Abstract #776, 224th ECS Meeting, © 2013 The Electrochemical Society

In Situ Oxygen Surface Exchange Coefficient Measurements on Lanthanum Strontium Ferrite Thin Films via a New Curvature Relaxation Method

Qing Yang, Dr. Richard R. Lunt and Dr. Jason D. Nicholas

Chemical Engineering and Materials Science Department, Michigan State University
2527 Engineering Building, 428 South Shaw Lane,
East Lansing, Michigan 48824, USA

Introduction

Mixed ionic electronic conducting (MIEC) materials are widely used in solid oxide fuel cell (SOFC) cathodes, oxygen sensors, and catalytic converters. The oxygen content of these materials can be dramatically altered through redox reactions that simultaneously produce changes in oxygen vacancy concentration, cation oxidation state, and lattice strain. Here we demonstrate that this mechano-chemical coupling can be used to determine oxygen chemical surface exchange coefficients (k*'s*) by measuring the curvature relaxation (κR) of mechano-chemically active thin film | inert substrate bilayers subjected to abrupt step changes in oxygen partial pressure (pO_2). For dense films thin enough to exhibit surface-controlled oxygen exchange, k can be determined from the following equation, which describes the response of the material to a small pO_2 step change:

$$\frac{\kappa - \kappa_o}{\kappa_\infty - \kappa_o} = 1 - \sum_{i=1}^{n} A_i \exp\left(-\frac{t\,k_i}{h_f}\right)$$

where κ, κ_0, and κ_∞ are the instantaneous, initial, and new-pO_2-equilibrated curvature, respectively, k_i is the surface exchange coefficient for a portion of the film with faction of surface area, A_i, t is time, and h_f is the film thickness.[1-4] This κR method provides an in-situ, electrode-free method to measure k*'s* and examine stress-k correlations.

Experimental Method

As shown in Figure 1, an in-situ Multi-beam Optical Stress Sensor apparatus was used to measure the κR of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF64) | $(Y_2O_3)_{0.08}(ZrO2)_{0.92}$ (YSZ) bilayers subjected to multiple pO_2 cycles.

Results

In Figure 2, each curvature relaxation (κR) was fit to two surface exchange coefficients, indicating the presence of two distinct decay processes. These κR-measured surface exchange coefficients agree well with low temperature extrapolation of the bulk sample studied by ten Elshof et al.,[5] as shown in Figure 3. However, these results differ significantly from those obtained on pulsed laser deposited thin films.[6,7]

Discussion

In this presentation, we will discuss the multiple relaxation processes in Figure 2 that likely correspond to oxygen incorporation into the lattice vs. grain boundaries. We will also examine whether the discrepancies between the Figure 3 thin film data is caused by differences in film stress and/or the presence/absence of electrodes. A comparison of the oxygen surface exchange processes of bulk and porous samples will also be presented.

Acknowledgements

This work was funded through a Michigan State University faculty startup grant.

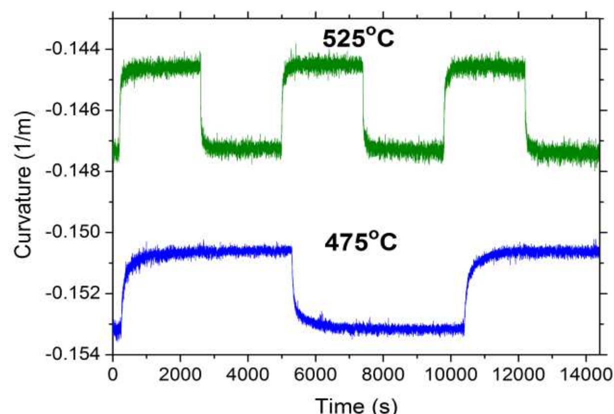

Figure 1. Multiple curvature relaxation cycles between pO_2=0.21 (air) and pO_2=0.021 (N_2-air).

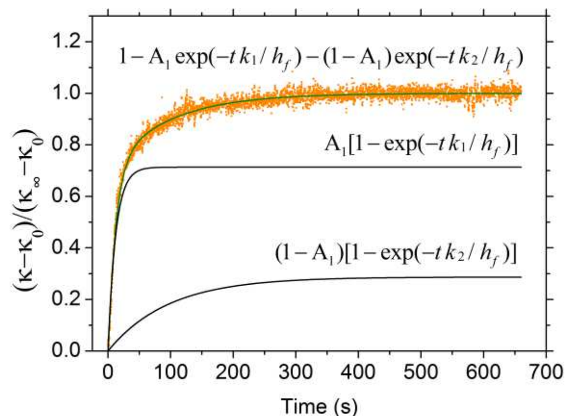

Figure 2. Normalized curvature relaxation of a 250 nm LSF64 film on reduction at 525°C. The top line is the combined fit to the data, while the lower lines show the separate contributions of each relaxation process.

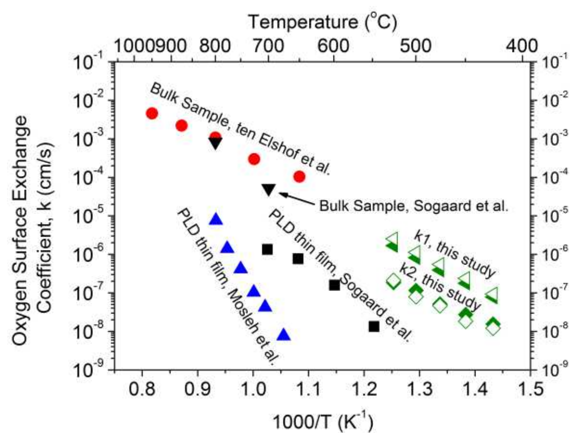

Figure 3. Arrhenius plot of the literature[5-7] and κR-measured LSF64 surface exchange coefficients.

References

1. J. Crank, The Mathematics of Diffusion, Oxford University Press, Oxford, UK (1975).
2. G. Kim, S. Wang, A. J. Jacobson and C. L. Chen, Solid State Ionics, **177**, 1461 (2006).
3. K. Kerman, C. H. Ko and S. Ramanathan, Phys. Chem. Chem. Phys., **14**, 11953 (2012).
4. Q. Yang, T. J. Burye, R. R. Lunt and J. D. Nicholas, Solid State Ionics, **Submitted** (2013).
5. J. E. tenElshof, M. H. R. Lankhorst and H. J. M. Bouwmeester, J. Electrochem. Soc., **144**, 1060 (1997).
6. M. Mosleh, M. Sogaard and P. V. Hendriksen, J. Electrochem. Soc., **156**, B441 (2009).
7. M. Sogaard, P. Vang Hendriksen and M. Mogensen, J. Solid State Chem., **180**, 1489 (2007).