Conductivity of porous Sm$_2$O$_3$-doped CeO$_2$ as a function of temperature and oxygen partial pressure

James Wright, Anil V. Virkar*

Department of Materials Science & Engineering, University of Utah, 122 S. Central Campus Drive, Salt Lake City, UT 84112, USA

ABSTRACT

Porous samples of Sm$_2$O$_3$-doped CeO$_2$ (samaria-doped ceria, SDC) of composition Sm$_{0.15}$Ce$_{0.85}$O$_{2-\delta}$ were made by conventional ceramic processing and sintering in air at 1400 °C. Crystal structure and microstructure of the samples were characterized, respectively, by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Electrical conductivity was measured using a four probe DC method over a temperature range from 200 °C to 800 °C, and over a wide range of oxygen partial pressures corresponding to testing in oxygen and in nearly dry hydrogen. Conductivity rapidly stabilized at any given temperature consistent with the attainment of thermodynamic equilibrium corresponding to the imposed conditions. At and below 300 °C, the conduction was predominantly due to oxygen ion transport. At and above 400 °C, however, significant electronic conduction occurred in reducing atmospheres. The ionic transference number of SDC at 400 °C in hydrogen is only ∼0.4. This result shows that the electrolytic domain of SDC at and above 400 °C is rather narrow. These results also suggest that SDC (and possibly other rare earth oxide-doped CeO$_2$) is not a suitable electrolyte without a thin electron blocking layer such as yttria-stabilized zirconia (YSZ).

1. Introduction

Much of the current development of solid oxide fuel cells (SOFC) is based on yttria-stabilized zirconia (YSZ) as the electrolyte which exhibits ionic transference number near unity over wide temperature and oxygen partial pressure ranges. Rare earth oxide doped ceria (RDC) is an excellent oxygen ion conductor. Its ionic conductivity is typically two or three times that of yttria-stabilized zirconia (YSZ) at a given temperature, and thus is of interest for low to intermediate temperature SOFC (500–700 °C) [1–17]. RDC at low oxygen partial pressures and at high temperatures, however, becomes a mixed ionic electronic conductor (MIEC) [1,18–20]. Catalytic and electro-catalytic properties of undoped ceria and RDC have also been extensively investigated. In a porous form, RDC mixed with nickel is a candidate for the anode functional layer of an SOFC. Similarly, RDC mixed with perovskites such as Sr-doped LaCoO$_3$ (LSC), Sr-doped LaMnO$_3$ (LSM), Sr-doped LaFeO$_3$ (LSF), etc. are also known to be candidates for the cathode functional layer. Thus, RDC is a constituent in all three components in low to intermediate temperature SOFCs and it is important to determine its transport properties as a function of temperature and atmosphere. For application as an electrolyte, an ionic transference number close to one is necessary. For application as a constituent in the electrodes, mixed ionic-electronic conducting properties are beneficial.

There is extensive literature on the measurement of transport properties of RDC as a function of temperature and oxygen partial pressure and its potential use as a constituent in SOFC [1,18–22]. Much of the reported work on the measurement of conductivity of RDC is on fully dense samples or on samples sufficiently dense with negligible contiguous porosity [15,17,20–23]. Typical thickness of samples used in such measurements is ∼2 mm. The design of electrolyte and electrodes used in SOFC is typically based on such measurements made on dense samples. At low temperatures in air, such measurements indicate that RDC is a predominantly oxygen ion conductor with negligible electronic conductivity. However, at low temperatures, even if the oxygen ion conductivity of RDC may be quite high, the chemical diffusion coefficient of neutral oxygen, which is proportional to the product of ionic and electronic conductivities, is rather low. This means the equilibration of a fully dense sample of a typical thickness (∼2 mm) with the imposed atmosphere, whose kinetics is dictated by the chemical diffusion coefficient of oxygen, is very sluggish. Suppose for example the chemical diffusion coefficient of oxygen through RDC is $\tilde{D}_O$ at a given temperature and in a given atmosphere. For a sample of thickness $2d$, the time required for sample equilibration with the imposed atmosphere to occur will be $t \sim d^2/\tilde{D}_O$. For an assumed $\tilde{D}_O$ of 10^{-7} cm^2 s^{-1} at 500 °C, the time required for the equilibration of

* Corresponding author. Tel.: +1 801 581 5396; fax: +1 801 581 4816.
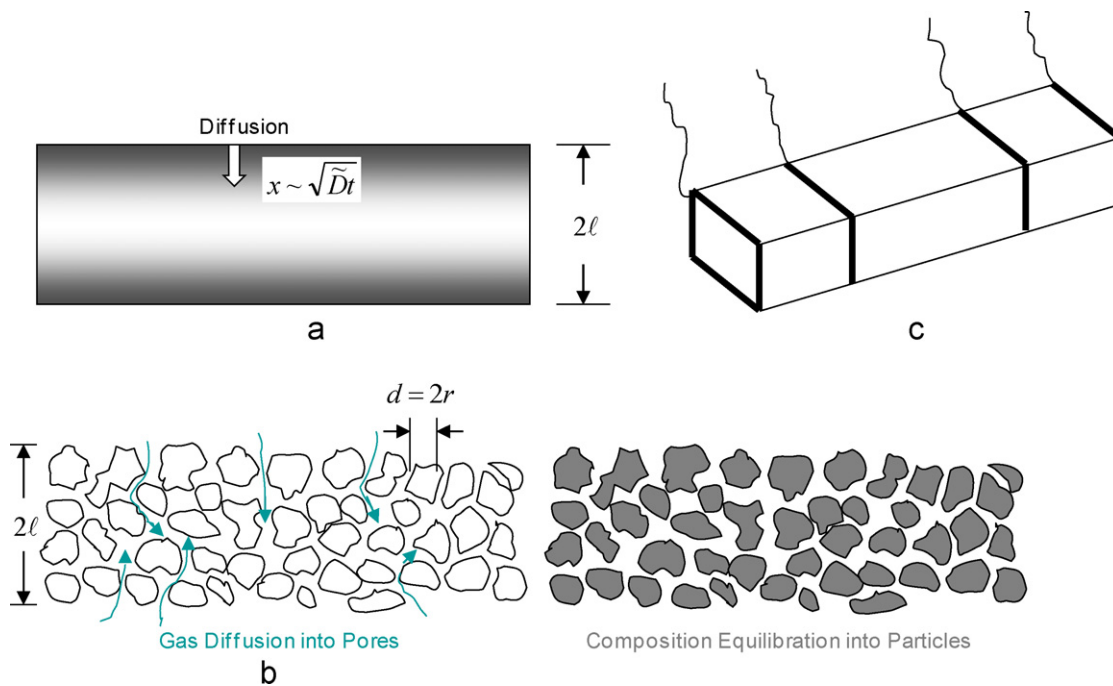*E-mail address:* anil.virkar@m.cc.utah.edu (A.V. Virkar).

Fig. 1. (a) A schematic of the equilibration kinetics in a dense sample. The diffusion distance is given by $x \sim \sqrt{\tilde{D}t}$ where $\tilde{D}$ is the chemical diffusion of the diffusing species (e.g., oxygen). (b) A schematic showing the equilibration kinetics in a porous sample of the same external dimensions as the dense sample. The process involves gas phase diffusion within the porous interstices and solid state diffusion within the particles. Gas phase equilibration occurs rapidly due to the high effective gas phase diffusivity (~ 0.1 cm^2 s^{-1}). Rapid solid state diffusion occurs due to the small particle size. (c) A schematic of the samples used for the four probe DC conductivity measurements.

a 2 mm thick sample is $\sim 10^5$ s; that is ~ 28 h or over a day. Rarely are experiments conducted for more than a few hours of equilibration. This means often equilibration of the sample with the imposed atmosphere may not occur over the duration of the experiment. The lower the temperature, the lower is the $\tilde{D}_O$, and the longer will be the time required for equilibration. If the kinetics are extremely sluggish, stable values of conductivity may be observed. However, stable values in such cases are representative of metastable conditions and do not correspond to the thermodynamically equilibrated state. Thus, reliable measurements corresponding to thermodynamically equilibrated conditions can only be made on dense bulk samples ~ 2 mm thick at sufficiently high temperatures. For RDC, this temperature is probably about 600 °C or may be even higher.

The objective of the present work was to explore the use of porous samples instead of dense samples for the measurement of transport properties of RDC. If a porous sample is used for conductivity measurements, gas transport through the sample will generally be very rapid. Suppose the open (contiguous) porosity in a porous sample is $\sim 30\%$. Typical effective gas diffusivity of air through a porous sample, estimated using the binary O$_2$–N$_2$ diffusivity [24], porosity, and tortuosity is ~ 0.1 cm^2 s^{-1}. Thus, in a porous sample of 2 mm thickness, gas phase equilibration will occur in $(0.1)^2/0.1$ or in ~ 0.1 s. Suppose now that the particle size in the porous sample is ~ 2 μm. Equilibration of composition in the solid phase of the porous sample corresponding to the imposed gas phase will occur in $\sim (1 \times 10^{-4})^2/10^{-7}$ or in ~ 0.1 s. That is, the solid phase in a porous sample of 2 mm thickness will equilibrate a million times faster than a dense sample of the same external dimensions (~ 2 mm). Since the equilibration of a gas phase in porous interstices of porous samples and compositional equilibration within the particles of the porous sample by solid state diffusion are sequential/concurrent steps, the overall time required for thermodynamic equilibration of a porous material with the imposed atmosphere may only be a fraction of the time required for bulk, dense samples. This orders of magnitude difference between the

kinetics of equilibration of dense and porous samples is schematically depicted in Fig. 1(a) and (b).

The preceding shows that the equilibration of a porous sample with the atmosphere can occur in a reasonable time, which is often not possible on a dense sample. Properties of fully dense materials may then be estimated using the measured values on porous samples provided appropriate geometric factors which can relate the conductivity of the porous sample to the corresponding dense sample, are known. Such geometric or correction factors depend upon volume fraction porosity and morphology of the solid phase within the porous body such as the particle size and the inter-particle neck size [25]. If the inter-particle necks in a porous body are relatively wide, a simple correction factor based solely on the volume fraction porosity may be used [25]. Alternatively, if the morphological features such as the particle size and the inter-particle neck size are accurately known, and if the inter-particle necks are narrow, the conductivity of the porous sample can be related to that of the corresponding dense sample by the use of a geometric parameter derived using these parameters [25]. The estimation of such correction or geometric factors requires a thorough characterization of the microstructure.

It is important to have accurate information on the conductivity of dense samples under thermodynamically equilibrated conditions. This is because dense membranes typically used in many electrochemical devices may eventually equilibrate with the atmosphere in the actual device application over the long duration in service. For example, solid electrolytes several tens of microns thick may equilibrate with the imposed atmosphere over hundreds or thousands of hours of operation. If the design of such devices however is based on measurements made on bulk dense samples, which only give the initial values under non-equilibrated conditions, the predictions of long term performance made using such measurements may likely be inaccurate. Measurements made on porous samples, and corrected using appropriate geometric factors to obtain the corresponding properties of dense samples, on the other hand provide a way to estimate properties

of dense materials necessary for use in actual devices such as an electrolyte in SOFC. Additionally, the measurement of conductivity on porous bodies is important in its own right since electrodes are porous and rapidly equilibrate with the imposed atmosphere. Thus, measurements made on porous samples can be directly used for the design of SOFC electrodes. This was the principal motivation for the present study. The experimental procedure used, the results obtained and the discussion of results are given in the following paragraphs.

2. Experimental procedure

Samaria-doped ceria powder of composition $Sm_{0.15}Ce_{0.85}O_{2-\delta}$ (SDC) was obtained from fuel cell materials. The reported surface area of the SDC powder was $40\,m^2\,g^{-1}$. The SDC powder was mixed with carbon powder (HTW, Sigradur K-spherical powder ~10–20 μm in diameter) and ethanol with ethylene glycol added as a binder. Zirconia milling media were then added and the mixture was ball milled for 12 h. The milling media were subsequently removed from the jar, the mixture was placed in a beaker, and heated on a hotplate to evaporate away ethanol. The dried powder was then dry milled. Rectangular, bar-shaped samples were formed by uniaxial pressing. Samples were sintered in air at 1400 °C for 2 h. The approximate dimensions of the sintered samples were: 4.5 cm × 1 cm × 2 mm. The porosity of the samples was measured using a fluid immersion method with water as the fluid. Fracture surfaces of the sintered samples were examined on a scanning electron microscope (SEM).

Platinum stripes were painted using platinum paste on the samples in a four probe configuration. The distance between the inner stripes was 2 cm while that between the outer stripes was 4 cm. Platinum wires were connected to the four stripes. Fig. 1(c) shows a schematic of the samples used for four probe DC conductivity measurements. In a typical experiment a sample with four platinum wires connected was placed inside a tubular furnace equipped with end fixtures and feed-throughs. The wires attached to the outer probes were connected to a Keithley 6517A electro-meter (which is also a DC power supply) and the wires attached to the inner probes were connected to a Keithley 2100 multi-meter. Data collection was accomplished using a laptop computer and LabView software.

Conductivity was measured over a range of oxygen partial pressures achieved using various gas mixtures: (a) ultra-high purity hydrogen, (b) ultra-high purity argon, (c) 10% O_2 + 90% N_2, (d) air, and (e) pure O_2. An oxygen sensor (CoorsTek) was used to measure the Nernst voltage of the atmosphere in the furnace referenced to air. The corresponding oxygen partial pressures in the furnace near the sample were estimated. Conductivity measurements were made over a temperature range between 200 °C and 800 °C in 50 or 100° intervals during heating as well as during cooling.

3. Results and discussion

The typical measured porosity of the samples was ~45%. Fig. 2(a) shows an SEM micrograph of a typical sintered sample. Fig. 2(b) is a higher magnification SEM image of the sample showing the morphological details. The typical particle size within the sample is on the order of 5 μm. Individual particles contained several grains of ~1–2 μm in size. The SEM image also shows that inter-particle necks are well developed in this sample. If the inter-particle necks are sufficiently wide, the relationship between the conductivity of a fully dense sample, σ_{dense}, the conductivity of the porous sample, σ, and the volume fraction porosity, V_v, is simply given by [25]

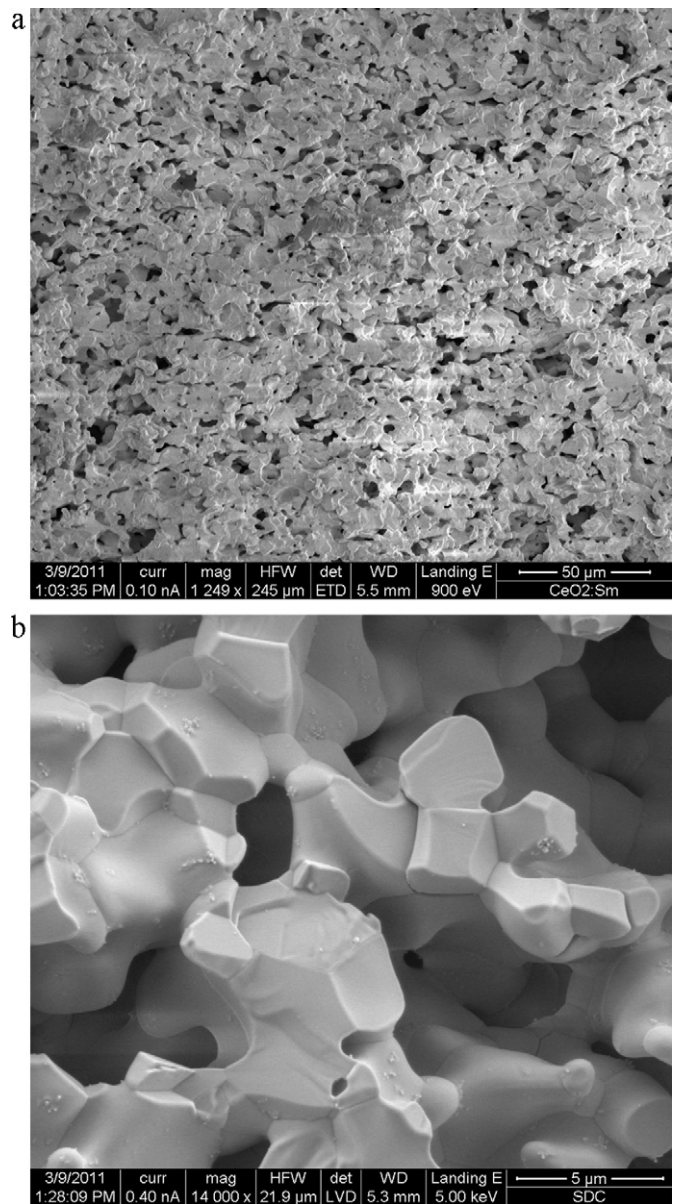$$\sigma_{dense} \approx \frac{\sigma}{(1 - V_v)} \tag{1}$$

Fig. 2. (a) An SEM micrograph of a porous SDC sample. The volume fraction porosity is ~0.45. (b) A higher magnification SEM micrograph showing the morphology; the particle size and the inter-particle neck size.

A more accurate relationship between particle size, neck size, volume fraction porosity, conductivity of particles, and the conductivity of the dense body is given in [25]. If the necks are narrow (poorly sintered materials), it is necessary to use the more accurate equation [25]. In the present work, for the sample whose SEM image is shown in Fig. 2(b), the simple relation is satisfactory. Thus, the conductivity values of dense samples can be readily estimated from measurements made on most of the porous samples in the present work. In this work, only the conductivity values of porous samples are reported.

Fig. 3 shows the measured conductivity of a porous SDC sample by a four probe DC method over the temperature range between 250 and 800 °C in humidified hydrogen, plotted vs. time during the experiment. This particular sample did not have well developed necks. Thus, it is expected that the more accurate correction factor given in [25] will be needed to obtain the corresponding conductivity of a dense sample. This correction factor is higher than $1/(1 - V_v)$ given in Eq. (1) [25]. The profound effect of morphol-
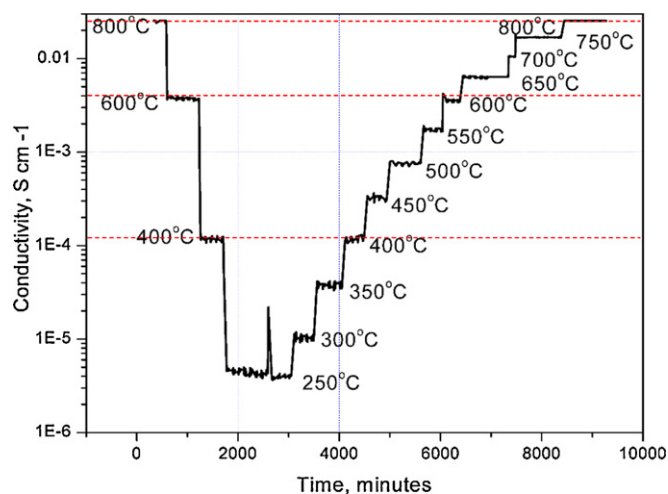
Fig. 3. Conductivity of a porous SDC sample measured by a four probe DC technique in humidified hydrogen over a temperature range from 250 °C to 800 °C. Measurements were made during cooling and heating. Conductivity rapidly equilibrated even at the lowest temperature of 250 °C. Also, conductivity at a given temperature was the same during both cooling and heating. The spike at 250 °C is due to temporary malfunction of the recording instrument.

Fig. 4. Estimated oxygen partial pressure as a function of temperature in hydrogen. Above 300 °C, the estimated oxygen partial pressure at a given temperature is about the same during cooling and heating.

ogy on conductivity has been discussed in detail in Ref. [25]. The purpose of this experiment to determine if rapid equilibration can be achieved using a porous sample. In this experiment, the sample was initially heated to 800 °C and its conductivity was measured. Measurements thereafter were made at 600 °C, 400 °C, and 250 °C during cool down. For each measurement, the sample was maintained at a given temperature for a sufficient period of time to ensure that stable values of conductivity were recorded. The sample was subsequently heated and measurements were again made during heating to 800 °C in 50° intervals. These data are also shown in Fig. 3.

Two observations can be made based on this experiment. (a) The conductivity rapidly equilibrated once the sample reached a given temperature. For example, as the temperature was lowered from 800 °C to 600 °C, the conductivity decreased from ~0.02 S cm^{-1} to ~0.004 S cm^{-1}, and then remained constant. The time dependence of the decrease in conductivity coincided with the rate of change of the sample temperature. Once the temperature reached 600 °C, no further change in conductivity occurred. This observation indicates that rapid equilibration of the sample conductivity occurred under the imposed atmosphere. The observation that stable values were obtained at the lowest temperature (250 °C) at which measurements were made on this sample also indicates that solid state equilibration (by oxygen chemical diffusion) was sufficiently rapid even at such a low temperature due to the small diffusion distance in the sample containing micron size particles. That is, much of the time required for equilibration to occur at a new temperature was the time required for the sample temperature to stabilize to the new value. Approximate time required for equilibration to occur in the sample containing ~5 μm size particles at the lowest temperature of 250 °C from Fig. 3 is ~10 min. The estimated chemical diffusion coefficient of oxygen thus is $(2.5 \times 10^{-4})^2/(10 \times 60)$ or $\tilde{D}_O \approx 10^{-10}$ cm^2 s^{-1}. No independently measured data on the chemical diffusion coefficient of oxygen in SDC at such a low temperature are available. The present measurements however show that even with such low values of the chemical diffusion coefficient, rapid equilibration is expected in porous samples. A dense sample of 2 mm in thickness, on the other hand, would require 3 years to equilibrate. Thus, any stable values observed in short term experiments (a few hours) would be indicative of metastable conditions, and not equilibrated conditions. (b) Measurements at 800 °C,
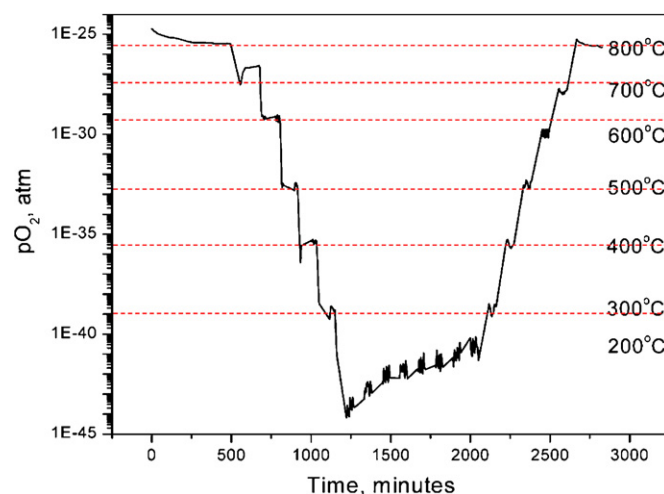
700 °C, and 600 °C made during both cooling and heating show that identical conductivity values were obtained at any given temperature. This observation also shows that the sample truly equilibrated with the atmosphere. Thus, the present measurements represent the true values of conductivity of the *porous* sample under equilibrated conditions.

Fig. 4 shows the estimated oxygen partial pressure in the hydrogen feed gas near the sample in the furnace as a function of temperature obtained from the measured sensor voltage. Depending upon temperature, the oxygen partial pressure measured in pure hydrogen by the oxygen sensor ranged between ~10^{-52} and ~10^{-25} atm. At any given temperature, the pO$_2$ was high enough to ensure the thermodynamic stability of YSZ in the sensor. A significant drift in the measured sensor voltage was observed at the lowest measurement temperature of 200 °C reflecting a drift in the estimated oxygen partial pressure. Thus, the accuracy of the oxygen partial pressure measurement at such a low temperature is probably not good. The horizontal broken lines in Fig, 4 however show that at 300 °C and above, the estimated oxygen partial pressure at a given temperature is approximately the same during both cooling and heating. Thus, it was assumed that sensor response is accurate above 300 °C. The estimated oxygen partial pressures from the sensor voltages should correspond to a certain pH$_2$/pH$_2$O ratio. Using the calculated pO$_2$ from the measured sensor voltages and using the Ellingham diagram [26], the corresponding pH$_2$/pH$_2$O ratios were estimated over the temperature range from 300 °C to 800 °C. The estimated pH$_2$/pH$_2$O ratio at 300, 600, 700, and 800 °C was about 2×10^3 or pH$_2$O ~5×10^{-4} atm. The estimated value of pH$_2$O at 400 and 500 °C was ~5×10^{-3} atm. This variation is believed to be due to some experimental scatter. It is also possible that there may have been leaks in the fixtures allowing some air in thus raising the H$_2$O content. It is thus concluded that the pH$_2$O in the hydrogen gas circulated was approximately in the range 5×10^{-4}–5×10^{-3} atm. Such a low value of pH$_2$O is consistent with the reasonably dry H$_2$ used in the experiment.

Fig. 5 shows the plots of log(conductivity) vs. log(oxygen partial pressure) over the temperature range from 200 to 800 °C. These data were obtained on another sample. This sample had well-developed inter-particle necks. The representative SEM micrograph is given in Fig. 2. Thus, the correction factor of $1/(1 - V_v)$ given in Eq. (1) is considered satisfactory. The broken lines show the minimum conductivity values at a given temperature. From Fig. 5, at 800 °C in air, the measured conductivity is ~0.024 S cm^{-1}. The volume fraction porosity of this samples was ~0.45. Thus, the
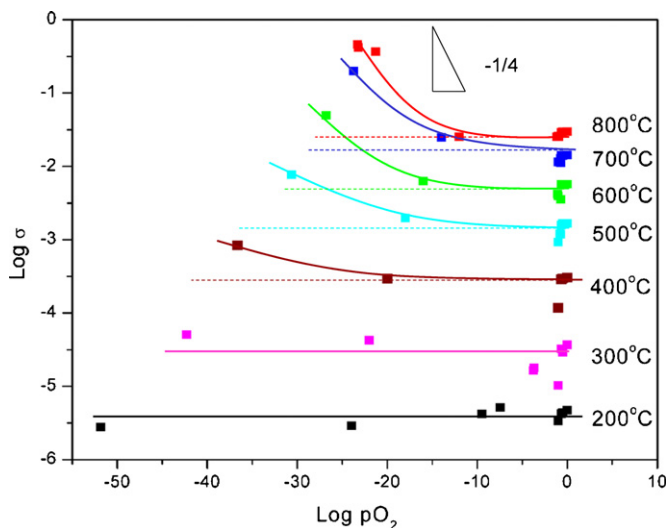
Fig. 5. Conductivity as a function of oxygen partial pressure over a temperature range from 200 °C to 800 °C. These data were obtained on another sample. Representative SEM micrographs are given in Fig. 2. The horizontal broken lines correspond to the ionic conductivity. Higher total conductivity at lower oxygen partial pressures is due to the contribution from electronic conduction. Significant electronic conduction occurs at 400 °C (and above) in hydrogen. The oxygen partial pressure dependence of electronic portion of the conductivity is given by $\sigma_{elec} \propto p_{O_2}^{-1/4}$. The inset shows a line with a slope of $-1/4$.

Fig. 6. Arrhenius plot of (conductivity × temperature) vs. 1/temperature for the sample tested in hydrogen. Fit to data points at 200 °C and 300 °C extrapolated to higher temperatures corresponds to ionic conductivity. The corresponding activation energy is ~74 kJ mol^{-1}. Fit to data points between 300 °C and 800 °C gives an activation energy of ~101 kJ mol^{-1}. Despite a linear plot on the semi-log scale, this does not represent unique activation energy because of the significant electronic conduction at higher temperatures. The triangles are the data corresponding to the minimum values of the measured conductivity as a function of oxygen partial pressure at various temperatures. These correspond to ionic conduction.

estimated value of conductivity of a fully dense sample would be ~0.043 S cm^{-1}. This value is in reasonably good agreement with many reported data on SDC in air at 800 °C.

The oxygen partial pressure given on the x-axis is as estimated using the oxygen sensor voltage. The oxygen partial pressures at 200 °C are probably not accurate. At any given temperature, the data point corresponding to the lowest pO$_2$ is that corresponding to the conductivity measured in dry hydrogen. As stated above, this corresponds to pH$_2$O approximately between 5×10^{-4} and 5×10^{-3} atm. Since the pH$_2$O is much higher than pO$_2$ in the atmosphere, it is assumed that pH$_2$O/pH$_2$ ratio essentially fixes the pO$_2$ at any given temperature. Thus, the higher the temperature, the higher is the pO$_2$, which ranges is between ~10^{-52} atm at 200 °C and ~10^{-25} atm at 800 °C [26]. At the lowest measurement temperature of 200 °C, the conductivity is essentially independent of pO$_2$ (actually it somewhat decreases with decreasing pO$_2$, which may be related to some scatter). At 300 °C, the conductivity slightly increases with decreasing pO$_2$. At 400 °C and above, the conductivity clearly increases with decreasing pO$_2$. Also, the increase in conductivity with decreasing pO$_2$ occurs at progressively higher pO$_2$ at higher temperatures, in accord with the considerable literature on RDC which shows that the electrolytic domain narrows as the temperature increases [1,20].

The increase in conductivity at low pO$_2$ is thus due to electronic conduction. At any pO$_2$ at a given temperature, the difference between the broken straight line and the bold curved line in Fig. 5 is a measure of electronic conduction. At 800 °C, significant electronic conduction occurs at values of pO$_2$ less than about 10^{-10} atm. The typical pO$_2$ in 'dry' hydrogen as a fuel at 800 °C is ~10^{-25} atm. At this pO$_2$ and temperature, the electronic conductivity is about 15 times the ionic conductivity. This is of course well known and thus RDC is not a suitable electrolyte for SOFC at 800 °C (without an electron blocking layer such as YSZ) [4,27]. At 500 °C also, significant rise in electronic conduction occurs below about 10^{-16} atm.

Matsui et al. [20] have investigated the electrolytic domain of SDC over a temperature range from 400 °C to 800 °C. These authors also observed significant electronic conduction in hydrogen at a temperature as low as 400 °C. The measurements in the work by
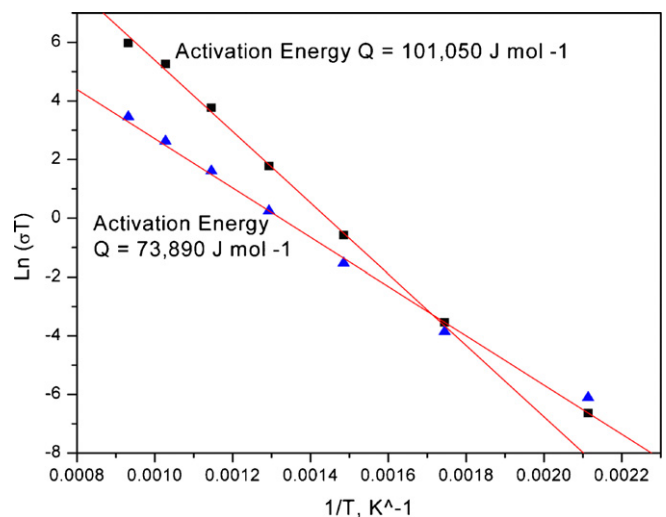
Matsui et al. [20] were conducted on dense bulk samples. A comparison of their Fig. 2 with Fig. 5 of the present work shows that in the present work the electrolytic domain is found to be much narrower. For example, Matsui et al. [20] observed electronic conduction at 400 °C below a pO$_2$ of 10^{-32} atm. By contrast, in the present work, electronic conduction is detected below a pO$_2$ of 10^{-20} atm at 400 °C. Similarly, Matsui et al. [20] observed electronic conduction at 800 °C below a pO$_2$ of 10^{-15} atm. In the present work, this transition at 800 °C occurs at a pO$_2$ of 10^{-10} atm. That is, the electrolytic domain measured in the present work is much narrower than reported by Matsui et al. [20]. The principal difference between the two studies is in the use of porous samples in the present work (instead of dense samples in [20]) which allowed rapid equilibration of the sample with the atmosphere thereby facilitating accurate determination of the electrolytic domain.

Fig. 6 shows a plot of ln(conductivity × temperature) vs. T^{-1} for the measurements made in pure hydrogen (squares). The data over the temperature range from 300 °C to 800 °C can be reasonably well described by a single activation energy of ~101 kJ mol^{-1} (the data point at 200 °C is slightly off the line). An additional line shown in the figure is obtained by joining the data points at 200 °C and 300 °C and extending it over the entire temperature range of the present study. From Fig. 5, the ionic conductivity at any given temperature regardless of the pO$_2$ is obtained as the minimum value at the temperature. This is based on the assumption that oxygen vacancy concentration is half the dopant (Sm) concentration in accord with simple defect chemistry. These values are given by the horizontal broken lines in Fig. 5. These values are also shown in Fig. 6 (triangles). These points (triangles) lie on the line joining the data points at 200 °C and 300 °C obtained in hydrogen (squares). As stated earlier, at any temperature, the difference between the two lines (bold and broken) in Fig. 5 gives the electronic conductivity at the corresponding oxygen partial pressure, pO$_2$. The data point corresponding to the lowest pO$_2$ at any temperature is that corresponding to the measurement in hydrogen. For example at 800 °C, the ionic conductivity is ~0.024 S cm^{-1} while the measured total conductivity in hydrogen is ~0.415 S cm^{-1}. Thus, the electronic conductivity at 800 °C in hydro-

gen is $\sim(0.415-0.024) = 0.391\,\mathrm{S\,cm^{-1}}$. At 500 °C, the measured minimum conductivity (ionic) is $\sim 1.698 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$ while the measured total conductivity in hydrogen is $\sim 7.079 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$. Thus, the electronic conductivity at 500 °C in hydrogen is $\sim(7.079 \times 10^{-3} - 1.698 \times 10^{-3}) = 5.381 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$. That is, the ionic transference number of SDC at 500 °C in hydrogen is only ~ 0.24. From Fig. 6, the estimated ionic transference number of SDC even at 400 °C in hydrogen is only ~ 0.4.

Triangles in Fig. 6 correspond to ionic conduction. The corresponding activation energy for oxygen ion conduction is estimated to be $\sim 74\,\mathrm{kJ\,mol^{-1}}$. In the extrinsic regime, the measured activation energy corresponds to that for oxygen vacancy migration. This measurement is in reasonably good agreement with the activation energy of $\sim 65\,\mathrm{kJ\,mol^{-1}}$ for oxygen vacancy migration given in a study by Wang et al. [11].

The observation that the electronic conductivity of SDC in hydrogen at 500 °C is about 3–4 times that of the ionic conductivity suggests that SDC is not a satisfactory electrolyte even at temperatures as low as 500 °C with pure hydrogen as a fuel. That is, the electrolytic domain is rather narrow at 500 °C [20]. The same is expected of ceria containing other rare earth oxides as dopants. For application as an electrolyte in SOFC, it would thus be necessary to block off the electronic current through ceria by depositing an electron blocking layer of a predominantly ionically conducting material such as YSZ [4,27]. The preceding conclusions are based on measurements made on samples in hydrogen. In an actual SOFC the cathode side is exposed to a relatively high pO₂ at which the RDC is a predominantly oxygen ion conductor. The overall transference number of the cell in such a case will be somewhat higher, as previously discussed by Riess [28]. Nevertheless, the general conclusion still is that it may be necessary to block off the electron current by depositing a thin layer of a material such as YSZ on RDC [4,27].

The data in Fig. 5 at 200 °C show that the electronic conductivity of SDC is negligible even at the lowest pO₂ corresponding to pure hydrogen. There is some measurable electronic conductivity at 300 °C at the lowest pO₂ at which measurements were made. It is known that electrodes with mixed ionic electronic conduction exhibit improved electrocatalysis. Any mixed (electronic) conductivity of the composite anode containing RDC as a constituent at low temperatures will be due solely to nickel. In order to introduce MIEC characteristics in single phase RDC at low temperatures (~ 300 °C), it may be necessary to dope ceria with an element which exhibits redox characteristics at higher oxygen partial pressures than does cerium.

4. Summary

Conductivity of porous samples of Sm_2O_3-doped CeO_2 (SDC) of composition $Sm_{0.15}Ce_{0.85}O_{2-\delta}$ was measured using a four probe DC method over a temperature from 200 °C to 800 °C in 'pure' oxygen, in 'pure' hydrogen and in humidified hydrogen. The conductivity rapidly equilibrated even at the lowest measurement temperature of 200 °C, which is attributed to fast equilibration of the gas phase in porous interstices and fast compositional (thermodynamic) equilibration in the few micron-sized ($\sim 5\,\mu m$) particles of the porous samples by solid state diffusion. For an assumed oxygen chemical diffusion coefficient, $\tilde{D}_O$ of $10^{-10}\,\mathrm{cm^2\,s^{-1}}$ at a low temperature of 250 °C, the required equilibration time in the porous SDC is only about 10 min. A dense sample of $\sim 2\,\mathrm{mm}$ in thickness, by contrast, would require over a year to equilibrate. The present work thus shows that in order to obtain conductivity values corresponding to thermodynamically equilibrated conditions, measurements should be made on porous samples instead of dense samples. Then the conductivity of dense samples under thermodynamically equilibrated conditions can be obtained using a geometric factor which accounts
for porosity and microstructural details [25]. If the inter-particle necks are sufficiently wide, the geometric factor is simply related to the volume fraction porosity as given in Eq. (1). A more accurate correction factor will be necessary if the inter-particle necks are too narrow [25].

It was observed that SDC became a mixed ionic electronic conductor with increasing temperature and decreasing pO₂. While this result is expected, the present work showed that even at a temperature as low as 500 °C, the electronic conductivity of SDC in hydrogen atmosphere is about 4 times the ionic conductivity. The use of porous samples allowed rapid equilibration and facilitated the measurement of true thermodynamically equilibrated properties, which is generally not possible using dense bulk samples due to the long equilibration times required. The present work thus shows that SDC may not be a satisfactory electrolyte for SOFC with pure hydrogen as a fuel without depositing a thin YSZ layer to block off the electronic current [4,27]. At temperatures below about 300 °C, however, the electrolytic domain of SDC is wide enough to permit the use of SDC as an electrolyte. The conductivity of SDC at 300 °C is, however, rather low and it will be necessary to use it as a thin film to minimize ohmic losses. The observation that SDC exhibits negligible electronic conductivity below ~ 300 °C even in a highly reducing environment implies that if used as a constituent in an anode functional layer of a low temperature SOFC, the mixed conductivity will be solely due to the addition of a metallic phase, such as nickel. It may be necessary to dope ceria with elements that exhibit redox properties at higher pO₂ to introduce mixed conductivity in SDC and thereby lower activation polarization.

Although the present experiments were conducted only on SDC, it is expected that the conclusions reached here would be broadly applicable to ceria doped with other rare earth oxides. The main conclusion of the work is that the electrolytic domain of RDC appears to be narrower than thought previously. The use of porous samples facilitated the accurate determination of the electrolytic domain of RDC as a function of temperature and pO₂.

Acknowledgements

References

[1] H.L. Tuller, A.S. Nowick, J. Electrochem. Soc. 122 (2) (1975) 255–259.
[2] D.Y. Wang, A.S. Nowick, J. Solid State Chem. 35 (3) (1980) 325–333.
[3] D. Braunshtein, D.S. Tannhauser, I. Riess, J. Electrochem. Soc. 128 (1) (1981) 82–89.
[4] H. Yahiro, Y. Baba, K. Eguchi, H. Arai, J. Electrochem. Soc. 135 (8) (1988) 2077–2080.
[5] T. Inoue, T. Setoguchi, K. Eguchi, H. Arai, Solid State Ionics 35 (34) (1989) 285–291.
[6] H. Yahiro, K. Eguchi, H. Arai, Solid State Ionics 36 (12) (1989) 71–75.
[7] K. Eguchi, T. Setoguchi, T. Inoue, H. Arai, Solid State Ionics 52 (1–3) (1992) 165–172.
[8] K. Yamashita, K.V. Ramanujachary, M. Greenblatt, Solid State Ionics 81 (12) (1995) 53–60.
[9] S.J. Hong, K. Mehta, A.V. Virkar, J. Electrochem. Soc. 145 (2) (1998) 638–647.
[10] Z. Zhan, T. Wen, H. Tu, Z. Lu, J. Electrochem. Soc. 148 (5) (2001) A427–A432.
[11] S. Wang, T. Kobayashi, M. Dokiya, T. Hashimoto, J. Electrochem. Soc. 147 (10) (2000) 3606–3609.
[12] F. Wang, S. Chen, S. Cheng, Electrochem. Commun. 6 (8) (2004) 743–746.
[13] T. Matsui, T. Kosaka, M. Inaba, A. Mineshige, Z. Ogumi, Solid State Ionics 176 (78) (2005) 663–668.
[14] D.A. Andersson, S.I. Simak, N.V. Skorodumova, I.A. Abrikosov, B. Johansson, Proc. Natl. Acad. Sci. U.S.A. (2006) 1–6.
[15] G.B. Balazs, R.S. Glass, Solid State Ionics 76 (1995) 155–162.
[16] R.T. Dirstine, R.N. Blumenthal, T.F. Kuech, J. Electrochem. Soc. 126 (1979) 264.
[17] H. Yahiro, Y. Eguchi, K. Eguchi, H. Arai, J. Appl. Electrochem. 18 (1988) 527–531.
[18] K. Eguchi, J. Alloys Compd. 250 (1997) 486–491.

[19] V.V. Kharton, F.M. Figueiredo, L. Navarro, E.N. Naumovich, A.V. Kovalevsky, A.A. Yaremchenko, A.P. Viskup, A. Carneiro, F.M.B. Marques, J.R. Frade, J. Mater. Sci. 36 (2001) 1105–1117.
[20] T. Matsui, M. Inaba, A. Mineshige, Z. Ogumi, Solid State Ionics 176 (2005) 647–654.
[21] H. Inaba, H. Tagawa, Solid State Ionics 83 (1996) 1–16.
[22] H. Yahiro, T. Ohuchi, K. Eguchi, H. Arai, J. Mater. Sci. 23 (1988) 1036–1041.
[23] Z. Tianshu, P. Hing, H. Huang, J. Kilner, Solid State Ionics 148 (2002) 567–573.
[24] E.L. Cussler, Diffusion: Mass Transfer in Fluid Systems, Cambridge University Press, Cambridge, UK, 1995.
[25] F. Zhao, A.V. Virkar, J. Power Sources 195 (2010) 6268–6279.
[26] D.R. Gaskell, Introduction to the Thermodynamics of Materials, third ed., Taylor & Francis, Washington, DC, 1995.
[27] A.V. Virkar, J. Electrochem. Soc. 138 (5) (1991) 1481–1487.
[28] I. Riess, J. Electrochem. Soc. 128 (10) (1981) 2077–2081.