INFLUENCE OF THE NATURE OF THE CONTACT ELECTRODE ON THE CONDUCTIVITY MEASUREMENTS OF DOPED CERIA

Hugues Duncan, Andrzej Lasia
University of Sherbrooke
Sherbrooke, Quebec J1K 2R1, Canada

ABSTRACT

Gadolinia doped ceria powders were prepared by the oxalate coprecipitation technique and pellets of these powders were sintered for 10 h at 1400°C. The impedance spectra were taken at temperatures ranging from 150°C to 800°C with different contact electrodes. Gold, platinum and silver from commercial paints and inks as well as sputtered platinum and La$_{0.3}$Sr$_{0.7}$Co$_{0.8}$Fe$_{0.2}$O$_3$ were used as contact electrodes. The total conductivities at temperatures higher than 500°C were roughly the same except when sputtered platinum electrodes were used. At lower temperatures, however, there is significant difference in the conductivity. While the grain interior resistivities are approximately the same regardless of the electrode nature, the grain boundary resistances are strongly influenced by the electrode nature.

INTRODUCTION

Doped ceria is considered as an alternative for the stabilized zirconia in solid oxide fuel cells (SOFCs). Many studies have been carried out on the doped ceria, mainly to determine total electrical, electronic and ionic conductivity and mechanical resistance (1,2). Impedance spectroscopy enables the determination of the total conductivity as well as the grain interior and grain boundary conductivity contributions at low temperatures, but requires use of contact electrodes (usually platinum or silver). To our knowledge no study focused on the effect of the contact electrode nature on the conductivity at high and low temperatures. The effect of the electrode nature on the impedance spectra of gadolinia doped ceria was studied. Specifically, the differences in grain interior and grain boundary capacitances and resistivities were analyzed.

EXPERIMENTAL

The powders were prepared by oxalate coprecipitation (3). Nitrates of cerium (Alfa Aesar, 99.5%) and gadolinium (Alfa Aesar, 99.9%) were weighted in the desired stoichiometric amounts and dissolved in de-ionized water to form a 1 M solution. This solution was added drop by drop to a 0.06 M oxalic acid solution that was adjusted to pH 6.7 with ammonia. The white precipitate was filtered, rinsed five times with water and five times with ethanol, and dried at 110°C overnight. The white precipitate was gently crushed in a mortar and calcinated at 600°C for 2 h. The powder was pressed into pellets of 2.54 cm in diameter and 1.2 mm in thickness and sintered at 1400°C for 10 h (2°C /
min). Platinum, silver and gold electrodes were applied to the electrolytes from commercial paints and inks and dried. Sputtered platinum and \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 \) (LSCF) deposited by screen-printing were also used as electrodes. Impedance spectroscopy measurements were carried by a Solartron 1260 frequency response analyzer and 1287 Electrochemical interface (for measures between 500°C and 800°C) or 1296 dielectric interface (for measures between 150°C and 500°C).

RESULTS

Grain Interior and Grain Boundary

The impedance spectra taken below 400°C were approximated by the equivalent circuit shown in Figure 1 (4). The experimental curves and their approximations are shown for 20% Gd in Figure 2 and for 10% Gd in Figure 3. The lower frequencies (on the right side of the graph) correspond to electrode reaction and are not considered here. The approximation yields the capacitance and the resistance of each process.

\[
Z = \frac{1}{T(j\omega)^\phi}
\]

where \( T \) is the capacity parameter and \( \phi \) is a constant that can assume values between 0 and 1. The CPE element in parallel with the resistance causes rotation of the semicircle by the angle of \( 90(1-\phi)^\circ \). The average capacitances, \( \bar{C} \), may be estimated as (6):

\[
T_{gi} = \bar{C}_{gi}\left(\frac{1}{R_{gi}}\right)^{1-\phi} \quad \text{and} \quad T_{gb} = \bar{C}_{gb}\left(\frac{1}{R_{gi}} + \frac{1}{R_{gb}}\right)^{1-\phi}
\]
for the first and the second semicircle, respectively, where indices $g_i$ and $g_b$ denote grain interior and grain boundary. The grain interior dielectric constant was determined from Eq. [3]:

$$C_{g_i} = \varepsilon_{g_i}\varepsilon_0 \frac{A}{L}$$

[3]

where $A$, $L$, $\varepsilon$, and $\varepsilon_0$ stand for the electrode area, sample thickness, dielectric constant and vacuum permittivity, respectively. Above 400°C only the total electrode resistance could be determined as the grain interior and grain boundary semicircles were not observed.

![Figure 2. Nyquist diagram of 20% Gd doped ceria with gold (V), platinum (ink) (□), sputtered platinum (Δ), silver (●) and LSCF (■) electrodes at 200°C.](image)

Figures 2 and 3 show the Nyquist diagrams of 10% and 20% Gd doped ceria (10% GDC and 20% GDC) at 200°C. It is obvious that the leftmost (the highest frequency) semicircle, corresponding to the grain interior, is approximately of the same diameter for all the electrodes except LSCF, which shows a lower grain interior resistivity. However, the grain boundary varies strongly with the nature of the contact electrode. While clearly resolved for silver, gold, sputtered platinum and LSCF electrodes, the semicircle overlaps with that of the electrode reaction semicircle for platinum ink. The grain interior and grain boundary conductivities for 20% GDC are shown in Table 1. There is only 4% difference in the grain interior conductivities at 200°C between gold and platinum (ink) ($1.90 \times 10^{-6}$ S cm$^{-1}$) and silver and sputtered platinum ($1.82 \times 10^{-6}$ S cm$^{-1}$). For the LSCF electrode the conductivity is 10% higher than that of the gold or platinum (ink) electrodes. However, there is a striking difference in the grain boundary conductivities. Samples covered with the sputtered platinum, silver paste and LSCF display essentially the same conductivities (ca. $5.95 \times 10^{-6}$ S cm$^{-1}$). For gold this parameter is slightly lower ($4.26 \times 10^{-6}$ S cm$^{-1}$) while for the platinum (ink) it is 2 times lower ($2.17 \times 10^{-6}$ S cm$^{-1}$). The grain interior and boundary conductivities for 10% GDC are shown in Table 2. The
Figure 3. Nyquist diagram of 10% Gd doped ceria with gold (▼), platinum (ink) (□) and silver (●) electrodes.

Grain interior conductivity is about the same for all three electrodes (the lowest being $1.34 \times 10^{-6}$ S cm$^{-1}$ with a silver electrode and the highest $1.48 \times 10^{-6}$ S cm$^{-1}$ with a platinum electrode, a difference of 10%). The grain boundary conductivity varies from $1.05 \times 10^{-5}$ S cm$^{-1}$ for a gold electrode to $2.02 \times 10^{-5}$ S cm$^{-1}$ for a platinum electrode. The grain interior conductivity for 10% GDC is 7 times higher than that of 20% GDC and the grain boundary conductivity is 2.5 times higher than for 20% GDC, in accordance with Zhang et al. (7). The electrode nature also has an effect on the capacitances. The grain interior capacitance is the same (within the experimental error) for 10% GDC (an average value of 4.6 pF cm$^{-1}$). The variations are larger for 20% GDC although for the gold, platinum (ink and sputtered) and silver electrodes the values are similar. Only for the LSCF electrode is characterized by higher capacitance (7.87 pF cm$^{-1}$). The reason for this deviation is unknown. The grain boundary capacitances are larger when a platinum (ink) electrode is used but approximately the same for the other electrodes. For 10% GDC the grain boundary capacitance with the gold and silver electrode is 1.96 and 1.60 nF cm$^{-1}$ while with platinum (ink) the value of 3.06 nF cm$^{-1}$ was obtained. The values obtained by Bae et al. (8) for 20% GDC with silver are quite similar: 3 pF cm$^{-1}$ for grain interior and 3 nF cm$^{-1}$ for grain boundary capacitances.

**Total Conductivity**

Table 1 shows the total conductivity of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ at 600°C and 800°C. The total conductivity is approximately the same when measured using gold, platinum (ink) and silver electrodes ($0.0183$ S cm$^{-1}$, $0.0179$ S cm$^{-1}$ and $0.0167$ S cm$^{-1}$, respectively) but higher by 20% when using an LSCF electrode at 600°C ($0.0208$ S cm$^{-1}$). The sample with a sputtered platinum electrode gave a total conductivity nearly 5 times lower than that found using other electrodes ($0.0035$ S cm$^{-1}$) due to the instability of this thin Pt layer.
Table 1. Grain interior (gi) and grain boundary (gb) conductivities at 200°C and total conductivities at 600°C and 800°C of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ with different contact electrodes.

| Electrode nature       | $\sigma_{gi}$ / S cm$^{-1}$ | $\sigma_{gb}$ / S cm$^{-1}$ | $\sigma_{total}$ / S cm$^{-1}$ |
|------------------------|-----------------------------|-----------------------------|---------------------------------|
|                        | 200°C                       | 600°C                       | 800°C                           |
| Gold                   | $1.90 \times 10^{-6}$       | $4.26 \times 10^{-6}$       | 0.0183                          |
| Platinum (ink)         | $1.90 \times 10^{-6}$       | $2.17 \times 10^{-6}$       | 0.0179                          |
| Platinum (sputtered)   | $1.82 \times 10^{-6}$       | $5.95 \times 10^{-6}$       | 0.0035                          |
| Silver                 | $1.82 \times 10^{-6}$       | $6.06 \times 10^{-6}$       | 0.0167                          |
| La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_3$ | $2.09 \times 10^{-6}$ | $5.75 \times 10^{-6}$ | 0.0208 |

Table 2. Grain interior (gi) and grain boundary (gb) conductivities at 200°C and total conductivities at 600°C and 800°C of Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ with different contact electrodes.

| Electrode nature       | $\sigma_{gi}$ / S cm$^{-1}$ | $\sigma_{gb}$ / S cm$^{-1}$ | $\sigma_{total}$ / S cm$^{-1}$ |
|------------------------|-----------------------------|-----------------------------|---------------------------------|
|                        | 200°C                       | 600°C                       | 800°C                           |
| Gold                   | $1.38 \times 10^{-5}$       | $1.05 \times 10^{-5}$       | 0.0186                          |
| Platinum (ink)         | $1.48 \times 10^{-5}$       | $2.02 \times 10^{-5}$       | 0.0182                          |
| Silver                 | $1.34 \times 10^{-5}$       | $1.47 \times 10^{-5}$       | 0.0178                          |

Table 3. Grain interior capacitances, dielectric constants and grain boundary capacitances of 20% Gd doped ceria at 200°C.

| Electrode nature       | $C_{gi}$ / pF cm$^{-1}$ | $\varepsilon_{gi}$ | $C_{gb}$ / nF cm$^{-1}$ |
|------------------------|------------------------|-------------------|------------------------|
| Gold                   | $4.85 \pm 0.26$        | $56 \pm 3$       | $2.10 \pm 0.09$         |
| Platinum (ink)         | $4.83 \pm 0.55$        | $54 \pm 6$       | $3.65 \pm 0.07$         |
| Platinum (sputtered)   | $5.27 \pm 0.03$        | $60 \pm 4$       | $2.17 \pm 0.09$         |
| Silver                 | $5.16 \pm 0.08$        | $58 \pm 1$       | $2.50 \pm 0.35$         |
| La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_3$ | $7.87 \pm 0.63$ | $89 \pm 7$ | $2.38 \pm 0.14$ |

Table 4. Grain interior capacitances, dielectric constants and grain boundary capacitances of 10% Gd doped ceria at 200°C.

| Electrode nature       | $C_{gi}$ / pF cm$^{-1}$ | $\varepsilon_{gi}$ | $C_{gb}$ / nF cm$^{-1}$ |
|------------------------|------------------------|-------------------|------------------------|
| Gold                   | $4.8 \pm 0.3$          | $54 \pm 3$       | $1.96 \pm 0.10$         |
| Platinum (ink)         | $4.7 \pm 0.3$          | $53 \pm 4$       | $3.06 \pm 0.36$         |
| Silver                 | $4.4 \pm 0.2$          | $50 \pm 2$       | $1.60 \pm 0.08$         |
at temperatures higher than 500°C. No measurements were taken above 700°C due to the
disintegration of this electrode. At 800°C the conductivities are again more or less the
same for the gold, platinum (ink) and silver electrodes but higher by 10% with an LSCF
electrode. Conductivities at 600°C and 800°C for 10% GDC are also in good agreement,
differing by a maximum of 4.6% at 600°C and 8.3% at 800°C from each other. While at
lower temperatures the conductivity of 10% GDC is higher than that of 20% GDC by
almost an order of magnitude, at higher temperatures (>500°C) 20% GDC is
characterized by a slightly higher conductivity.

CONCLUSIONS

It was shown that at temperatures above 500°C with a gold, silver, platinum (ink) or
LSCF the total conductivity is approximately similar (slightly higher when a LSCF
electrode is used). Sputtered platinum electrodes are not suitable for high temperature
measurements due to instability at these temperatures. The grain interior conductivity
does not vary much with the electrode nature but the grain boundary conductivity does.
Silver, gold, sputtered platinum and LSCF permit a better approximation of the grain
boundary arc on the Nyquist plot than platinum ink.

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REFERENCES

1. H. Inaba, H. Tagawa, Solid State Ionics, 83, 1 (1996).
2. M. Mogensen, N. M. Sammes, G. A. Tompsett, Solid State Ionics, 129, 63 (2000).
3. R. S. Torrens, N. M. Sammes, K. Kendall, J. C. Austin, in SOFC VI, S. C. Singhal
   and M. Dokiya, Editors, PV99-19, p. 209, The Electrochemical Society Proceedings
   Series, Pennington, NJ, (1999).
4. G. M. Christie, F. P. F. van Berkel, Solid State Ionics, 83, 17 (1996).
5. K. S. Cole, R. H. Cole, J. Chem. Phys, 9, 342 (1941).
6. G. J. Brug, A. L. G. van den Eeden, M. Sluyters-Rehbach, J. H. Sluyters, J.
   Electroanal. Chem., 176, 275 (1984).
7. T. S. Zhang, J. Ma, S. H. Chan, P. Hing, J. A. Kilner, Solid State Sciences, 6, 565
   (2004).
8. J.-M. Bae, B. C. H. Steele, Solid State Ionics, 106, 247 (1998)