Journal of the European Ceramic Society **19** (1999) 843–846
© 1999 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(98)00328-8
0955-2219/99/$ - see front matter

Study of Oxygen Exchange and Transport in Mixed Conducting Electroceramics

Alexandre Closset,* Stefan Diethelm, Kemal Nisancioglu,† Jan van Herle and A. J. McEvoy

Laboratoire de Photonique et Interfaces, École Polytechnique Fédérale de Lausanne, CH 1015 Lausanne, Switzerland

Abstract

Oxygen diffusion is treated in a dense electronically conducting perovskite pellet blocked ionically on one surface, electronically on the other, and sealed on the periphery. Oxygen exchange at the electronically blocked surface is assigned first order reaction kinetics. An equivalent circuit model is suggested for the cell impedance by the Laplace transform of Fick's second law. Asymptotic expressions are employed to extract the slope of the coulometric titration curve and the chemical diffusion coefficient from electrochemical-impedance-spectroscopy (EIS) data. NLLS fit with the theoretical model is performed to evaluate the surface oxygen exchange coefficient at the interface of the electrochemical cell. The methodology is applied to determine the chemical diffusion and surface exchange coefficients of oxygen in $SrCo_{0.5}Fe_{0.5}O_{3-\delta}$*, interfaced with a YSZ electrolyte. The experimental results are used to link the processes corresponding to the diffusion of oxygen vacancies to the ionic conductivity of the material. The data is applicable to solid oxide fuel cell cathodes, oxygen permeation membranes and related systems. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: impedance, spectroscopy, diffusion, perovskites, fuel cells.

1 Introduction

In the last decade, much attention has been focused on mixed conducting oxides as they appeared suitable for various industrial uses. As air electrodes for solid oxide fuel cells, oxidation catalysts, and gas separation membranes for oxygen recovery or purification, these nonstoichiometric oxides meet many potential applications.

To select the best material among many different compositions, flux measurements are commonly used[1,2] but reveal little information on the oxygen transport process. More recently, electrochemical techniques have been used to extract the chemical diffusion coefficient of oxygen in perovskites.[3,4] Despite accurate measurement, data analysis became problematic when the assumption of reversible boundary conditions at the electronically blocked surface was no longer valid because high bulk diffusivity implies that surface exchange then becomes rate determining.

For this purpose, oxygen exchange at the specimen/electrolyte interface was assigned first order reaction kinetics to solve the diffusion equations in the present study. Since the results are expressed in the frequency domain, Electrochemical-Impedance-Spectroscopy (EIS) was used to directly test the new model with no need to perform the often difficult and time consuming inverse Laplace transform. Asymptotic behaviors were derived following the A-C method developed by Ho *et al.*[5] for lithium diffusion in thin films. An electrochemical *blocked cell* design similar to that of Gür *et al.*[3] was used for the EIS measurements.

The material selected for the study is a highly defective cobaltate $SrCo_{0.5}F_{0.5}O_{3-\delta}$ with a focus on the validity of the theoretical model for diffusion of oxygen in such oxides and the proposed equivalent circuit model for data analysis.

2 Experimental

The powder used to produce $SrCo_{0.5}Fe_{0.5}O_{3-\delta}$ samples was obtained by mixing ground stoichiometric ratios of nitrates of Sr and Co, with Fe_2O_3, followed by repeated calcining and grinding until no impurities were detectable by X-ray powder diffraction.[4]

---

*To whom correspondence should be addressed.

†Permanent address: Department of Electrochemistry, Norwegian University of Science and Technology, N-7034 Trondheim, Norway.

The experimental arrangement is shown in Fig. 1 and involved the use of a single compartment electrochemical cell configuration. The $SrCo_{0\cdot5}Fe_{0\cdot5}O_{3-\delta}$ pellet is electronically blocked on one surface by an oxygen-ion conducting YSZ electrolyte, and on the opposite surface by a platinum foil blocking oxygen transport. Platinum paste was applied on the reverse side of the electrolyte to act as the porous counter and reference electrodes. This particular design has been developed and successfully used in the measurement of oxygen transport in A-site doped manganites.[3]

The perovskite pellet taken for this setup was 0·8 mm thick and had a diameter of 5·5 mm. The bulk density of the sample was 92% of the theoretical value, and presented a closed porosity of 8% while no open porosity was detectable.

Before the assembly of the cell, a little of the platinum paste was applied on the bare face of the sample. This very porous platinum layer was expected to catalyse oxygen exchange across the YSZ–perovskite interface and to produce a spacing between the two materials in order to avoid any undesired chemical reactions.

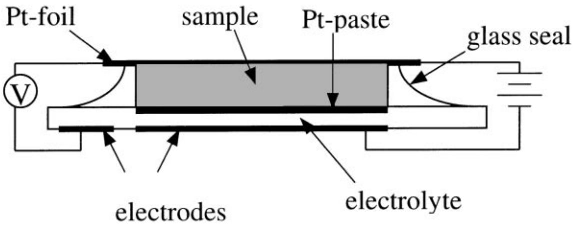

Fig. 1. Electrochemical cell design used for impedance-spectroscopy measurements.

3 Theory

Figure 2 represents the equivalent circuit model suggested for the following electrochemical cell:

$P_{O_2(air)}$Pt-paste/YSZ/Pt-paste/

$SrCo_{0\cdot5}Fe_{0\cdot5}O_{3-\delta}$/Pt-foil

The first part, the resistance R_{YSZ} in serial connection with an RC circuit simulates the platinum electrode interfacing the sample, as well as the ohmic drop within the electrolyte.[6] The second part represents the oxygen transport in and out of the perovskite pellet, where R_k is the surface exchange resistance, Z_d is the finite length diffusion element, and CPE_g is the distributed capacitance to account for gaseous and adsorbed oxygen at the sample's surface.

With the aim to calculate the complex impedance for oxygen transport within the specimen, one may solve Fick's second law in the Laplace plane while assuming first order reaction kinetics at the electronically blocked interface and no ion transport across the *sample/Pt (foil)* interface. This will lead to the definition of a complex impedance in the form of eqn (1)[7]

$$Z_T(j\omega) = \frac{\Delta\tilde{E}}{\tilde{I}} = \frac{V_M \mid \left(\frac{\mathrm{d}E}{\mathrm{d}\delta}\right)_\delta \mid}{zFSk} + \frac{V_M \mid \left(\frac{\mathrm{d}E}{\mathrm{d}\delta}\right)_\delta \mid}{zFS\sqrt{j\omega\tilde{D}}} \coth\sqrt{\frac{j\omega L^2}{\tilde{D}}} \qquad (1)$$

The first term in eqn (1), independent of frequency, is the surface exchange resistance R_k. A similar result has recently been reported by ten Elshof *et al.*[8] The second term of eqn (1), named Z_d, is a well known expression describing finite-length bulk diffusion.[9] At intermediate frequencies, small diffusion coefficient or thick samples, i.e. $\omega >> \tilde{D}/L^2$ the expression for Z_d reduces to

$$Re(Z_d)(\omega) = -\mathrm{Im}(Z_d)(\omega) \cong \frac{V_M \mid \left(\frac{\mathrm{d}E}{\mathrm{d}\delta}\right)_\delta \mid}{zFS\sqrt{2\omega\tilde{D}}} \qquad (2)$$

At very low frequencies, for very thin samples or large diffusion coefficient the real part of the impedance is independent of frequency and the imaginary part has the form

$$Im(Z_d)(\omega) \cong -\frac{V_M \mid \left(\frac{\mathrm{d}E}{\mathrm{d}\delta}\right)_\delta \mid}{zFS\omega L} \qquad (3)$$

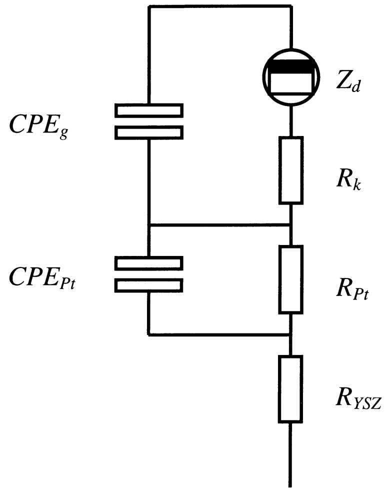

Fig. 2. Equivalent circuit model used to perform NLLS fit on the impedance data.

4 Results and Discussion

Figure 3 shows the plot of Im(Z) versus $1/\omega$ for frequencies from 500 μHz down to 70 μHz. Equation (3) gives $(\mathrm{d}E/\mathrm{d}\delta)_\delta = -2{\cdot}3$ V for the slope of the coulometric–titration curve. The same estimates of $(\mathrm{d}E/\mathrm{d}\delta)_\delta$ were done at 908 and 847°C and we obtained similar results which confirmed that the experiment was conducted within the linear part of the coulometric titration curve.

A Warburg response was observed in the frequency range of 3 mHz down to 700μHz. This is shown in Fig. 4 where the impedance adopts a diffusion like behavior predicted by the model at intermediate frequencies. The chemical diffusion coefficient obtained from the slope of these two straight lines using eqn (2) is $1{\cdot}4\times10^{-5}\,\mathrm{cm^2\,s^{-1}}$ for Im(Z) and $1{\cdot}0\times10^{-5}\,\mathrm{cm^2\,s^{-1}}$ for Re(Z). These values are one order of magnitude higher than those reported previously for the same material,[4] but the inadequacy of the reversible model used then to analyze the relaxation data may appear as lower coefficients.

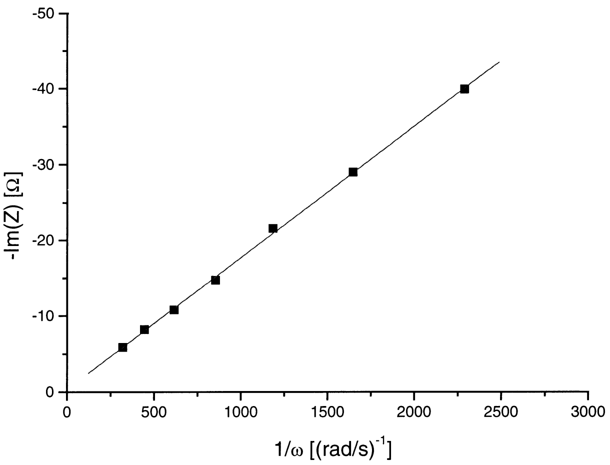

Fig. 3. Imaginary part of the measured impedance at 880°C versus $1/\omega$ in the frequency range of 70 to 500 μHz.

Impedance measurement at 880°C on this *blocked cell* is plotted in the complex plane in Fig. 5. The straight line at very low frequencies is the common response of a pure capacitor and it indicates that the electrochemical cell under investigation was perfectly sealed. Indeed, if oxygen molecules could reach the sample through some leaks, a leakage current would arise corresponding to a shunting of the capacitor and a third semicircle would replace this straight line.

The equivalent circuit model schematically represented in Fig. 2 was used to perform a Non-Linear Least Square fit on these data and the graphical result is also shown in Fig. 5. The chemical diffusion coefficient calculated from the fit results was $1{\cdot}2\times10^{-5}\,\mathrm{cm^2\,s^{-1}}$. Using eqn (1), the parameter R_k lead to a value for the surface exchange coefficient of $3{\cdot}0\times10^{-4}\,\mathrm{cm\,s^{-1}}$. From the latter two coefficients, one can estimate the critical thickness[10] $L_c = \tilde{D}/k$ around 4×10^{-2} cm. Since the thickness of the perovskite pellet used in the experimental set-up was $2\times L_c$, the limitation for oxygen transport rose from vacancy diffusion as well as from surface exchange and thus confirmed the assumption of irreversible boundary conditions at the specimen/electrolyte interface.

The fit displayed in Fig. 5 gave values for R_{Pt} and CPE_{Pt} well in accordance with the characteristics of platinum electrodes on YSZ reported by Van herle *et al.*[6] In addition, the consistency between the chemical diffusion coefficients derived by the asymptotic behaviors and the impedance fitting, justifies the proposed equivalent circuit model.

Assuming a nominal nonstoichiometry of $\delta = 0{\cdot}5$ given for a similar material,[10,11] one can estimate the thermodynamic enhancement factor[12]

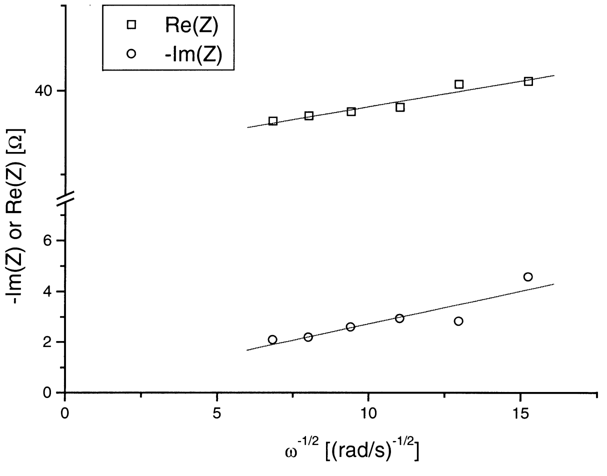

Fig. 4. Real and imaginary parts of the measured impedance at 880°C versus $1/\omega^{1/2}$ in the frequency range of 700 μHz to 3 mHz.

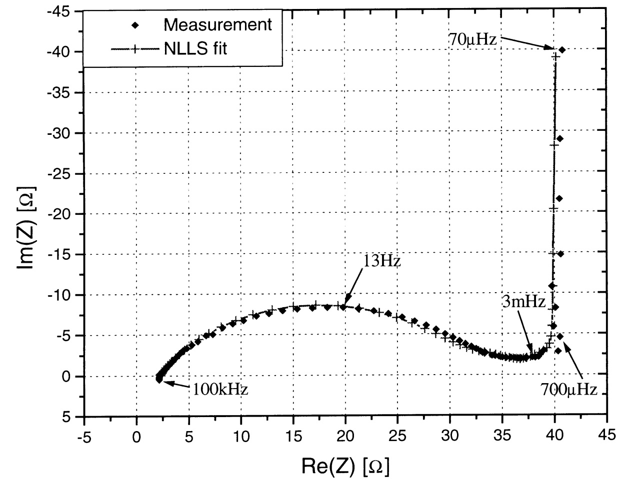

Fig. 5. Measured impedance of the electrochemical cell shown in Fig. 1 at 880°C plotted in the complex plane.

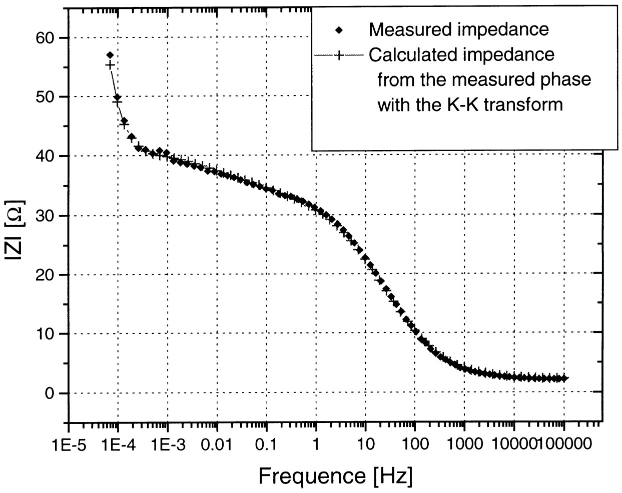

Fig. 6. Comparison of the measured impedance with the Kramers–Kronig transformation of the measured phase.

$\frac{\mathrm{d}\ln a}{\mathrm{d}\ln C} = -\frac{zF(3-\delta)}{RT}\frac{\mathrm{d}E}{\mathrm{d}\delta} \cong 116$, which appeared to be slightly larger than the value reported previously for the same material.[4]

One can also relate the chemical diffusion coefficient for oxygen vacancies to the ionic conductivity with the relation[5] $\sigma_i = \frac{zF\tilde{D}}{V_M(\mathrm{d}E/\mathrm{d}\delta)}$ which leads to an ionic conductivity of $3{\cdot}6\times10^{-2}\,\mathrm{s\,cm^{-1}}$, about two orders of magnitude lower than the data obtained by Teraoka *et al.*[2]

Because of chemical incompatibility between the cobaltate pellet and the YSZ electrolyte,[13] and the long measurement times (about 3 days), the question of whether the impedance data could be corrupted is crucial. For that reason, a Kramers–Kronig transformation was performed on the impedance data before the analysis, to test the stability of the electrochemical system during the measurements. Figure 6 shows a comparison between the measured impedance of the *blocked cell* and the impedance calculated from the phase with the Kramers–Kronig transform. The good match between the measured and calculated impedance within the experimental error proves the validity of the data. Note that the relatively good NLLS fit with the equivalent circuit model shown in Fig. 5 is by itself an indication of the stability of the system.[14]

5 Conclusion

If first order reaction kinetics is one of the boundary conditions in the resolution of the diffusion equations, the *blocked cell* design can still be used to study oxygen transport in highly defective cobaltates. An appropriate equivalent circuit model, including a finite length diffusion impedance and a surface exchange reaction resistance, leads to an accurate characterization of the electrochemical cell. Chemical diffusion and surface exchange coefficients of $1{\cdot}2\times10^{-5}$ and $3{\cdot}0\times10^{-4}\,\mathrm{cm\,s^{-1}}$, respectively, have been measured for oxygen vacancies in a $SrCo_{0{\cdot}5}Fe_{0{\cdot}5}O_{3-\delta}$ sample at 880°C. Similar values for the chemical diffusion coefficient have been extracted from the impedance data with asymptotic equations derived directly from the solution of Fick's second law, thus justifying the choice of the equivalent circuit model. Finally, both the NLLS fit with the model and the Kramers–Kronig test confirmed the validity of the impedance data.

Acknowledgements

The authors are grateful for the support of the Federal Office for Energy (CH), the Priority Program for Materials (CH), Norsk Hydro a.s.(N) and Statoil a.s. (N).

References

1. Kruidhof, H., Bouwmeester, H. J. M., Doorn, R. H. E. V. and Burggraaf, A. J., *Solid State Ionics*, 1993, **63-65**, 816.
2. Teraoka, Y., Zhang, H.-M., Okamoto, K., Yamazoe, N., *Mat. Res. Bull.*, 1988, **23**, 51.
3. Gür, T. M., Belzner, A., Huggins, R. A., *J. Membrane Sci.*, 1992, **75**, 151.
4. Nisancioglu, K., Gür, T. M., *Solid State Ionics* 1994, **72**, 199.
5. Ho, C., Raistrick I. D. and Huggins, R. A., *J. Electrochem. Soc.*, 1980, **127**, 343.
6. Van Herle, J. and McEvoy, A. J., *Ber. Bunsenges. Phys. Chem.*, 1993, **97**, 470.
7. Closset, A., Study of oxygen transport in $SrCo_{7\text{-}x}Fe_xO_{3\text{-}\delta}$ sintered pellets by impedance spectroscopy. Dipl. Thesis, EPFL, 1997.
8. ten Elshof, J. E., Lankhorst, M. H. R. and Bouwmeester, H. J. M., *J. Electrochem. Soc.*, 1997, **144**, 1060.
9. Raistrick, I. D. and Huggins, R. A., *Solid State Ionics* 1982, **7**, 213.
10. Bouwmeester, J. H. M., Kruidhof, H. and Burggraaf, A. J., *Solid State Ionics*, 1994, **72**, 185.
11. Harrison, W. T. A., Lee, T. H., Yang, Y. L., Scarfe, D. P., Liu, L. M. and Jacobson, A. J., *Mat. Res. Bull.*, 1995, **30**, 621.
12. Weppner, W. and Huggins, R. A., Electrochemical methods for determining kinetic properties of solids. *Annual Review of Materials Science*, ed. R. A. Huggins, Annual Reviews Inc., Palo Alto, 1978, pp. 269–309.
13. Stochniol, G., Syskakis, E. and Naoumidis, A. Patibility studies between $La_{7\text{-}x}Sr_xMnO_3$ and 8YSZ. In *SOFC Materials, Process Engineering and Electrochemistry, Proceedings of 5th IEA Workshop*, 2–4 March 1993. Forschungszentrum Jülich, Germany, pp. 25–31.
14. Boukamp, A., *Solid State Ionics*, 1993, **62**, 131.