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ACTIVE CATHODES FOR SUPER-HIGH POWER DENSITY SOLID OXIDE FUEL CELLS THROUGH SPACE CHARGE EFFECTS

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ABSTRACT

This report summarizes the work done during the eleventh quarter of the project. Conductivity relaxation experiments were conducted on porous La_{0.5}Sr_{0.5}CoO_{(3-δ)} (LSC50) samples over a temperature range from 350 to 750°C, and over an oxygen partial pressure, $p_{O_2}$, switch between 0.04 and 0.06 atm in order to determine the surface exchange coefficient, $k_{chem}$. The normalized conductivity data could be fitted to a first order kinetic equation. The time constant decreased with decreasing temperature between ~750 and ~450°C, but sharply increased with decreasing temperature between 450 and 350°C. The corresponding $k_{chem}$ was estimated using three models: (a) A porous body model wherein it is assumed that the kinetics of surface exchange is the slowest. (b) Solution to the diffusion equation assuming the particles can be approximated as spheres. (c) Solution to the diffusion equation assuming the particles can be approximated as cylinders. The values of $k_{chem}$ obtained from the three models were in good agreement. In all cases, it was observed that $k_{chem}$ increases with decreasing temperature between 750 and 450°C, but below 450°C, it sharply decreases with further decrease in temperature.
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INTRODUCTION

Electrode transport properties, namely ionic and electronic conductivities, and morphology have a profound effect on electrode polarization and thus on solid oxide fuel cell (SOFC) performance. A large part of the polarization loss is associated with the cathode in the form of activation polarization. Mixed Ionic and Electronic Conducting (MIEC) materials are often used as oxygen separation membranes, in gas sensors and as cathodes in solid oxide fuel cells. The description of transport in MIECs requires the knowledge of two parameters, the chemical diffusion coefficient, $D\tilde{}$, and the chemical surface exchange coefficient, $k_{chem}$ [1]. The former describes transport through bulk, while the latter describes transport across gas phase/solid phase interfaces. The parameters $D\tilde{}$ and $k_{chem}$ are functions of composition, microstructure, temperature and atmosphere. Conventional methods for determining $D\tilde{}$ and $k_{chem}$ include radio isotope, O18, exchange (analyzed using secondary ion mass spectroscopy - SIMS), oxygen permeation experiments [2-4] and conductivity relaxation. The conductivity relaxation technique has been widely used because of simplicity of procedure, which involves measurement of conductivity as a function of time upon an abrupt change in $p_{O_2}$. When exposed to a $p_{O_2}$ change, the sample under test re-equilibrates to the new $p_{O_2}$ with a concomitant change in conductivity. This change can be an increase or decrease, depending on the new atmosphere and upon the defect chemistry. An analysis of the change of conductivity with time can be used to estimate $D\tilde{}$ and $k_{chem}$.

The ratio of $D\tilde{}$ to $k_{chem}$ has units of length and is defined as the critical thickness, $l_{cr}$ [5]. For sample thickness $>> l_{cr}$, the kinetics of oxygen exchange is governed by $D\tilde{}$. For sample thickness $<< l_{cr}$, the kinetics of oxygen exchange is governed by $k_{chem}$. Typically conductivity relaxation is conducted on dense bar-shaped samples of thickness $\geq l_{cr}$. On many materials, experimental work on dense samples over a temperature range between ~600 and 900°C has shown that both $D\tilde{}$ and $k_{chem}$ increase with increasing temperature, and follow an Arrhenius behavior [6-8]. The use of a porous sample with average particle size $<< l_{cr}$ to determine $k_{chem}$ has been demonstrated by this group in previous work [9-11]. The experimental approach is identical to that used on dense bodies but the kinetics of equilibration was shown to depend only on $k_{chem}$ without any influence from $D\tilde{}$. The equilibration times for porous MIEC samples of composition La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC40) and La$_{0.8}$Sr$_{0.2}$FeO$_{3-\delta}$ (LSF20) increased with decreasing temperature over a temperature range from 600 to 800°C, especially at lower $p_{O_2}$'s [9-11]. That is, the relaxation time was smaller at lower temperatures and the corresponding calculated $k_{chem}$ increased with decreasing temperature over the temperature range investigated. That is, the temperature dependence of $k_{chem}$ obtained using dense samples reported in the literature and porous samples are opposite. Clearly, the temperature dependence of $k_{chem}$ obtained from porous samples cannot be described by a thermally activated process. Increasing $k_{chem}$ with decreasing
temperature appears to be consistent with its possible dependence on oxygen surface coverage, in turn governed by an adsorption isotherm such as Langmuir.

This report presents further conductivity relaxation work on La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (LSC50) using porous samples of a very fine particle size in an attempt to investigate surface exchange kinetics over a wider temperature range, down to 350°C. LSC50 was chosen as the MIEC material of choice because of its excellent ionic conductivity even at low temperatures. The critical thickness, $l_{cr}$, is expected to decrease with decreasing temperature. For this reason, samples of a very fine particle size were made so that the average particle size would be below $l_{cr}$ to as low a temperature as possible. It is expected that surface kinetics will be rate limiting down to some temperature below which diffusion becomes sluggish – and a transition from surface exchange control to diffusion control is expected at lower temperatures.

The analysis of data is done using the porous sample model developed previously [9-11], and also by approximating the particle shape in the porous sample to spherical and cylindrical geometries and using the mathematical solutions of diffusion equations given by Crank [12]. The mathematical solutions to diffusion equations for flux across a surface and into the bulk involve both diffusion and surface exchange terms. However, for a particle size well below $l_{cr}$ at a given temperature, the solutions are sensitive to surface exchange kinetics only. The spherical and cylindrical models are then used to obtain values of $k_{chem}$ down to a temperature where transition from surface exchange control to diffusion control occurs.
EXECUTIVE SUMMARY

Solid oxide fuel cells (SOFC) can operate over a wide temperature range, from ~600 to 1000°C, and can use a variety of hydrocarbon fuels, once appropriately processed. The current target for SOFC is about 800°C, although efforts are presently underway to lower the operating temperature below 700°C. The largest voltage loss (polarization) in SOFC is known to occur at the cathode, especially at relatively low temperatures (<800°C). There are two types of cathodic polarizations: (1) Concentration polarization – that associated with gas transport. (2) Activation polarization – that associated with the occurrence of the overall electrochemical cathodic reaction of charge transfer. Two types of material sets are used for cathode in SOFC: (1) Composite materials containing two phases – one capable of transporting predominantly oxygen ions, and the other capable of transporting predominantly electronic defects. In such cathodes, the relevant parameters governing electrocatalysis are the charge transfer resistivity, $\rho_{ct}$, the ionic resistivity, $\rho_i$, and the three phase boundary length, $\ell_{TPB}$. Report No. 10 (for the period January 1, 2005 through March 31, 2005) described in detail methods used to measure $\rho_{ct}$ using patterned electrodes. (2) Single phase mixed ionic – electronic conductors or MIEC. These materials transport both ionic and electronic defects. The relevant parameters which govern electrocatalysis are the surface exchange coefficient, $k_{chem}$, the chemical diffusion coefficient, $D_\text{~}$, and the net specific pore surface area, $S_p$. This report describes theory, experimental procedure, and results obtained on the measurement of $k_{chem}$ on MIEC cathode materials using conductivity relaxation. The material selected for the work was La$_{0.5}$Sr$_{0.5}$CoO$_{(3-\delta)}$ or LSC50.

The traditional approach consists of using dense samples of an MIEC, apply electrical contacts, heat the sample to the desired temperature and expose to a given atmosphere containing certain oxygen partial pressure, $p_{O_2}$. The electrical conductivity of the sample is measured. Then, an abrupt change of atmosphere is made such that the sample is now exposed to a different $p_{O_2}$. This leads to uptake of oxygen by (or expulsion of oxygen from) the sample, simultaneously changing its conductivity. The time dependence of conductivity is measured, and the response is analyzed using two adjustable parameters - the surface exchange coefficient, $k_{chem}$, the chemical diffusion coefficient, $D_\text{~}$. Depending upon the sample dimensions and temperature, often the kinetics are predominantly governed by only one parameter – making it difficult to accurately estimate the parameters.

In the present work, porous samples were used instead of dense samples. In the porous samples used, the particle size was on the order of a few microns or a fraction of micron. Under such conditions, diffusion into the particles is rather rapid, and the kinetics are exclusively controlled by the surface exchange coefficient, $k_{chem}$. The analysis of conductivity response affords an accurate method of estimating $k_{chem}$ - the parameter which governs cathodic electrocatalysis. This report describes the theory, experimental procedure used, the results obtained, and discussion of the results.
EXPERIMENTAL

Theoretical Basis:

When a porous MIEC sample placed in a chamber is subjected to an abrupt \( p_{O_2} \) change, four processes occur, each having a different time constant or a characteristic time. The four processes are: (a) Change of atmosphere in the chamber. (b) Transport of the gaseous atmosphere into the porous interstices of the porous sample. (c) Surface exchange on the interior surfaces of the porous body. (d) Chemical diffusion of oxygen into the particles of the sample. In order to determine \( k_{chem} \) by this technique, step (c) must be the slowest; that is, having a time constant or a characteristic time greater than for the other three processes. Figure 1 shows a schematic of the 4 processes that occur.

By selecting a small chamber size, and by using a high gas flushing rate, the time constant/characteristic time for process (a) can be made quite small. In reality the assumed ‘step change’ in \( p_{O_2} \) is not instantaneous and there is a finite gas exchange time. Gas exchange times of more than a few seconds can adversely affect the accuracy, especially at short time periods [13]. The time constant, \( \tau_{ch} \), to flush the chamber with the new atmosphere, as defined by den Otter et al. [14], is given by

\[
\tau_{ch} = \frac{V_r}{\Phi_{v,\text{tot}}} \frac{T_{STP}}{T_r}
\]

where \( V_r \) and \( T_r \) are the reactor volume and temperature, respectively, \( \Phi_{v,\text{tot}} \) is the flow rate of the gas and \( T_{STP} \) refers to room temperature. Equation (1) assumes that the chamber can be treated as a continuously stirred tank reactor (CSTR), which requires perfect mixing (extreme limit of turbulent mixing) [15]. The experiments were conducted in a specially designed and built quartz tube. The effective volume of the sample chamber, i.e. chamber volume minus volume of sample and insulated current leads, was \( \sim 6.3 \pm 0.5 \text{ cm}^3 \). At a gas flow rate of 600 ml/min, the time constant for switching the atmosphere in the chamber at 800°C was approximately 0.17 sec. This calculation assumes a continuously stirred tank reactor (CSTR), which requires complete mixing, typical of extreme limit of turbulent behavior. Calculations using the effective tube diameter and volume flow rate, however, yield a Reynolds number of \( \sim 45 \) to 40 between 600 and 800°C, which corresponds to laminar flow and well below that for a turbulent flow. For a laminar flow, the change of atmosphere in the chamber cannot be described by a first order kinetic equation (implied in equation (1) as a time constant). Rather, the change of atmosphere essentially occurs as a step function (plug flow reactor (PFR)) [15]. Based on flow rates, chamber geometry, and sample dimensions, the estimated time for this step change across the sample was \( <0.09 \text{ second} \). That is, the time required for a complete change of atmosphere across the length of the sample in the chamber from the initial to final is \( <0.09 \text{ second} \). Thus, the assumption of CSTR overestimates the time required for chamber equilibration, and in reality the chamber flush time was closer to the
plug flow behavior. Even with the assumption of CSTR, however, the time constant is rather small. This gas exchange process is illustrated schematically by Figure 1-(a).

The application of conductivity relaxation technique to porous bodies assumes gas transport in the porous interstices to be much faster than kinetics of surface exchange. By ensuring that the sample is sufficiently porous and relatively thin, the time constant/characteristic time for process (b) can similarly be made very small. An estimate of the time required for gas diffusion to occur into the pores of such samples was made. This calculation was based on binary diffusion into the porous body. The effective diffusion coefficient, \( D_{\text{eff}} \), of oxygen-nitrogen through porous bodies is given by [16]:

\[
D_{\text{eff}} = \frac{D_{O_2-N_2} V_v}{\varepsilon} \tag{2}
\]

where \( D_{O_2-N_2} \) is the binary diffusion coefficient of oxygen-nitrogen, which can be calculated using the Chapman-Enskog model [17], \( V_v \) is the porosity, and \( \varepsilon \) is the tortuosity factor. A one dimensional diffusion equation was solved numerically using \( D_{\text{eff}} \) and the time required for the \( p_{O_2} \) in the center of the sample to reach 99% of the \( p_{O_2} \) after the switch was calculated. For an assumed tortuosity factor of 5, the estimated time was between 0.055 and 0.14 sec over the temperature range investigated. This gas transport into the pores, process (b), is illustrated in Figure 1-(b).

Process (a) is not affected by the microstructure. Process (b), in general, is only weakly dependent on the microstructure of the porous sample\(^1\). However, processes (c) and (d) are clearly dependent on the sample microstructure. The time constant for process (c), \( \tau_c \), governed by \( k_{\text{chem}} \) can be defined approximately by:

\[
\tau_c \propto \frac{1}{S_V k_{\text{chem}}} \approx \frac{d}{k_{\text{chem}}} \tag{3}
\]

where \( S_V \) is the specific surface area of the body and \( d \) is the average particle size of the porous body. Similarly the time constant/characteristic time for process (d), \( \tau_D \), which is governed by \( \tilde{D} \), can be described by:

\[
\tau_D \propto \frac{d^2}{\tilde{D}} \tag{4}
\]

Clearly process (d) is more influenced by the average particle size due to the \( d^2 \) dependence and \( \tau_D \) decreases more rapidly with decreasing particle size than \( \tau_r \). A critical particle size,

\(^1\) Assuming porosity is high enough and pore size is sufficiently large (so that Knudsen diffusion is ignored).


d_{cr}, can be defined at which \( \tau_r \) and \( \tau_D \) are equal. For \( d < d_{cr}, \tau_r > \tau_D \), and for \( d > d_{cr}, \tau_r < \tau_D \). By ensuring that \( d << d_{cr} \), one can ensure that \( \tau_D << \tau_r \). Under such conditions, process (c), illustrated by Figure 1-(c), is the slowest and a porous body can be used to measure \( k_{chem} \) by conductivity relaxation. The use of a porous sample instead of a dense sample also closely resembles actual SOFC cathodes, which are porous and of a fine microstructure. The objective of this work was to investigate this regime of kinetic behavior.

In porous samples of very fine microstructure, diffusion in very small particles is assumed fast, so that the concentration is essentially uniform within the solid at any time during equilibration (for \( \tau_D << \tau_r \)). If the specific surface area of the porous body of volume fraction porosity \( V_v \) is given by \( S_V \) (in \( \text{cm}^2/\text{cm}^3 \) or \( \text{cm}^{-1} \)), the average concentration at time \( t \) is \( C(t) \) and the final equilibrated concentration is \( C_o \), the mass balance of oxygen incorporation (or expulsion) is given by

\[
S_V k_{chem} (C_o - C(t)) dt = (1 - V_v) dC(t)
\]

the integration of which gives

\[
\frac{C_o - C(t)}{C_o - C(0)} = \exp \left[ -\frac{t}{\frac{1 - V_v}{S_V k_{chem}}} \right] = \exp \left[ -\frac{t}{\tau_r} \right]
\]

which represents first order kinetics with time constant given by

\[
\tau_r = \frac{(1 - V_v)}{S_V k_{chem}}
\]

Note that the time constant \( \tau_r \) is defined in terms of the specific surface area of the porous body, \( S_V \), rather than the average particle size, \( d \). This also means that if the above conditions are satisfied, the only relevant parameters are \( S_V \) and \( V_v \), and the kinetics of equilibration is independent of other microstructural features, such as particle shape. In terms of the normalized conductivity, \( g(t) \), the above may also be written as

\[
g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma_{\infty} - \sigma(0)} = 1 - \exp \left[ -\frac{t}{\tau_r} \right]
\]

where \( \sigma(0) \) is the conductivity of the sample before the switch in \( p_{O_2} \), \( \sigma(t) \) is the conductivity at time \( t \) after the switch and \( \sigma_{\infty} \) is the conductivity after the sample is equilibrated to the new \( p_{O_2} \). The experimental procedure consists of measuring the time
dependence of conductivity after an abrupt change in atmosphere, fitting a first order kinetic equation to the normalized conductivity, \( g(t) \) vs. \( t \) plot, and determining the time constant, \( \tau \), which is related to \( k_{chem}, V_v \), and \( S_v \) by equation (7). The \( S_v \) can be determined using quantitative stereology [18]. Volume fraction porosity, \( V_v \), can be measured by the fluid immersion method as well as by systematic point count using quantitative stereology [18]. From these measurements, \( k_{chem} \), can be determined using porous samples, given in terms of measured parameters using equation (7).

Transport kinetics in porous samples can also be analyzed assuming that the particle geometry is approximately spherical or cylindrical. For spherical geometry, data can be analyzed using the diffusion equation:

\[
\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) \quad 0 \leq r \leq a
\]

where \( a \) is the particle radius, with the initial condition

\[
C(r, 0) = C(0) \quad 0 \leq r \leq a
\]

and boundary conditions

\[
C(a, t) = C_o \quad t > 0
\]

and

\[
-\frac{D}{r} \frac{\partial C(r, t)}{\partial r} \bigg|_{r=a} = k_{chem} (C_o - C_s(t)) \quad t > 0
\]

where \( C_o \) is the concentration of oxygen in the particle after equilibration to a new \( P_{O_2} \), \( C(0) \) is the initial concentration of oxygen in the particle corresponding to the initial \( P_{O_2} \), and \( C_s(t) \) is the concentration of oxygen just inside the particle surface at time \( t \). Using the solution to the diffusion equation given by Crank [12], the normalized conductivity, \( g(t) \), for porous body containing spheres of radius \( a \), assuming a linear relation between conductivity and concentration, can be described by2:

\[
g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma_{\infty} - \sigma(0)} = \frac{C(t) - C(0)}{C_o - C(0)} = \frac{M(t)}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{6L^2 \exp(-\beta_n^2 \frac{D}{a^2})}{\beta_n^2 L^2 + L(L-1)}
\]

2 For the spherical geometry, this is only an approximation, and not valid rigorously.
where $\sigma(0)$ is the initial conductivity, $\sigma_\infty$ is the conductivity after the sample is equilibrated to the new $p_{O_2}$ (that corresponding to $C_o$), and $\sigma(t)$ is the conductivity after time $t$, which corresponds to $C(t)$, the average concentration at time $t$, defined as:

$$C(t) = \frac{3}{a^3} \int_0^a C(r,t)r^2dr$$

(12)

$M(t)$ is the net amount of oxygen that entered (left) in time $t$ after the change in $p_{O_2}$ and $M_\infty$ is the net amount of oxygen that entered (left) after an infinite time following the change in $p_{O_2}$. The $\beta_n$’s are the positive roots of the transcendental equation

$$\beta_n \cot \beta_n + L - 1 = 0$$

(13)

where

$$L = \frac{ak_{chem}}{D} = \frac{a}{l_{cr}}$$

(14)

For a cylindrical geometry transport is analyzed in a long circular cylinder (length $>> r$) using the diffusion equation:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) \quad 0 \leq r \leq a$$

(15)

The same initial condition and boundary conditions given for the spherical geometry are applicable here. The normalized conductivity is given by [12]³:

$$g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma_\infty - \sigma(0)} = \frac{C(t) - C(0)}{C_o - C(0)} = \frac{M(t)}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4L^2}{\beta_n^2} \exp(-\beta_n^2 \tilde{D}t / a^2)$$

(16)

The $\beta_n$’s are now given by the positive roots of the transcendental equation [12]

$$\beta_n J_1(\beta_n) - LJ_0(\beta_n) = 0$$

(17)

where $J_0$ is the Bessel function of the first kind and of zeroth order, $J_1$ is the Bessel function of the first kind and of first order and $L$ is defined in equation (14). The corresponding average concentration $C(t)$ at time $t$ is given by:

---

³ This also assumes a linear relationship between $\sigma(t)$ and $C(t)$, which is strictly valid only for cylinders aligned in one direction – the direction conductivity is measured.
Frequently a ‘sum-of-least-squares’ fitting program is used to fit experimental data to these models, where a numerical procedure is necessary to obtain solutions to equations (13) and (17). Values of $\beta_n$ can be easily obtained using a numerical procedure given by den Otter et al. [14] or root finding operations built into commercially available mathematical softwares. However, as noted previously, in the limit of $a << l_{cr}$ the solutions to the diffusion equations are sensitive only to the kinetics of surface exchange. Thus, although the ‘least-squares’ procedure gives values for both $\widetilde{D}$ and $k_{chem}$, only the surface exchange term is meaningful as large variations in $\widetilde{D}$ have little or no effect on the best fit. The objective of this report is to present the results of a study on LSC50 from 350 to 800°C and compare values of $k_{chem}$ obtained using the porous body analysis as well as using both spherical and cylindrical solutions for the diffusion equation particles in the porous body.

**Experimental Procedure:**

LSC50 powder (Praxair Specialty Ceramics) was mixed with 25 wt.% carbon (HTW – Germany, 10-20 µm spherical particles) and attrition-milled in ethanol for 4 hrs. The dried powder was mixed with 3 wt.% ethylene glycol (as binder) and bars were die pressed uniaxially, and then isostatically pressed at 32,000 psi. The bars were heated at 1°C/min in air to 500°C to burn off carbon and create porosity, and sintered in air at 1000°C to fabricate porous bars fine particle size and large specific surface area. A few bar samples were also impregnated with epoxy and polished to a level finish for stereological analysis on a scanning electron microscope (SEM).

Silver mesh and paste were used to attach silver leads in a four-probe configuration. The sample was placed in a quartz chamber and inserted into a tube furnace for conductivity relaxation measurements. A thermocouple was placed inside the sample chamber to measure possible temperature fluctuations during measurements. Experiments were carried out between 350 and 800°C in 50 degree intervals for the $p_{O_2}$ switch from 0.06 to 0.04 atm and 0.04 to 0.06 atm. Measurements were also made at the larger $p_{O_2}$ step changes of 0.21 to 0.10 atm. Voltage and current were measured using a Solartron 1287 Electrochemical Interface and recorded using ‘CorrWare’ software from Scribner Associates.

**RESULTS AND DISCUSSION**

Figure 2 is a plot of the normalized conductivity, $g(t)$ vs. time for the LSC50 porous sample sintered at 1000°C. The plots are given for the $p_{O_2}$ step change from 0.06 to 0.04 atm at 750, 600, and 450°C (with data for 350°C given as an inset due to relatively long relaxation time). Data at other temperatures are not shown for the sake of clarity. The sample equilibration times decreased monotonically from 750°C (~55 sec) down to a minimum at ~500°C (~26
sec) to 450°C (~28 sec). Below this threshold the sample equilibration times increased quite sharply; 400°C (~45 sec) and 350°C (~150 sec) with decreasing temperature.

The $k_{chem}$ is related to $\tau_r$, $S_v$, and $V_v$, by equation (7) for the porous model. The pore surface area per unit volume, $S_v$, of the randomly oriented surfaces of a porous body can be obtained from the equation from quantitative stereology given by [18]

$$S_v = 2P_L \text{ cm}^{-1} \quad \text{(19)}$$

From the measurements of $P_L$, the $S_v$ for the porous LSC50 sample sintered at 1000°C was estimated to be ~29,000 cm$^{-1}$. The $V_v$ was measured to be ~0.71. The $k_{chem}$ obtained between 750°C and 350°C from the measured $\tau_r$, $S_v$ and $V_v$ for the porous sample model are plotted in Figure 3 vs. 1000/T for a $p_{O_2}$ step change from 0.06 to 0.04 atm. This figure clearly shows a monotonic increase in $k_{chem}$ with decreasing temperature, from $1.35 \times 10^{-6}$ cm/s at 750°C to $2.1 \times 10^{-6}$ cm/s around 450°C. Below 450°C the $k_{chem}$ appears to be thermally activated and decreases rapidly with decreasing temperature, to $\sim 1 \times 10^{-7}$ cm/s at 350°C.

The normalized conductivity data from the above sample were also fitted to the solutions for the spherical and cylindrical models, equations (11) and (16). SEM micrographs of the sample revealed a uniform microstructure with average particle size ~0.5 microns. Hence, the radius $a$ was chosen as 0.25 micron. Figure 3 also shows plots of $k_{chem}$ vs. 1000/T obtained from the spherical and cylindrical models for the LSC50 sample sintered at 1000°C. The results from the spherical and cylindrical geometry solutions show similar trends, with $k_{chem}$ increasing with decreasing temperature between ~750 and ~500°C, and thereafter sharply decreasing with further decrease in temperature from ~500 to 350°C. The agreement between the results from the spherical and cylindrical geometry solutions and the porous sample model is very good. The value of $k_{chem}$ obtained from the porous sample model, in which it is a-priori assumed that $\tau_r >> \tau_D$, lies between the values obtained from the spherical and cylindrical models.

**CONCLUSION**

The present work has shown that the chemical surface exchange coefficient, $k_{chem}$, can be determined using porous MIEC materials such that over a temperature range, the slowest process is that of surface exchange. Such a condition is realized when the particle size, $d$, in the porous body is much smaller than the critical length, $l_{cr}$. Under such conditions, the time response of normalized conductivity to an abrupt $p_{O_2}$ change can be described by a simple first order kinetics and the time constant can be uniquely related to $k_{chem}$. In the present work, three models were used for the estimation of $k_{chem}$; (a) Porous body model which
depends only on $S_v$ and $V_v$ as the microstructural parameters, (b) A solution to the diffusion equation assuming the particles in the porous body to be spherical, and (c) A solution to the diffusion equation assuming the particles in the porous body to be cylindrical. For LSC50, the $k_{chem}$ was determined for a $P_{O_2}$ step change between 0.04 and 0.06 atm. over a range of temperatures between 350 and 750°C. It was observed that the $k_{chem}$ increased with decreasing temperature between 750 and ~450°C. This is in contrast to results on dense samples, which show that the $k_{chem}$ decreases with decreasing temperature over the same range. Increasing $k_{chem}$ with decreasing temperature determined using porous samples may indicate a role for surface adsorption by a model such as Langmuir. For temperatures in the range from 450 to 350°C, the $k_{chem}$ determined using porous bodies sharply decreased with decreasing temperature, consistent with a thermally activated process over this range.
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FIGURE CAPTIONS

Figure 1: A schematic of the 4 processes that occur when an abrupt change in $p_{O_2}$ is made: (a) change of atmosphere in the chamber; (b) gas transport into the porous interstices; (c) surface exchange on the interior surfaces; (d) chemical diffusion of oxygen into the particles.

Figure 2: Normalized Conductivity vs. time at 450, 600 and 750°C for the porous LSC50 sample sintered at 1000°C: $p_{O_2}$ change from 0.06 to 0.04 atm. The inset shows data for 350°C.

Figure 3: $k_{chem}$ vs. 1000/T for the porous sample, spherical and cylindrical geometry models: 350 to 700°C for the porous LSC50 sample sintered at 1000°C; $p_{O_2}$ change from 0.06 to 0.04 atm.
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LIST OF ACRONYMS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>CSTR:</td>
<td>Continuously Stirred Tank Reactor</td>
</tr>
<tr>
<td>LSC:</td>
<td>Sr-doped LaCoO\textsubscript{3}</td>
</tr>
<tr>
<td>LSF:</td>
<td>Sr-doped LaFeO\textsubscript{3}</td>
</tr>
<tr>
<td>MIEC:</td>
<td>Mixed Ionic Electronic Conductor</td>
</tr>
<tr>
<td>PFR:</td>
<td>Plug Flow Reactor</td>
</tr>
<tr>
<td>SEM:</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>SOFC:</td>
<td>Solid oxide fuel cell</td>
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