreases, from $6.5\mu\text{m}$ to 10nm , the half width changed from 53.8 to 85.6cm^{-1} respectively and the line asymmetry increased up to 2,6 (Fig.4). The shape of YSZ Raman lines was described using the spatial correlation model (Eq.1) and obtained results are presented in Fig.4. As can be seen this model correlates well with the experimental data when the microstructure is changed from the micro- to nanocrystalline region. Note that for those calculations the parameter Γ_0 of 15.9cm^{-1} has been chosen for all YSZ specimens. This value corresponds to the double width determined from the high-frequency site of Raman line and represents virtually ordered YSZ.

Fig.5 The coherence length as a function of the grain size of YSZ.

Fig.5 presents the relationship between so determined coherence length and the grain size. As can be seen, the coherence length is not microstructure dependent for the grain size larger than $1\mu\text{m}$ and equals 0.41nm . This value corresponds to the distance between the oxygens in the nearest neighbor shells, which as determined from EXAFS study is 0.44nm [17]. This coincidence strongly suggests that the coherence length in YSZ is attributed to short-range disorder that is induced by acceptor doping and each elemental cell includes an oxygen vacancy resulting a decrease in the oxygen coordination number from 8 to 7 [17]. Due to the extensive disorder, when the grain size of YSZ decreases from $1\mu\text{m}$ to 10nm , the coherence length only decreased from 0.41 to 0.35nm (Fig.5).

Since the coherence length determined for CeO_2 and YSZ is dependent upon the grain size, it is possible to determine the concentration of defects related to the coherence length:

$$N = \frac{1}{\frac{4}{3} \cdot \pi \cdot L^3} \quad (2)$$

This concentration corresponds to the spheres with diameters equal to the distance between two near-neighbor oxygens and with their center localized on the defect in the oxygen sublattice. Fig.6 shows the defect concentration determined in this manner for CeO_2 and YSZ as a function of the grain size. As can be seen this concentration for nominally pure CeO_2 is changes about 3 orders of magnitude from 10^{17} to 10^{21}cm^{-3} when the microstructure is decreased from 330 to 4nm . This behavior corresponds to the same changes of oxygen vacancy concentration obtained from coulometric titration studies on 10nm and $5\mu\text{m}$ grain sized CeO_2 [18] and those estimated from electrical conductivity measurements performed for 15nm [19] and 30nm [20] specimens.

The observed changes in the defect concentration in nanocrystalline CeO_2 can be explained as resulting from a reduction in the enthalpy of oxygen vacancy formation. This enthalpy determined from the electrical conductivity measurements was found to be changed from 4.8 to 1.77eV when the microstructure of CeO_2 decreases from 150 to 10nm respectively [4,7-9]. Such a large reduction implies increased non-stoichiometry in nanocrystalline CeO_2 , which is consistent with the observed increase in electronic conductivity [8,9]. Fig.6 presents the grain size dependence of the oxygen vacancy concentration, which was calculated from the experimentally determined relationship between the formation enthalpy and the grain size [4,8]. The good correlation between the defects determined from the Raman spectra and conductivity measurements suggests that the changes in the coherence length of CeO_2 are related to the oxygen vacancy concentration which can be controlled by the microstructure.

Fig.6 The comparison between the defect concentration related to the coherence length and the oxygen vacancy determined from the electrical conductivity as a function of grain size nanocrystalline CeO₂ and YSZ.

A different behavior of the defect concentration attributed to the coherence length has been observed for YSZ. In this case the calculated value of $4 \cdot 10^{21} \text{ cm}^{-3}$ is practically independent of the grain size and correlates well with the oxygen vacancy concentration estimated from the concentration of acceptors (16%Y) assuming the charge carriers are compensated by oxygen vacancies:

$$[Y_{Zr}'] = 2[V_o''] \quad (3)$$

From this equation the oxygen vacancy concentration of $[V_o''] = 0.08 \cdot N_o = 3.9 \cdot 10^{21} \text{ cm}^{-3}$ (where $N_o = 4.75 \cdot 10^{22} \text{ cm}^{-3}$ is the density of oxygen atoms in ZrO₂) has been estimated. This value is in good correlation with the concentration of oxygen vacancy determined for bulk CeO₂:20%Gd specimen (Fig.6). For highly doped CeO₂ and YSZ, the coherence length is spatially confined by the acceptor impurities and the crystalline quality is related to the oxygen distances in the first coordination sphere. Therefore, YSZ and CeO₂:20%Gd are characterized by

extrinsic controlled non-stoichiometry and only at very low grain size ($<20\text{nm}$) does the concentration of oxygen vacancies show any dependence upon the microstructure (Fig.6).

The observed correlation between the lattice defects determined from the analysis of the Raman spectra and the concentration of oxygen vacancies show that the dynamical and electrical properties of oxygen conductors are interrelated and can be attributed to the spatial correlation length. It also shows that Raman spectroscopy can be used for the determination of the lattice defects in CeO_2 and YSZ specimens and the study their non-stoichiometry, which is controlled by the microstructure and extrinsic impurities.

CONCLUSIONS

The results of the study of micro- and nanocrystalline CeO_2 and YSZ by Raman spectroscopy are presented and correlated with the specimens microstructure and impurity level.

The Raman spectra have been described using the spatial correlation model from which the coherence length was determined. This parameter is related to the average distance between the defects in the oxygen sublattice. It has been found that the Raman spectra are influenced by the defects attributed to grain size controlled non-stoichiometry or acceptor impurities.

A direct comparison between the defects related to the spatial correlated effects and the concentration of oxygen vacancies in CeO_2 and YSZ specimens has been achieved.

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extrinsic controlled non-stoichiometry and only at very low grain size ($<20\text{nm}$) does the concentration of oxygen vacancies show any dependence upon the microstructure (Fig.6).

The observed correlation between the lattice defects determined from the analysis of the Raman spectra and the concentration of oxygen vacancies show that the dynamical and electrical properties of oxygen conductors are interrelated and can be attributed to the spatial correlation length. It also shows that Raman spectroscopy can be used for the determination of the lattice defects in CeO_2 and YSZ specimens and the study their non-stoichiometry, which is controlled by the microstructure and extrinsic impurities.

CONCLUSIONS

The results of the study of micro- and nanocrystalline CeO_2 and YSZ by Raman spectroscopy are presented and correlated with the specimens microstructure and impurity level.

The Raman spectra have been described using the spatial correlation model from which the coherence length was determined. This parameter is related to the average distance between the defects in the oxygen sublattice. It has been found that the Raman spectra are influenced by the defects attributed to grain size controlled non-stoichiometry or acceptor impurities.

A direct comparison between the defects related to the spatial correlated effects and the concentration of oxygen vacancies in CeO_2 and YSZ specimens has been achieved.

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Appendix C

“Lattice Defects and Electrical Transport in Nanocrystalline CeO₂”

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PART A

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LATTICE DEFECTS AND ELECTRICAL TRANSPORT IN NANOCRYSTALLINE CeO_2

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The results of studies of the electrical conductivity and Raman scattering of CeO_2 thin films obtained by a polymeric precursor spin coating technique are presented. The electrical conductivity has been studied as a function of temperature and oxygen activity and correlated with the grain size. When compared to microcrystalline specimens, nanocrystalline specimens showed enhanced electronic conductivity and different stoichiometry, which are related to microstructure. The transition from extrinsic to intrinsic type of the conductivity has been observed as the grain size decreases below 100nm and it is shown that the enthalpy of formation for oxygen vacancies in CeO_2 becomes greatly reduced. The Raman spectra have been described using the spatial correlation model, which the crystalline quality has been determined as a function of grain size. A direct comparison between the concentration of defects related to coherence length and non-stoichiometry of CeO_2 has been achieved.

1. INTRODUCTION

Nanocrystalline materials are of interest due to their ability to improve the electrical transport and catalytic activity¹⁻⁴. Understanding these phenomena is of importance for the development of electroceramic devices, such as gas sensors, fuel cells and ionic membranes^{3,4}. For such devices, CeO_2 has been one of candidates and intensively studied. Microcrystalline CeO_2 is characterized as an extrinsic conductor, whose conductivity is related to impurity effect, while nanocrystalline CeO_2 shows an intrinsic conductivity. It is also shown that there is an increase of over 4 orders of magnitude in the electronic conductivity of nanocrystalline CeO_2 (10nm grain size) compared with microcrystalline CeO_2 (5 μm)^{5,6}. However, few experimental data are available related to the influence of microstructure on properties, because of difficulties in stabilizing the microstructures. To meet this requirement, the polymeric precursor spin coating technique has proven to be useful since it allows the formation of dense nanocrystalline thin film materials at lower temperatures. This method has recently used for preparation of nanocrystalline oxides of $\text{ZrO}_2\cdot\text{Y}$ ⁷, CeO_2 ^{6,8} and $\text{SrCeO}_3\cdot\text{Yb}$ ^{2,4}.

One of the most important aspects of the study of nanocrystalline materials is the ability to determine their nanostructure-property relationships. Since Raman scattering can yield important information on the atomic scale level, it can be used to study the microscopic nature of nanocrystalline materials and its combination with the electrical conductivity measurements can bring more extended information about the nature of nanocrystalline materials. In this paper the results of a study of the electrical conductivity and Raman scattering of nanocrystalline CeO_2 thin films are presented. The purpose of this study is to understand how microstructure influences the electrical transport and dynamical properties. The electrical conductivity and Raman scattering measurements of CeO_2 with different microstructure as a function of temperature and oxygen activity have been performed systematically over the grain size range from 10 to 330nm.

2. EXPERIMENTAL

Dense nanocrystalline CeO_2 thin films were prepared on sapphire substrates using a polymeric precursor spin coating technique reported in detail elsewhere^{6,8-11}. This process allows the preparation of the oxides from a precursor, which can be converted to dense oxide films by spin coating, drying and crystallizing at temperatures in the range of 300-1200°C. Such low temperatures compared to those typically required by normal powder processing techniques (1400-1800°C), allow the formation of dense nanocrystalline specimens. The precursor solutions were prepared by quantitatively dissolving water soluble cation sources such as nitrates and carbonates into solutions, which contain chelating and polymerizing agents such as ethylene glycol and water. The thickness of the films is about 0.3µm and depends upon the number of depositions and the concentration of the precursor. For this study, 13 depositions of a 2% cation concentrated precursor were applied.

The crystallinity, integrity and phase purity obtained specimens were investigated by x-ray diffraction and electron microscopy. Since the nucleation of the oxides from the polymeric precursor occurs on the molecular level, the films are characterized by very uniform microstructures. The microstructure was determined by the analysis of the shape of x-ray lines. It has been found that the grain size of CeO_2 thin films is dependent upon the annealing temperature and can be changed from 4 to 330nm over the annealing temperature range of 400-1200°C^{10,11}. Note, that for temperature below 1000°C no preferential orientation is observed. However at 1000°C an out-of-plane texture growth is observed. For temperatures higher than 1000°C in-plane texturing starts to occur with preferential orientation of (200).

One of the most important aspects of the study of nanocrystalline materials is the ability to determine their nanostructure-property relationships. Since Raman scattering can yield important information on the atomic scale level, it can be used to study the microscopic nature of nanocrystalline materials and its combination with the electrical conductivity measurements can bring more extended information about the nature of nanocrystalline materials. In this paper the results of a study of the electrical conductivity and Raman scattering of nanocrystalline CeO_2 thin films are presented. The purpose of this study is to understand how microstructure influences the electrical transport and dynamical properties. The electrical conductivity and Raman scattering measurements of CeO_2 with different microstructure as a function of temperature and oxygen activity have been performed systematically over the grain size range from 10 to 330nm.

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The electrical conductivity of CeO₂ thin films was studied using a Solartron 1260 frequency response analyzer with a 1296 Interface operating over the frequency of 1-5×10⁶Hz and impedance up to 10¹⁰Ω. Measurements were performed in the temperature range of 600-900°C in oxygen, air, helium and CO/CO₂ mixtures for the oxygen activity range of 10⁻²⁶ - 1atm over the temperature range of 600-900°C. Silver electrodes were used for all electrical measurements. The impedance spectra were analyzed to yield the high-frequency semicircle related to conductivity, which for nanocrystalline materials is attributed to the superposition of the bulk and grain boundary contribution^{2,3,6,7,10,11}.

The Raman spectra were recorded at room temperature using XY Dilor spectrograph equipped with a Spex CCD detector (2000x800 pixels). Spectra were recorded in the micro-configuration with the laser beam impacting a region of about 1μm in diameter. The excitation source was the 514.5nm line of an argon laser at the power level of 5mW. The spectra have been described using the spatial correlation model^{12,13} from which the coherence length has been determined and correlated with the concentration of defects estimated from electrical conductivity measurements.

3. ELECTRICAL CONDUCTIVITY OF NANOCRYSTALLINE CeO₂

From the measurements of electrical conductivity as a function of oxygen partial pressure and temperature, it is possible to obtain the information about the type of conductivity and thermodynamic parameters of the defects. Fig.1 shows the electrical conductivity as a function of P_{O2} and temperature of CeO₂ thin films whose grain size varies from 20 to 150nm. As can be seen in Fig.1a, the electrical conductivity of the 150nm grain sized specimen is P_{O2} independent at high oxygen activity, and follows P_{O2}^{-1/4} behavior at low P_{O2}, which is characteristic for extrinsic ionic and electronic conductivity respectively. Such behavior was also observed for microcrystalline specimens^{8,10,11}, and is considered to be an impurity effect. On the other hand, the electrical conductivity of the 65 and 30nm specimens displayed in Fig.1 (b and c) shows the transition from P_{O2}^{-1/4} to P_{O2}^{-1/6} behavior with increasing temperature. The P_{O2}^{-1/6} relationship corresponds to the intrinsic charge compensation, $n = 2[V_O^{\bullet\bullet}]$. This observation is consistent with the intrinsic electronic conductivity reported for nanocrystalline CeO₂ specimens at 600°C^{5,14}. It is seen that the onset temperature for intrinsic behavior decreases as grain size decreases until only intrinsic is observed for 20nm grain sized specimen (Fig.1d). However, for d_g = 20nm at lower P_{O2} the conductivity follows less as -1/6 power dependence. This suggests a change in either the model or compensation mechanism. It is possible that at the low grain size, the surface and grain boundary effects dominate the exchange reactions due to the increased grain boundary volume and surface

area. This supposition is supported by the study of Horita, et al.¹⁵, who measured oxygen surface exchange for $Y_{0.2}Ce_{0.8}O_{2-x}$ and showed that the surface exchange coefficient varied with $P_{O_2}^{-1/20}$. This may explain the behavior seen in Fig. 1d, but further investigation is required.

Figure 1
The electrical conductivity as a function of P_{O_2} for CeO_2 specimens with different microstructure

The analysis of the temperature dependence of the conductivity can provide information regarding defect thermodynamics related to the microstructure. Assuming that the ionic and electronic conductivity are controlled by oxygen vacancies and electron concentration respectively and that the electronic transport is attributed to small polaron hopping with a thermally activated electron mobility, then expression for electrical conductivity is given by^{5,10,11}.

$$\sigma = \sigma_i + \sigma_e'' \cdot P_{O_2}^r \quad (1)$$

where σ_i is P_{O_2} -independent ionic conductivity and σ_e'' denotes the temperature dependent small polaron conductivity, $\sigma_e'' T = \sigma_0 \exp(-E_{act}/kT)$. For the extrinsic region, the electronic conductivity follows the relationship with $r = 1/4$ and $E_{act} = \Delta H/2 + E_h$ where ΔH and E_h are the enthalpy of oxygen vacancy formation and electron hopping respectively. In the intrinsic region, the electronic conductivity should follow the relationship with $r = 1/6$ and $E_{act} = \Delta H/3 + E_h$ ^{5,8,10,14}.

Eq.1 when fit to the experimental data can be used to deconvolute and determine the ionic and electronic contribution to the total conductivity as a function of temperature and oxygen activity. The isothermal conductivity reported in Fig.1 has been interpreted in terms of the above defect model and the solid curves represent the result of fitting the experimental data to the model (Eq.1). From these results, the temperature dependence of the electronic conductivity for different grain sized CeO_2 are presented in Fig.2. In this figure the data obtained for bulk CeO_2 with 10nm grain size are also shown^{5,14}. As can be seen, the electronic conductivity is strongly dependent upon the microstructure and increases with decreasing grain size resulting in an enhancement of over 6 orders of magnitude (at 600°C) when the grain size is changed from 5 μm to 10nm. Note that the ionic conductivity obtained from the fitting procedure increased by a factor of 1.5 as the grain size decreases from 5 μm to 10nm with the same activation energy of 1.04eV^{8,11}.

Figure 2
Temperature dependence of electronic conductivity determined for CeO_2 with different grain size

Figure 3
The enthalpy of oxygen vacancy formation of CeO_2 as a function of microstructure

The electronic conductivity activation energy is decreased from 2.8 to 1eV when the grain size changed from the micro- into nanocrystalline range. Such behavior is quite unique and is probably related to the reduction in the enthalpy of formation of oxygen vacancies, which can be determined from the conductivity activation energy. This energy includes also the contribution due to small polaron hopping - E_h , which is much lower than the energy of oxygen vacancy formation which for CeO_2 is about 5eV¹⁶. Recently reported data for bulk nanocrystalline CeO_2 (15nm grain size) showed that the electron hopping energy does not changes with microstructure and is similar to that for microcrystalline specimens¹⁷, which agrees with the predictions that the changes in the activation energy are related to the enthalpy of formation of oxygen vacancies term. Thus, assuming this to be the case and taking the electron hopping energy of $E_h = 0.4\text{eV}$ (value determined for monocrystalline CeO_2 ¹⁶) and using the above presented expression for E_{act} in extrinsic and intrinsic region, the enthalpy of oxygen vacancy formation, ΔH as the function of grain size has been determined (Fig.3). As can be seen this enthalpy is microstructure independent for grain size higher then 100nm and equals 4.8eV. When the grain size decreases to the nanometer range, the enthalpy rapidly decreases reaching the value of 1.77eV for 10nm grain sized specimens. These values are consistent with the oxygen vacancy formation enthalpy of 1.84eV reported for nanocrystalline (15nm grain size) bulk CeO_2 specimens¹⁷. Such a large reduction in the enthalpy implies greater nonstoichiometry in nanocrystalline materials consistent with the higher electron conductivity. Therefore, the defect formation enthalpy is controlled by the CeO_2 microstructure and can decrease about 3 times when the grain size changes from the micro- to nanocrystalline scale.

Using the determined values of ΔH , changes of the concentration of oxygen vacancy can be calculated and correlated with the microstructure. In the intrinsic region of the conductivity this concentration can be described as¹⁸:

$$[V_o^{\bullet\bullet}] = N_o \cdot \exp\left(\frac{-\Delta H}{3kT}\right) \quad (2)$$

where $N_o = 4.99 \cdot 10^{22} \text{cm}^{-3}$ is the density of oxygen atoms in the CeO_2 lattice.

Another way to estimate the concentration of oxygen vacancy can be achieved from the analysis of the Raman spectra which are very sensitive to any disorder in the oxygen sublattice resulting from thermal, doping or grain size induced effects^{19,20}.

4. RAMAN SCATTERING OF NANOCRYSTALLINE CeO_2

Since the defect formation in nanocrystalline CeO_2 is controlled by the microstructure, it can also influence the dynamical properties, which are sensitive to lattice disorder and are extremely important due to its influence on the ionic conductivity. From this point of view, Raman spectroscopy, which yields information about the interaction between the ions can be very helpful in the study of the microscopic nature of nanocrystalline materials.

Fig.4 presents the Raman spectra obtained for single crystal and nanocrystalline (4nm) CeO_2 specimens. The Raman-active mode in this material corresponds to the frequency of $\omega_R = 466\text{cm}^{-1}$, which is attributed to a symmetrical stretching mode of CeO_8 octahedron vibrational unit. The influence of the microstructure of CeO_2 on the shape of Raman spectra was observed by the broadening of the line and increases in its asymmetry what is attributed to reduction of phonon life-time in the nanocrystalline regime^{12,13,21}.

Figure 4
Raman spectra of single crystal and nanocrystalline (4nm) CeO_2 together with the curve fit according to Eq.3 (solid line)

Important information regarding the lattice disorder can be obtained from the analysis of the shape of the Raman line, which has been performed using a spatial correlation model^{12,13}. According to this model, the Raman line intensity, $I(\omega)$ at the frequency, ω can be written as:

$$I(\omega) = \int_0^1 \exp\left(\frac{-q^2 L^2}{4}\right) \cdot \frac{d^3 q}{[\omega - \omega(q)]^2 + \left(\frac{\Gamma_o}{2}\right)^2} \quad (3)$$

where q is the wave vector expressed in units of $2\pi/a$ (a is the lattice constant) and Γ_o is the half width of the Raman line. The expression of $\exp(-q^2 L^2/4)$ represents a Gaussian spatial correlation function with parameter L as the coherence length, $\omega(q)$ is the function of Raman phonon dispersion. This function has been determined for CeO_2 based on a rigid-model calculation²¹ and was used in this analysis.

Fig.4 shows the Raman spectra of CeO_2 and the corresponding line-shape fit performed using the spatial correlation model, (Eq.3). As can be seen this model appears to fit the shape of Raman line of CeO_2 . Note that this procedure used only one fitting parameter, which is the phonon coherence length. Therefore, the disorder induced by the microstructure could be well defined by the coherence length rather than the half width or line asymmetry.

Figure 5

The coherence length as a function of the grain size of nanocrystalline CeO_2 . Dashed line is the coherence length estimated from spherical model

Figure 6

The comparison between the defect concentration related to the coherence length and the enthalpy of oxygen vacancy formation (Fig.3 and Eq.3) as a function of grain size of nanocrystalline CeO_2

Fig.5 presents the relationship between the so determined coherence length and the grain size of CeO₂ specimens. As can be seen, the coherence length is not microstructure dependent for grain size larger than 100nm and equals 105Å. This value corresponds to about 20 lattice constants. The observed independence between the correlation length and grain size illustrates the limit above which the line broadening and asymmetry are not detectable. Note that for the specimens with grain size larger 150nm the Raman line is practically the same as that of a single crystal^{19,20}. When the grain size is smaller than 100nm, the coherent length decreases rapidly and equals 11Å for a 4nm grain sized specimen, which corresponds to 2 lattice constants. Such large changes in the coherence length can be attributed to the grain boundary phase whose volume increases with decreasing grain size. The observed decrease in the coherence length was described in the model in which the fraction of atoms on the surface of each grain was considered. Assuming spherical symmetry of the grains, the coherence length should depend upon the grain size to the 1/3rd power the grain size - $L \sim d_g^{1/3}$. Fig.5 shows the results of such modeling^{19,20}.

Since the correlation length is dependent upon the grain size, probably the changes of correlation length are attributed to the oxygen vacancies. Fig.6 shows the defect concentration calculated from the correlation length - $\frac{3}{4\pi L^3}$ as a function of grain size. As can be seen this concentration changes ca. 3 orders of magnitude from 10¹⁷ to 10²⁰cm⁻³ which corresponds to the same changes of oxygen vacancy concentration what were determined from the study of coulometric titration (10nm)²² and electrical conductivity measurements for 15nm¹⁷, and 30nm⁶ grain sized specimens. Fig.6 also shows the changes of the oxygen vacancy concentration, which was calculated from the experimentally determined relationship between the formation enthalpy and the grain size (Fig.3) using the Eq.2.

The observed correlation between the defects determined from Raman spectra and conductivity measurements shows that the changes in coherence length are related to the concentration of oxygen vacancies which can be controlled by the microstructure.

5. CONCLUSIONS

The results of a study of the electrical and dynamical properties of nanocrystalline CeO₂ thin films obtained by a polymeric precursor spin coating technique have been presented. The electrical conductivity of these films has been investigated as a function of grain size, temperature and oxygen partial pressure. The results show that the electrical transport in nanocrystalline specimens is dominated by grain boundary effects and is related to the grain size-dependent stoichiometry.

Nanocrystalline CeO_2 possesses greatly enhanced electronic conductivity due to a grain size dependent reduction in the enthalpy of oxygen vacancy formation. The concentration of the oxygen vacancy related to the changes of the enthalpy formation has been estimated. The results have been correlated with the concentration of the lattice defects determined from the Raman spectra.

The Raman spectra have been described using the spatial correlation model from which the coherence length was determined. This parameter is related to the average distance between the defects in the oxygen sublattice. It has been found that the Raman spectra are influenced by the defects which are attributed to grain size-controlled non-stoichiometry. The observed correlation between the lattice defects determined from the analysis of the Raman spectra and the concentration of oxygen vacancy shows that the dynamical and electrical properties of CeO_2 are interrelated and can be attributed to the spatial correlation length. It also shows that Raman spectroscopy can be used for the determination of the concentration of lattice defects, which are controlled by the microstructure.

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Appendix D

“Electrical Conductivity of Nanocrystalline Ceria and Zirconia Thin Films”

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Electrical conductivity of nanocrystalline ceria and zirconia thin films

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Electrical conductivity of nanocrystalline ceria and zirconia thin films

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Abstract

The results of studies of the preparation, structure and electrical conductivity of ZrO_2 :16% Y and CeO_2 thin films are presented. Dense films with grain size controlled in the region of 1–400 nm have been obtained on monocrystalline sapphire and polycrystalline Al_2O_3 substrates using a polymeric precursor spin coating method. The electrical conductivity of nanocrystalline thin films has been studied as a function of oxygen activity and temperature and correlated with the microstructure. Nanocrystalline specimens are characterized by enhanced electrical conductivity and different stoichiometry compared with microcrystalline material. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Nanocrystals; Oxygen conductors; Nonstoichiometry; Zirconia; Ceria; Electrical conductivity; Impedance spectroscopy

1. Introduction

Nanocrystalline oxides are characterized by unique electrical properties and chemical reactivity which are vastly different than those of microcrystalline grained materials [1,2]. Such effects are due to increased interfacial area and size-dependent defects, which enhance the nonstoichiometry and reaction kinetics. These results have been recently reported for ZrO_2 :Y, CeO_2 and SrCeO_3 :Yb nanocrystalline specimens [3–5]. The observed properties shows that these materials may be very useful for applications related to gas sensors, fuel cells and ionic membranes [6,7]. However, for the development of such devices their microstructural stabilization is required. A number of recent studies have shown that it can be achieved by formation of nanocrystalline thin films

using the preparation techniques which allow the formation of dense specimens at reduced processing temperature to yield stable nanocrystalline microstructures. For such requirements, the polymeric precursor spin coating technique has proved to be particularly useful since it allows the formation of dense nanocrystalline oxide thin films at temperature about 1000°C lower than those required to prepare microcrystalline sized specimens. Such processing was recently used for the formation of nanocrystalline ZrO_2 :Y and CeO_2 thin films [8–10]. As has been shown, the optical properties of these films are influenced by their microstructure resulting in quantum confinement effects [10,11].

A study of electrical conductivity correlated with the microstructure showed that the electrical transport in nanocrystalline materials is dominated by grain boundary effects [3–5,12]. In recognition of the influence of the microstructure on the electrical transport, a direct comparison has been achieved

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between the electrical conductivity of single crystal, micro- and nanocrystalline $\text{ZrO}_2\text{:Y}$ [3]. The results shown that nanocrystalline $\text{ZrO}_2\text{:Y}$ possesses greatly enhanced electrical conductivity which is probably related to grain boundary defect segregation effects [3,13]. This segregation can change the stoichiometry and also the type of electrical conductivity as has been recently reported for CeO_2 [4,12].

In order to explain the observed enhancement in the electrical conductivity of nanocrystalline $\text{ZrO}_2\text{:Y}$ and CeO_2 it is necessary to examine the relationship between the stoichiometry and microstructure. In the present work, the results of the electrical conductivity measurements as a function of oxygen activity and temperature for micro and nanocrystalline $\text{ZrO}_2\text{:16% Y}$ (YSZ) and CeO_2 specimens are presented and correlated with their microstructure. The results have been correlated with the defect model and the enthalpy of defect formation was determined.

2. Experimental

Thin films of YSZ and CeO_2 were prepared by using a polymer precursor spin coating process reported in detail elsewhere [3,8–10]. This process allows the preparation of the oxides from polymeric precursor, which can be converted to oxide films by spin coating, drying and crystallizing at temperatures in the range of 300–1200°C. Such low temperatures compared to those typically required by powder processing techniques (1400–1800°C), allow the formation of dense nanocrystalline specimens. For this study YSZ and CeO_2 thin films with the thickness in the range of 0.4–0.7 μm have been deposited on sapphire single crystal or polycrystalline Al_2O_3 substrates. The crystallinity, integrity and phase purity of YSZ and CeO_2 thin films were investigated by X-ray diffraction and electron microscopy.

The electrical conductivity was studied using a Solartron 1260 frequency response analyzer with a 1296 Interface operating over the frequency range of 1 Hz–5 MHz and impedance up to $10^{10} \Omega$. Measurements were performed in the temperature range of 450–900°C in oxygen, air, helium and CO/CO_2 mixtures for the oxygen partial pressure range of

10^{-26} –1 atm. Silver electrodes were used for all electrical measurements.

The impedance spectra were analyzed to yield the high-frequency semicircle related to conductivity, which for nanocrystalline materials is attributed to the superposition of the bulk and grain boundary contributions [3–5,7,12]. Such determined conductivity for nanocrystalline specimens was compared with similar data for microcrystalline material, which are related to the sum of bulk and grain boundary semicircles.

3. Microstructure of YSZ and CeO_2 thin films

The crystallization and grain growth of YSZ and CeO_2 films was observed by X-ray diffraction (XRD). Fig. 1 shows XRD patterns for CeO_2 specimens deposited on sapphire substrate and sintered at different temperatures. As can be seen the spectra for the films correlate well with the standard indicating the successful preparation of the materials with a single fluorite phase. No preferential orientation was observed for CeO_2 films sintered at temperatures up to 800°C, however at higher temperatures changes in the peaks intensities were observed. The (111) line, which is the most intensive for the polycrystalline powder standard begins to decrease while at a same time the (200) and (400) lines increase (Fig. 1). These changes are consistent with the texturing with (200) preferential orientation. The same phenomena were observed for YSZ films where texturing has been observed at temperatures above 1200°C [9]. The evaluation of the cubic phase in YSZ thin films can be observed by the profile of the X-ray diffraction lines. Fig. 2 presents the (111) line at different sintering temperatures. As can be seen, crystallization and grain growth are observed by increasing the line intensity and its sharpening when sintering temperature is changed from 450 to 1100°C. However at higher temperatures the development of monoclinic phase with the decreasing amount of the cubic phase has been observed and is probably due to a reaction between the film and substrate (Fig. 2).

The analysis of the shape of X-ray lines has been used to determine the grain size for each specimen.

Fig. 1. X-ray diffraction patterns of CeO_2 thin films deposited on monocrystalline sapphire substrate sintered under different temperatures. The insert is the dependence of grain size with sintering temperature for CeO_2 deposited on sapphire and polycrystalline Al_2O_3 substrates.

Fig. 2. The evaluation of the (111) X-ray diffraction line for YSZ thin films sintered under different temperatures. The insert is the dependence of grain size with sintering temperature deposited on sapphire and polycrystalline Al₂O₃ substrates.

As can be seen in the inserts in Figs. 1 and 2 the microstructure of YSZ and CeO₂ thin films strongly depend upon the sintering temperature and the grain size can be varied from 1 to 400 nm for CeO₂ and from 1 to 220 nm for YSZ over the temperature range of 300–1200°C.

The crystallographic orientation and phase stability can also be effected by the substrate. As can be seen in the insert in Fig. 1, up to 1000°C the type of the substrate has little influence on the microstructure of CeO₂, however at higher sintering temperatures the CeO₂ films deposited on polycrystalline Al₂O₃ substrate have the larger grain size than those deposited on sapphire. Such behavior has also been observed for YSZ where the substrate influenced the

microstructure. The comparison of the microstructure of YSZ thin films obtained on polycrystalline Al₂O₃ and on sapphire substrates showed that the cubic phase of YSZ is much more stable when the film is deposited on sapphire. As can be seen in the insert in Fig. 2 the microstructure of YSZ films is the same for the specimens obtained at temperatures below 800°C on both substrates. At higher temperatures rapid grain growth starts to occur in the films deposited on polycrystalline Al₂O₃ substrates whereas on sapphire substrates rapid growth does not occur until 1000°C (Fig. 2). The observed influence of the substrate is probably connected with the nucleation mechanism which can expect to be faster when the substrate is polycrystalline.

4. Electrical properties of YSZ and CeO₂ thin films

The difference in stoichiometry of micro- and nanocrystalline YSZ and CeO₂ specimens influence the electrical conductivity which has been studied as a function of temperature and oxygen activity. Fig. 3

presents the relationship between the conductivity and oxygen partial pressure for micro- and nanocrystalline YSZ determined at 900°C. As can be seen the conductivity of nanocrystalline YSZ is about one order of magnitude higher compared with a microcrystalline specimen and an anomalous decrease of the conductivity at low p_{O_2} has been

Fig. 3. The behavior of the electrical conductivity of YSZ nanocrystalline thin film and microcrystalline bulk specimen as a function of p_{O_2} . The insert is the temperature dependence of electrical conductivity at p_{O_2} -independent region.

observed. In contrast, the electrical conductivity of microcrystalline YSZ is p_{O_2} -independent everywhere which strongly suggests that the extrinsic ionic conductivity is controlled by acceptors.

The observed anomalies in electrical conductivity for nanocrystalline YSZ can be explained by a model in which a defect pair formation was proposed [14,15]. In this model an association between oxygen vacancies and acceptors has been considered, which result in the formation of a donor center — $[Y'_{Zr} - V_{O\bullet}] = D^\circ$. In this case YSZ can be considered as a compensated semiconductor with acceptor and donor levels whose concentration in ionized and unionized states can be described by the Fermi equations [15]. Based on this model, an expression for the concentration of ionized centers as a function of oxygen activity has been obtained and the resulting behavior related to the ionic conductivity. A comparison of the experimental results with model predictions suggests that electrical conductivity in micro and nanocrystalline YSZ has the same extrinsic ionic character. An anomalous decrease of the conductivity at low p_{O_2} is probably related to a different mechanism of the charge carrier compensation resulting in a decrease of the concentration of ionic species [14]. The enhancement in the conductivity observed for nanocrystalline YSZ can be explained as the result of the decrease in activation energy, which is related to ion mobility. The insertion in Fig. 3 shows the temperature dependence of the conductivity for micro- and nanocrystalline YSZ. Determined from this relationship the activation energy is 1.23 and 0.93 eV for micro- and nanocrystalline specimen respectively. The observed decrease is probably due to extended interfacial area in the nanocrystalline material and the unique defect thermodynamics, which determine the hopping energy for oxygen ions.

A different behavior between the conductivity and oxygen partial pressure has been observed for CeO_2 . In this material the microstructure induces the change of the type of the conductivity and charge carrier compensation. Fig. 4 shows the conductivity determined for micro (5 μm grain size) and nanocrystalline (30 nm grain size) CeO_2 as a function of oxygen activity. At low temperatures ($<800^\circ C$) both specimens show the similar conductivity behavior with p_{O_2} -independent region at high oxygen activity and $p_{O_2}^{-1/4}$ relationship at low

p_{O_2} , which is characteristic for extrinsic ionic and electronic conductivity respectively [12]. However, at higher temperatures ($>800^\circ C$), the conductivity of nanocrystalline CeO_2 shows a transition into intrinsic behavior following the $p_{O_2}^{-1/6}$ relationship which corresponds to the charge compensation by electrons and oxygen vacancies. This observation is consistent with the intrinsic electron conductivity reported for nanocrystalline bulk (10 nm grain size) CeO_2 specimens [4,12]. As can be seen in Fig. 4, the microstructure of CeO_2 controls the electronic conductivity significantly increasing its value for nanocrystalline specimens. The analysis of the temperature dependence of the conductivity can provide information regarding defect thermodynamics related to the microstructure. Assuming that the ionic and electronic conductivity are controlled by oxygen vacancies and electron concentration respectively and that the electronic transport is attributed to small polaron hopping with a thermally activated electron mobility, then the expression for total conductivity is given by:

$$\sigma = \sigma_i + \sigma_e^\circ p_{O_2}^{-r} \quad (1)$$

where σ_i is p_{O_2} -independent ionic conductivity and σ_e° denotes the temperature-dependent electronic conductivity, $\sigma_e^\circ T = \sigma_o \exp(-E_{act}/kT)$. For extrinsic region, the electronic conductivity follows relationship with $r=1/4$ and $E_{act} = \Delta H/2 + E_h$, where ΔH and E_h are the enthalpy of oxygen vacancy formation and electron hopping energy, respectively. In the intrinsic region electronic conductivity should follow the relationship with $r=1/6$ and $E_{act} = \Delta H/3 + E_h$.

Eq. (1) when fit to the experimental data, can be used to deconvolute and determine the ionic and electronic contribution to the total conductivity as a function of temperature and oxygen activity. The isothermal conductivity reported in Fig. 4 has been interpreted in terms of the above defect model and the solid curves represent the result of fitting the experimental data to the model Eq. (1). From these results, the temperature dependencies of the electronic conductivity for CeO_2 with different grain size are presented in the insertion in Fig. 4. In this figure the data obtained for bulk CeO_2 with 10 nm grain size are also shown [4,12]. As can be seen, the electronic conductivity is strongly dependent upon

Fig. 4. The electrical conductivity as a function of p_{O_2} for CeO_2 specimens with different microstructure. The insert is the temperature dependence of electronic conductivity determined for CeO_2 with different grain size.

the CeO_2 microstructure and the increases with decreasing the grain size resulting the enhancement over six orders of magnitude (at 600°C) occurs when the grain size is changed from $5\text{ }\mu\text{m}$ to 10 nm . The electronic conductivity activation energy is decreased from 2.8 to 0.99 eV in a same range of microstructure changes. Such observations are quite unique and are probably related to the reduction in the enthalpy of oxygen vacancy formation, which can be determined from the conductivity activation energy. This energy includes also the contribution of the polaron hopping (E_h), which is much lower compared to the energy of oxygen vacancy formation that for CeO_2 which is about 5 eV [16]. Recently reported data for nanocrystalline CeO_2 (15 nm grain size) showed that electron hopping energy do not change with material microstructure and is similar to that of bulk specimen [17] which supported the predictions that the changes in activation energy are related to the enthalpy of lattice defect formation. For this reason we assume, that such a large decrease (about three times) in electron conductivity activation energy is the result of changes of oxygen vacancy formation energy. Taking the electron hopping energy of $E_h = 0.4\text{ eV}$ (value determined for monocrystalline CeO_2) [16], and using the above presented expressions for E_{act} in the extrinsic and intrinsic region, the enthalpy of oxygen vacancies formation, ΔH has been estimated. This enthalpy depends upon the grain size and equals 4.8 , 3.8 and 1.77 eV for $5\text{ }\mu\text{m}$, 30 nm and 10 nm grain sized CeO_2 specimens, respectively. These values are consistent with data reported for 15 nm grain sized bulk CeO_2 of 1.84 eV [17]. Such large reduction in the enthalpy implies greater nonstoichiometry in nanocrystalline specimens consistent with the higher electron conductivity. Note that the ionic conductivity obtained from fitting (Eq. (1)) procedure slightly increases (for a factor of 1.5) with decreasing grain size from $5\text{ }\mu\text{m}$ to 10 nm with the same activation energy of 1.04 eV [10].

5. Summary

The results of a study of the formation and microstructure of YSZ and CeO_2 thin films obtained by a polymeric precursor spin coating technique have been presented. This preparation technique allowed

crystalline dense film formation with the grain size in range of $1\text{--}400\text{ nm}$ on sapphire and polycrystalline Al_2O_3 substrates.

The electrical properties of YSZ and CeO_2 nanocrystalline thin films were studied by impedance spectroscopy as a function of temperature and oxygen activity. The electrical transport of nanocrystalline specimens is determined by grain boundary effects and is related to the grain size-dependent stoichiometry.

Examples are given which illustrate enhancement of both the ionic and electronic conductivity. This can be achieved by the control of the microstructure in the nanometer range. An enhancement of about two orders of magnitude (at 600°C) in the ionic conductivity for nanocrystalline YSZ is observed. This is a result of a decrease of the activation energy from 1.23 to 0.93 eV for micro- and nanocrystalline material, respectively. An anomalous decrease in ionic conductivity in nanocrystalline YSZ at oxygen partial pressure lower than 10^{-17} atm has been observed and correlated with a defect pair model. A direct comparison has been achieved between the electrical conductivity and microstructure of CeO_2 . The results show that the nanocrystalline CeO_2 possess greatly enhanced electronic conductivity due to reduced enthalpy of oxygen vacancy formation.

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