Role of the reference position on overpotential measurements

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Steady state polarisation measurements can be affected by electrode microstructure and geometrical arrangement. In particular, the relative position of the reference electrode with respect to the working and counter electrodes may influence the reference potential and therefore effect the overvoltage readings. The influence of the geometrical arrangement of the electrodes on the electrolyte potential lines, was simulated by solving the appropriate Maxwell equations. Simulations were in relatively good agreement with steady state polarisation and impedance spectroscopy results obtained with YSZ | LaMnO₃-based cells. The use of impedance spectroscopy to assess the appropriateness of a given electrode configuration is suggested.

Keywords: SOFC, Polarisation, Reference electrode

Papel de la posición del electrodo de referencia en las medidas de sobrepotencial

La medida de los estados de polarización fijos puede estar afectada por la microestructura del electrodo y su configuración geométrica. En particular, la posición relativa del electrodo de referencia en relación con los electrodos de trabajo y conteo puede influenciar el potencial de referencia y por lo tanto afectar las lecturas de sobrevoltaje. La influencia de la configuración geométrica de los electrodos sobre las líneas potenciales del electrolito fue simulada por resolución de las ecuaciones de Maxwell apropiadas. Las simulaciones estuvieron en relativamente buen acuerdo con el estado de polarización fijo y los resultados de espectroscopía de impedancia obtenidos con células basadas en YSZ | LaMnO₃. Se sugiere el uso de espectroscopía de impedancias para valorar la conveniencia de una configuración de electrodo.

Palabras clave: SOFC, Polarización, electrodo de referencia

1. INTRODUCTION

Polarisation measurements are one of the most important techniques for the characterisation of electrode materials for Solid Oxide Fuel Cells. However, the polarisation results obtained by different authors for similar compositions often show inconsistencies. One of the main causes for such scatter is the electrode microstructure due to the use of a variety of deposition techniques (1). However, the electrodes geometrical arrangement is also recognised as a key factor to ensure the reproducibility of polarisation measurements (2,3,4,5).

The use of reference electrodes in solid state systems is far more complex than in classical liquid electrochemistry. It is difficult to imagine the solid state equivalent to the Luggin capillary (6). For this reason, an external reference is commonly deposited onto the surface of the solid electrolyte. Figure 1 shows several examples of electrode arrangements.

Physical models show that certain electrode arrangements may cause sharp changes in the potential across the solid electrolyte (4,7). It is therefore difficult to ensure a constant reference electrode (RE) potential, a key issue for a true reference. Hammouche et al. (8) suggested a lateral RE on the electrolyte, with a potential intermediate to those of the working and the counter electrodes (WE and CE, respectively). Nagata et al. (3) used a dc equivalent circuit to confirm experimental observations in YSZ solid electrolytes with platinum electrodes suggesting the use of a symmetrical arrangement of WE and CE (eg. Figure 1.B or E). Boukamp et al. (7) pointed out the impor-

Figure 1. Different electrode geometrical arrangements in solid electrolytes.

tance of the distance between the RE and the symmetrical couple WE-CE. The accuracy of the symmetrical arrangement was also suggested by Hsieh et al. (4) based on simulations of the ac behaviour. Asymmetrical arrangements often lead to deviations of up to 20 % between measured and simulated values of the electrolyte resistance, and introduce spurious arcs on the electrode impedance spectra. More recently, a new RE concept inspired in the Luggin capillary was proposed for solid electrolytes (Figure 1.E) (9). Although accurate, this particular configuration is quite complex from an experimental point of view. Furthermore, it is impossible to implement this method in thin electrolytes ($< 200 \mu\text{m}$)

A number of simulations are reported in the literature but their experimental verification are still absent, especially in the case of ceramic electrodes. In this work the potential distribution across the electrolyte is derived for different electrode geometries by solving the appropriate Maxwell equations. These simulations are compared to experimental results obtained with air,Pt|YSZ|La_{0.9}MnO_{3- δ} air cells.

2. EXPERIMENTAL

Porous La_{0.9}MnO_{3- δ} ceramic cathodes were screen printed onto YSZ disks with different thicknesses and fired at 1275°C. Porous counter and reference electrodes were painted and thermally treated at 1000°C. Potentiometric cathodic polarisation measurements were carried out and the ohmic drop between the different electrodes evaluated by impedance spectroscopy. A complete description of the experimental procedure can be found elsewhere (10). The working electrode overvoltage (η_{WE}) can be obtained by

$$\eta_{\text{WE}} = V_{\text{WE-RE}} - R_{\text{WE-RE}} \cdot I \quad [1]$$

where $V_{\text{WE-RE}}$ is the potential difference between the working and reference electrodes, $R_{\text{WE-RE}}$ the corresponding ohmic resistance and I the current flowing through the cell.

Figure 2. Schematic view of the two dimensional model cell used in the calculations and in cathodic polarisation measurements. δ_{CE} is a measure of the degree of asymmetry.

3. MODEL BEHAVIOUR

3.1. Basic Approach

The problem under study can be solved starting from the two dimensional model cell shown in Figure 2, surrounded by air. Simulations were carried out for electrolyte thicknesses ranging from 0.2 to 20 mm with both symmetrical and asymmetrical electrode arrangements. The WE diameter (d_{WE}) was 5 mm, while the CE diameter (d_{CE}) ranged from 5 to 18 mm. The assumed electrolyte conductivity was 10 S/m. The electrodes were treated as almost equipotential lines with a conductivity higher than 10000 S/m and possess a negligible interior electric field. Two types of interfaces were considered: i) the electrode/electrolyte boundaries in which the current is perpendicular to the interface (modelled as equipotentials

Figure 3. Calculations of ϕ_d in: **A** - asymmetrical cells ($d_{\text{WE}}=5 \text{ mm}$ and $d_{\text{CE}}=13 \text{ mm}$) with different electrolyte thickness; **B** - symmetrical cells ($d_{\text{WE}}=d_{\text{CE}}=5 \text{ mm}$); **C** - symmetrical and asymmetrical ($d_{\text{WE}}=5 \text{ mm}$ and $d_{\text{CE}}=5+\delta_{\text{CE}} \text{ mm}$) thin cells ($L=0.2 \text{ mm}$).

with $V_{\text{WE/electrolyte}}=1$ V and $V_{\text{CE/electrolyte}}=0$ V); ii) the electrolyte/air in which the current is parallel to the interface.

The problem was solved in both ac and dc conditions using the finite element technique-based commercial application Maxwell 2D Field Simulator V.1.7.65 (Ansoft, Co.). Results are discussed by inspection of the potential (ϕ_d) along a line parallel and close to the electrolyte surface, where the WE is located. Both ac and dc simulations show good agreement, therefore only the dc results are presented. This is an expected consequence of the low permittivity of the electrolyte. Note that the electrode polarisation is not considered and the electrodes are assumed almost perfect conductors.

3.2. Results

Figure 3.A shows the variation of ϕ_d in asymmetric cells for different values of electrolyte thickness. It can be seen that the RE potential (ϕ_{RE}) changes with location, and also with the electrolyte thickness. For example, ϕ_d for a point 3 mm distant from the WE is ≈ 0.7 V when $L=20$ mm, and is close to 0 when $L \leq 1$ mm. In asymmetric cells with typical dimensions close to those of laboratory samples (1 mm thick and 20 mm diameter), the potential difference between WE and RE ($V_{\text{WE-RE}}=\phi_{\text{WE}}-\phi_{\text{RE}}$) approaches the total potential difference across the cell ($V_{\text{WE-CE}}=\phi_{\text{WE}}-\phi_{\text{CE}}$). Therefore, $\phi_{\text{RE}} \approx \phi_{\text{CE}}$ and the existence of polarisation in the CE is likely to affect ϕ_{RE} and thus the $V_{\text{WE-RE}}$ reading.

Results obtained with symmetrical cells are presented in Figure 3.B. These calculation show that, in symmetrical arrangements, the potential of the RE converges to a value $(\phi_{\text{WE}}+\phi_{\text{CE}})/2$ when the electrolyte thickness is lower than 8 mm. In this case, the potential distribution is uniform in nearly all the electrolyte cross section irrespective of L and ϕ_d .

The parameter δ_{CE} is defined as the difference between d_{WE} and δ_{CE} and is a measure of the degree of asymmetry. The role of d_{CE} is shown in Figure 3.C for a thin electrolyte layer. When d_{CE} equals half the electrolyte thickness (100 μm) the values of ϕ_d are already considerably affected and the potential of the RE is close to the CE potential. This means that in thin electrolytes the influence of the CE can be a critical factor.

Figure 4. Cathodic polarisation obtained with different electrolyte thickness and different electrode configurations: a - 0.2 mm/asy; b - 1 mm/asy; c - 3 mm/asy; d - 7.7 mm/asy; e - 19.5 mm/asy; f - 0.2 mm/sym. Lines are a guide to the eye. Symmetrical configuration: $d_{\text{WE}}=d_{\text{CE}} \approx 5$ mm. Asymmetrical configuration: $d_{\text{WE}} \approx 5$ mm and $d_{\text{CE}} \approx 13$ mm.

In general, these results are in good agreement with those based in physical models (4,7), equivalent circuits (3) and finite element-based techniques (5). The general conclusion is that the symmetrical cells should be preferred to ensure an homogeneous potential distribution, especially with thin electrolytes. However, obtaining symmetrical cells may not be a simple task. In fact, normal deposition techniques (eg., screen-printing, sputtering) do not allow an accurate control of the electrode dimensions in a scale of a few μm (11). Nevertheless, one can validate a given electrode configuration with a careful evaluation of the potential differences between the different possible electrode combinations ($V_{\text{WE-RE}}$, $V_{\text{RE-CE}}$, $V_{\text{WE-CE}}$).

The simulations have shown that for a symmetrical cell, the potential of a reference electrode, far enough from the other electrodes, is

$$\phi_{\text{RE}} \approx (\phi_{\text{WE}} + \phi_{\text{CE}})/2 \quad [2]$$

or

$$V_{\text{WE-RE}}/V_{\text{RE-CE}} = (\phi_{\text{WE}} - \phi_{\text{RE}})/(\phi_{\text{RE}} - \phi_{\text{CE}}) \approx 1 \quad [3]$$

Equation 3 is valid whenever the WE and CE overpotentials (η_{WE} and η_{CE}) are equal or negligible. The ratio $V_{\text{WE-RE}}/V_{\text{RE-CE}}$ will be greater than one if $|\eta_{\text{WE}}| \gg |\eta_{\text{CE}}|$ or smaller than one if $|\eta_{\text{WE}}| \ll |\eta_{\text{CE}}|$. Experimentally, one can obtain the resistances associated to $V_{\text{WE-RE}}$ and $V_{\text{RE-CE}}$ for a small ac signal when $\eta \approx 0$. Equation (3) can thus be rewritten as a function of such resistive terms:

$$R_{\text{WE-RE}}/R_{\text{RE-CE}} \approx 1 \quad [4]$$

where $R_{\text{WE-RE}}$ and $R_{\text{RE-CE}}$ are the ohmic resistances measured between electrode combinations (WE-RE and RE-CE). Impedance spectroscopy is a suitable technique to determine $R_{\text{WE-RE}}$ and $R_{\text{RE-CE}}$.

4. RESULTS

Figure 4 shows cathodic overpotential (η_{WE}) curves for $\text{La}_{0.9}\text{MnO}_{3-\delta}$ ceramic cathodes screen-printed onto YSZ substrates with an asymmetrical electrode distribution. This figure

Figure 5. $V_{\text{WE-RE}}/V_{\text{RE-CE}}$ for the same samples as in Figure 4: a - 0.2 mm/asy; b - 1 mm/asy; c - 3 mm/asy; d - 7.7 mm/asy; e - 19.5 mm/asy; f - 0.2 mm/sym. Lines are a guide to the eye.

shows an apparent increase in h_{WE} when the electrolyte thickness is reduced. Assuming reproducibility of the electrode microstructures, differences suggest that the RE deviates from an ideal RE. Note also that the overpotentials tend to a limiting value when the electrolyte thickness is $L \geq 8$ mm. When $L < 8$ mm, ϕ_{CE} can influence the potential of the RE. The values of h_{WE} obtained with the symmetrical 200 μm thick cell (Figure 4 - curve f) are similar to those obtained for asymmetrical cells with thick electrolyte layers. This result suggests that ϕ_{RE} is far from ϕ_{CE} (between 30 and 60% of ϕ_{CE}) which is in good agreement with the resistance data shown in Table I, and the estimates presented in Figure 3.B.

The scattering in the overpotential values obtained with the same material and the same microstructures can be explained by an additional non-ohmic contribution to V_{WE-RE} that may lead to inaccurate estimates of η_{WE} . This disturbance in the electrolyte potential distribution could be caused by a polarised CE. The importance of this disturbance could be minimised by using a symmetrical arrangement of the electrodes which would lead to a potential distribution where ϕ_{RE} is almost an average of ϕ_{WE} and ϕ_{CE} .

Polarisation data reported in Figure 4 were also represented in terms of the ratio V_{WE-RE}/V_{RE-CE} in Figure 5. These data show an increase of V_{WE-RE}/V_{RE-CE} with increasing current density, again suggesting the influence of the electrode polarisation. However, the observation that $V_{WE-RE}/V_{RE-CE} \approx 1$ for the asymmetrical cells with $L \geq 8$ mm, and for the symmetrical one with $L = 0.2$ mm, is in good agreement with the polarisation curves and suggests the use of Equation [3] to verify the location of ϕ_{RE} .

The dependence of the ratio V_{WE-RE}/V_{RE-CE} on the electrode geometrical arrangement is confirmed by the equivalent resistance ratio R_{WE-RE}/R_{RE-CE} . The different combinations of electrode resistances, as measured by impedance spectroscopy, are shown in Table I. The close agreement with the simulation is strong evidence for the accuracy of the measurement and shows that the values of resistance are not affected by electrode polarisation. The ratio R_{WE-RE}/R_{RE-CE} can thus provide a quick inspection of the suitability of the location of the RE, in order to predict the accuracy of a given electrode configuration. This is specially useful when working with thin electrolytes (typically under 200 μm).

5. CONCLUSIONS

The potential distribution in a three electrode solid electrolyte cell was calculated assuming a simple two-dimensional model cell. Calculations showed that an asymmetrical arrangement of WE and CE can introduce sharp potential variations in the electrolyte regions where the RE is commonly placed.

The simulated data were found in close agreement with experimental results obtained with $\text{La}_{0.9}\text{MnO}_{3-\delta}$ | YSZ cells, showing an equivalent behaviour for thick-asymmetrical and thin-symmetrical cells. The good agreement between simula-

TABLE I. RESISTANCES BETWEEN THE DIFFERENT POSSIBLE ELECTRODE COMBINATIONS OBTAINED BY IMPEDANCE SPECTROSCOPY AT 900 °C.

L (mm) R (Ω)	0.2 asym	1 asym	3 asym	7.7 asym	19.5 asym	0.2 sym
R_{WE-CE}	2.09	6.56	11.77	14.56	23.10	2.15
R_{WE-RE}	2.03	6.41	10.53	9.14	11.90	1.13
R_{RE-CE}	—	0.11	0.89	5.30	11.08	1.02
R_{WE-RE}/R_{RE-CE}	—	58.27	11.83	1.72	1.07	1.11

tions and experiments is particularly evident at low polarisation, suggesting the use of impedance spectroscopy as a quick method in order to identify the relative potential of the RE, a key point in the accuracy of polarisation measurements.

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REFERENCES

1. K. Sasaki, J-P. Wurth, R. Gschwend, M. Gödickemeier, L.J. Gaukler, "Microstructure-Property Relations of SOFC Cathodes and Current Collectors", *J. Electrochemical Soc.* **143** [2], 530.
2. J. Newman, W. Tiedemann, Potential and Current Distribution in "Electrochemical Cells. Interpretation of the Half Cell Voltage Measurements as a Function of Reference-Electrode Location", *J. Electrochemical Soc.* **140** [7], (1961).
3. Nagata M., Itoh Y., Iwahara H., "Dependence of Observed Overvoltages on the Positioning of the Reference Electrode on the Solid Electrolyte", *Solid State Ionics* **67** 215. (1994)
4. Hsieh G., Ford S.J., Mason T.O., Pederson L.R., "Experimental Limitations in Impedance Spectroscopy: Part III - Effect of Reference Electrode Geometry/Position", *Solid State Ionics* **96** 153. (1997)
5. Winkler J. , Hendriksen P.V., Bonanos N., Mogensen M., "Geometric Requirements of Solid Electrolyte Cells with a Reference Electrode", *J. Electrochemical Soc.* **145** [4] 1184. (1998)
6. Besson J, "Precis de Thermodynamique et Cinétique Electrochimiques", ed. Marketing p. 251. (1984)
7. Boukamp B.A., Vinke I.C., Seshan K., Vries K.J., Burggraaf A.J., "Influence of Electrode Geometry and NLLS Fit Analysis of I-V Measurements in a Three-Electrode Cell", *Solid State Ionics* **28-30** 1187. (1988)
8. Hammouche A., Siebert E., Kleitz M., Hammou A., "Oxygen Reduction at the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ /Zirconia Electrode", in Proc. 1st Int. Symp. on SOFC's, eds. Singhal S.C., The Electrochemical Society, Pennington, NJ p. 265. (1989)
9. Østergård M.J.L., Clausen C., Bagger C., Mogensen M., "Manganite-Zirconia Composite Cathodes for SOFC: Influence of Structure and Composition", *Electrochimica Acta* **40** [12] 1971. (1995)
10. F.M. Figueiredo, J.R. Frade, F.M.B. Marques, "Geometrical Effects on Polarization Measurements of $\text{La}_{0.9}\text{MnO}_{3-\delta}$ Cathodes Deposited on YSZ Substrates", *Electroceramics* V, vol. 2, eds. J.L. Baptista et al., Fundação João Jacinto Magalhães, Aveiro p. 179 (1996)
11. Minh N.Q., "Ceramic Fuel Cells", *J. Amer. Ceram. Soc.* **76** [3] 563. (1993)