

Surface Exchange Coefficient Measurements on Porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ by Conductivity Relaxation

Ramanan Ganeshanathan and Anil V. Virkar
Department of Materials Science and Engineering,
University of Utah
Salt Lake City, Utah 84112, USA

A novel technique using conductivity relaxation on porous bodies was introduced at the ECS Conference in Orlando in 2004 [1,2]. This technique is based on analyzing the 4-probe conductivity response of a porous sample to an abrupt change in oxygen partial pressure p_{O_2} , to determine the chemical surface exchange coefficient k_{chem} . For a porous sample with an average particle size of a few microns or less, the rate limiting step is expected to be controlled exclusively by k_{chem} , where all other equilibration processes are tailored to be much faster (with the appropriate choice of sample geometry and fast gas exchange times in the experimental chamber) [2]. The objective of this work was to investigate this regime of kinetic behavior for mixed conducting Strontium doped Lanthanum Ferrite (LSF20).

The experimental procedure consists of measuring the time dependence of conductivity after an abrupt change in atmosphere, and fitting a first order kinetic equation to the normalized conductivity, $g(t)$ vs. time plot, where

$$g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma_{\infty} - \sigma(0)} \quad (1)$$

$\sigma(t)$ is the conductivity of the sample at a given time t , $\sigma(0)$ is the conductivity before the p_{O_2} switch and σ_{∞} is the conductivity after equilibration to the new p_{O_2} . In this case, diffusion in very small particles is assumed fast, so that the concentration is essentially uniform within the solid at any time during equilibration. If the specific surface area of the porous body of volume fraction porosity V_v is given by S_v (in cm^2/cm^3), where the average concentration at time t is $C(t)$ and the final equilibrated concentration is C_o , the rate of oxygen incorporation (or expulsion) is given by

$$S_v k_{\text{chem}} (C_o - C(t)) dt = (1 - V_v) dC(t) \quad (2)$$

the integration of which gives

$$\frac{C_o - C(t)}{C_o - C(0)} = \exp\left[-\frac{t}{\left(\frac{1 - V_v}{S_v k_{\text{chem}}}\right)}\right] = \exp\left[-\frac{t}{\tau_r}\right] \quad (3)$$

which represents first order kinetics with time constant given by τ_r . In terms of the measured parameter, namely the normalized conductivity function $g(t)$, the above may also be written as

$$g(t) = 1 - \exp\left[-\frac{t}{\tau_r}\right] = 1 - \exp\left[-\frac{t}{\left(\frac{1 - V_v}{S_v k_{\text{chem}}}\right)}\right] \quad (4)$$

where the time constant, τ_r , is related to k_{chem} , V_v , and S_v as shown in equation (4). Volume fraction porosity, V_v , can be measured by the conventional Archimedes fluid immersion method as well as by a systematic point count by quantitative stereology [3]. The specific pore

surface area, S_v , can also be determined using quantitative stereology [3].

Conductivity relaxation experiments were carried out from 600 to 800°C for small p_{O_2} step changes, both decreasing and increasing, from 0.02 to 0.21 atm. Samples of varying volume fraction porosity V_v and specific surface area per unit volume S_v were tested to confirm the relationship of these parameters to the time constant τ_r and hence the surface exchange coefficient k_{chem} . Fig 1 is a plot of k_{chem} vs. p_{O_2} for 2 porous samples of LSF20 of different S_v and V_v . The dependence of k_{chem} with p_{O_2} is essentially the same for the two samples. The dependence of k_{chem} on p_{O_2} is typical of doped perovskites of this type and has been reported extensively in the literature. However, for a given p_{O_2} switch, the k_{chem} is found to increase with decreasing temperatures, a trend which is unique to studies on porous samples. Similar results were also found for Strontium doped Lanthanum Cobaltite [2]. Temperature dependence and comparisons of the two systems will be presented to contrast the similarities and differences of the transport kinetics over the temperature range and oxygen partial pressure range measured.

Attempts were also made to fabricate a porous sample with an ultra-fine microstructure that exhibits extremely fast kinetics, for use as an oxygen sensor at lower temperatures (down to 350°C). In this instance a porous sample of strontium doped lanthanum cobaltite of composition LSC50, with excellent mixed conducting properties, was used for the experiments. These results will also be presented.

References-

1. Ramanan Ganeshanathan and Anil V. Virkar, *Electrical Conductivity Relaxation on Dense and Porous $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$* , High Temperature Materials Chemistry Symposium in Honor of Professor C. B. Alcock – Q1, 204th ECS Meeting, October 12-16, 2003, Orlando FL.
2. Ramanan Ganeshanathan and Anil V. Virkar, submitted for publication to the *Journal of the Electrochemical Society*, April 19th 2004.
3. Erwin E. Underwood, *Quantitative Stereology*, p. 23, Addison-Wesley Publishing Co., Reading, MA (1970).

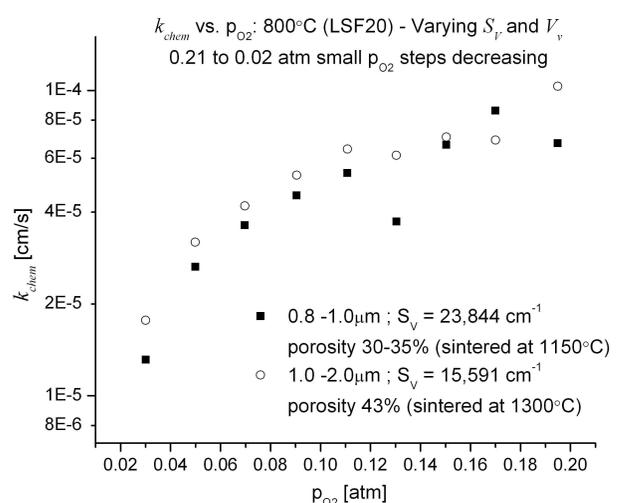


Fig. 1. k_{chem} vs. p_{O_2} – LSF20 porous samples with differing particle size, specific surface area S_v and volume fraction porosity V_v .