DEPOSITION, ELECTRICAL PROPERTY AND DIRECT POROSITY MEASUREMENT OF Ni-ZrO₂ CERMET ELECTRODES

K.C. Chou, S. Yuan and U. Pal

Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

ABSTRACT

Porous Ni-ZrO₂ cermet anodes were deposited over dense yttria-stabilized zirconia electrolyte tubes by a technique consisting of slurry coating, pressure infiltrating and sintering. The deposition process was reproducible, the electrodes had high porosity (30%-37%), low sheet resistance (0.0064-0.019 ohms per square at room temperature) and were stable at high temperature (1273K-1473K). A unique Archimedean method was employed to measure the overall porosity of the cermet. Optical micrographs were also taken to show the cermet structure, and demonstrate the reliability of the porosity measurement and the stability of the cermet electrodes.

1. BACKGROUND

State of the art solid oxide fuel cells are based on the oxygen ion conducting yttria-stabilized zirconia electrolyte. Usually, a porous perovskite electrode is deposited on one side of the electrolyte and a porous zirconia based cermet electrode is deposited on the other side. The perovskite is stable under oxidizing conditions and it serves as the cathode. The cermet is stable under reducing conditions and it serves as the anode. For the cell to perform efficiently, the electrodes must adhere well during operation and under thermal cycle (must have matching thermal expansion coefficients). In addition, the electrodes must have the lowest possible resistance and remain porous (not sinter) during operation in order to allow easy gas phase diffusion to and from the electrolyte interface for effective charge transfer reaction. Hence, in short, a good electrode is one which is adhering,
has high stable porosity and low sheet resistance. In this paper the deposition and characterization of such Ni-ZrO₂ cermet electrodes are described.

2. DEPOSITION OF THE Ni-ZrO₂ CERMET ELECTRODES

The porous Ni-ZrO₂ cermet was deposited over the outer walls of a closed end zirconia tube which had an internal diameter of 9.5 mm and was 1.6 mm thick. Some deposition experiments were also conducted wherein the cermet was deposited over the inner walls of the tube. The cermet was between 30 to 150 microns thick, around 34% porous, contained approximately 75 wt.% Ni and had a room temperature sheet resistance between 0.0064 and 0.19 ohms per square. The flow chart for depositing the cermet electrode is shown in Figure 1; it is a modified version of an earlier reported process (1). Some of the other processing techniques for depositing these electrodes include screen printing or tape casting a layer of NiO and ZrO₂ over the electrolyte followed by reduction of the NiO to Ni (2). These processes are sensitive to the particle size of the NiO because the contact area between the particles changes during the course of the reduction process. Furthermore, the reduced Ni particles often have a core of NiO. As a result, these electrodes have higher sheet resistance. A combination of slurry coating and EVD is often used as an alternative method to deposit the cermet (3). This process results in stable cermets, however, it involves the use of the expensive EVD process.

Briefly, the process reported in Figure 1 consists of dipping (or filling) the zirconia tube (closed at one end) at room temperature with a slurry of Ni powder (60 wt.%), ZrO₂ powder (5 wt.% of Ni powder), and PVA solution (40 wt.% of a 6% PVA solution). The tube is then inverted and the slurry is allowed to run out leaving a layer of the slurry adhering to the outer (inner) wall of the tube. The tube is then turned horizontally and it is slowly rotated at a steady speed during the drying process to get a uniform layer of the slurry. After the slurry has dried the tube is sintered at 1100 °C for 17 hours under an atmosphere of nitrogen with 2% water vapor followed by natural cooling under an atmosphere of nitrogen with 5% hydrogen. At the end of this sintering step, a porous layer of nickel adhering to the outer (inner) walls of the zirconia tube is obtained. The zirconia tube is then introduced into a vacuum infiltration chamber shown in Figure 2. The vacuum chamber is maintained at a pressure of 5 torr and a zirconia slurry containing 30 vol.% ZrO₂, 70
vol.% water and 3 ml of (4N) nitric acid is introduced into the chamber in order to completely immerse the zirconia tube in the slurry. Then the vacuum chamber is opened to the atmosphere and the zirconia slurry partially infiltrates the pores of the nickel layer that is present on the outer (inner) walls of the zirconia tube. Following this infiltration step the zirconia tube is sintered for the second time at 1200 °C for 7 hours under an atmosphere of nitrogen with 5% hydrogen. The final product is a zirconia tube with a layer of nickel-zirconia cermet adhering to the outer (inner) walls of the tube. It may be noted that it was not possible to physically remove the cermet from the zirconia tube without fracturing the electrode. This demonstrated that the cermet adhered well to the zirconia substrate.

The procedure outlined above is ideally suited for depositing the Ni-ZrO$_2$ cermet on either the outer or the inner walls of the electrolyte in tubular solid oxide fuel cells. However, the process can also be used to deposit the cermet (anode) on planar cells if the cathode on the other side of the electrolyte can be successfully kept isolated from the processing environment of the cermet.

3. POROSITY MEASUREMENT

The Ni-ZrO$_2$ cermet consists of a three phase structure which includes the Ni particles, the ZrO$_2$ particles and the pores (gas phase). The porosity ($\eta$) of the cermet is defined as:

$$\eta = \frac{V_p}{V_p + V_N + V_Z} \times 100 \quad [1]$$

where $V_p, V_N, V_Z$ are the volumes occupied by the pore, nickel and the zirconia particles, respectively in the cermet.

The method used for measuring the porosity, while depositing the Ni-ZrO$_2$ cermet over the zirconia tube, is outlined below:
(1). The zirconia tube to be coated with the cermet is weighed \( (W^9) \).

(2). The weight fraction of nickel in the nickel-zirconia slurry \( (\xi) \), that is used for coating the tube, is noted.

(3). The slurry coated tube is sintered and weighed \( (W^9) \).

(4). The tube is weighed again at the end of the zirconia infiltration and the second sintering step \( (W^9) \).

(5). Next, petroleum jelly is heated to around 60 °C and the tube with the cermet is dipped into the liquid petroleum jelly. After dipping, the tube is immediately removed, forced air cooled and weighed \( (W^9) \); the petroleum jelly coats the outer cermet layer without penetrating into the pores.

(6). The same cermet tube coated with the petroleum jelly is weighed again in liquid water \( (W^9) \); due to the petroleum jelly coating the water does not enter the pores of the cermet.

It should be noted that, in step (5), instead of petroleum jelly one could use any other material having a low melting point. However, it is important that the material in its liquid state must have a high contact angle (greater than 90 degrees) with the cermet and also preferably a high surface tension. This way the material will cover the exterior (outer surface) of the cermet without penetrating into the pores. From these measurements, the volumes of the nickel and zirconia particles and the pores can be calculated as follows:

\[
V_N = \frac{(W^9 - W^9)}{(p_N - p^9)} \quad [2]
\]

where \( p_N \) and \( p^9 \) are the densities of nickel and air, respectively.
\[ V_z = \frac{(\rho_T - \rho_L)(1 - \epsilon)}{(\rho_L - \rho_P)} \]  

where \( \rho_z \) is the density of the zirconia particles.

\[ V_p = \frac{\left[\frac{\rho_T - \rho_L}{\rho_T - \rho_P}\right] - \frac{\rho_L}{\rho_T} - \frac{\rho_L - \rho_P}{\rho_T - \rho_P} - \frac{\rho_L - \rho_P}{\rho_T - \rho_P} - \frac{\rho_L - \rho_P}{\rho_T - \rho_P}}{(\rho_P - \rho_P)} \]  

where \( \rho_T, \rho_P \) and \( \rho_J \) are the densities of the zirconia tube, petroleum jelly and liquid water, respectively.

Expressions for \( V_N, V_Z \) and \( V_P \) from the above equations can be substituted in equation (1) and the porosity can be expressed as:

\[ \eta = \frac{\left[\frac{\rho_T - \rho_L}{\rho_T - \rho_P}\right] - \frac{\rho_L}{\rho_T} - \frac{\rho_L - \rho_P}{\rho_T - \rho_P} - \frac{\rho_L - \rho_P}{\rho_T - \rho_P} - \frac{\rho_L - \rho_P}{\rho_T - \rho_P}}{(\rho_P - \rho_P)} \]  

The measurement described above gives us a much more accurate quantitative description of the actual average porosity of the cermet than that obtained from microscopic evaluation. However, this type of measurement does not give information about the tortuosity in the cermet.

Several Ni-ZrO\(_2\) cermet electrodes were deposited as described earlier and the porosity measurements conducted on three of these electrodes are tabulated in Table I. These three porosity measurements typically represent the average (33.7%), the lowest (30.4%) and the highest (36.6%) porosity values. These measurements indicate that the process outlined earlier can consistently deposit cermet electrodes having porosity within a narrow range (30% to 37%). The optical micrograph picture of the sectioned cermet electrode used in porosity measurement #1 is shown in Figure 3. This micrograph shows the typical structure of the cermet in terms of the distribution of the nickel and zirconia particles, and the pores.
4. SHEET RESISTANCE MEASUREMENT

The sheet resistance or the spreading resistance of the Ni-ZrO₂ cermet electrodes is measured using the four terminal technique. A schematic of the setup is shown in Figure 4. The two end terminals are 3 to 7 cm apart and are connected to a power supply (KEPCO MSK 10-10M) in series with an amperemeter. The two inner terminals are 1.7 to 3 cm apart and are connected to a voltmeter. The four terminals are constructed by tightly wrapping 0.5 mm diameter nickel wires around the cermet that is deposited over the yttria-stabilized zirconia tube. A ceramic paste is also applied at the areas of contact between the nickel wires and the cermet to ensure proper contact when the system is heated to high temperatures (1273K-1473K). The high temperature measurements were all made in a 5% H₂-N₂ environment in order to prevent the oxidation of the nickel. The sheet resistance (spreading resistance) of the Ni-ZrO₂ cermet \( (S_R) \) in such an arrangement can be expressed as:

\[
S_R = \frac{\rho}{6} \frac{V}{I} \frac{C}{L} \quad [6]
\]

where \( \rho \) is the resistivity of the cermet

\( \delta \) is the thickness of the cermet layer

\( V \) is the voltmeter reading

\( I \) is the amperemeter reading

\( C \) is the circumference of the tube and

\( L \) is the spacing between the two inner terminals.

The thickness of the deposited cermet electrodes varied from 150 microns to 30 microns. The room temperature sheet resistance of these electrodes varied from 0.0064 ohms per square to 0.019 ohms per square. Three typical room temperature sheet resistance measurements are tabulated in Table II. In order to evaluate the long term stability of these electrodes, the sheet resistance of these electrodes were measured as a function of time at 1273K, 1373K and 1473K. These measurements...
are plotted in Figure 5. It can be seen from Figure 5 that the sheet resistance of the cermet, between 1273K and 1473K, did not decrease with holding time. This indicated that the electrodes did not undergo any major sintering at these temperatures. However, interestingly we do see a very slight initial increase in the value of the sheet resistance of these electrodes. For instance, when the cermet electrodes are held at 1473K, 1373K and 1273K the corresponding increases in the value of the sheet resistance during the first 30 hours of annealing are 9.1%, 5.6% and 2.2% respectively. But, after 30 hours, the sheet resistances of these electrodes do not continue to increase and they become quite stable. This observation suggests that, during the first 30 hours of annealing, the nickel particles may be undergoing some slight shrinkage which interrupts their connectivity. Optical micrographs of the cermet electrode before and after the 100 hour annealing treatment at 1373K is shown in Figure 6. From these micrographs it is evident that the cermet electrodes do not undergo any noticeable structural changes during annealing. Furthermore, since the overall increase in sheet resistance is very small in 100 hours, it is also not possible to distinctly identify the micro-structural changes associated with this increase.

From equation (6) it is apparent that by increasing the thickness of the cermet electrode one can decrease the spreading resistance of the electrode. However, by increasing the thickness and depending on the porosity of the cermet one would also increase the resistance to gas phase diffusion which could in turn result in higher polarization losses. Therefore, there is an optimum cermet thickness beyond which the polarization losses begin to dominate. We obtained best cell performance when these electrodes had thickness between 50 and 150 microns.

Solid oxide fuel cells having these Ni-ZrO₂ cermet electrodes were successfully operated at 1473K to extract oxygen out of molten metals (4). Each cell could operate for more than 100 hours at 1473K and could also undergo at least ten thermal cycles between 1473K and room temperature. Hence, it is expected that these Ni-ZrO₂ cermet electrodes can also be easily used in solid oxide fuel cells that are operated at 1273K for power generation purposes.
5. SUMMARY

A process consisting of slurry coating, pressure infiltrating and sintering is described for depositing adhering Ni-ZrO₂ cermet electrodes over yttria-stabilized zirconia (electrolyte) tubes. The deposited electrodes were characterized in terms of porosity, sheet resistance and long term stability at elevated temperatures (1273-1473K). Using this deposition process, we could consistently deposit Ni-ZrO₂ cermet electrodes having porosities between 30 to 37 percent and sheet resistances between 0.0064 to 0.019 ohms per square depending on the thickness. These electrodes were also stable at high temperatures (1273K-1473K).

ACKNOWLEDGEMENT

The authors are pleased to acknowledge financial support of this research by the National Science Foundation, Division of Design and Manufacturing, Grant No. DDM 9113480.

REFERENCES

1. R. E. Jensen, "Method of Electrode Fabrication for Solid Oxide Electrochemical Cells", U. S. Patent No. 4,971,830, Issued Nov. 20, (1990).

2. P. H. Middleton, M. E. Seiersten and B. C. H. Steele, "Morphology and Electrochemistry of Porous Nickel/Zirconia Cermets", in Proceedings of the First International Symposium on Solid Oxide Fuel Cells, Edited by Subhash C. Singhal, The Electrochemical Society, Inc., Princeton, NJ, (1989), p.90.

3. A. O. Isenberg and G. E. Zymboly, "High Performance cermet Electrodes", U. S. Patent No. 4,582,766, Issued April 15, (1986).
4. S. Yuan, K. C. Chou and U. B. Pal "Deoxidation of Molten Metals Using Oxygen Ion Conducting Yttria-Stabilized Zirconia Electrolyte", Accepted for Publication in EPD Congress 1993, Edited by J. P. Hager, TMS, Warrandale, PA, (To Appear in February 1993).

Table I. Typical Data on Porosity Measurement

| Variables | #1     | #2     | #3     |
|-----------|--------|--------|--------|
| W₀(g)     | 14.0765| 11.5322| 11.1410|
| W₁(g)     | 14.8085| 12.0897| 11.5971|
| W₂(g)     | 15.0150| 12.1683| 11.6707|
| W₃(g)     | 15.3190| 12.4874| 12.2916|
| W₄(g)     | 12.4010| 10.0535| 9.5942 |
| Porosity η| 36.6%  | 33.7%  | 30.4%  |

ρᵣ = 5.937 g/cm³ (measured)  \( \rho^N = 8.910 \) g/cm³ (measured)
ρ₂ = 5.600 g/cm³ (ZIRCOA Co) \( \rho^f = 1.000 \) g/cm³ (water)
ρ₃ = 0.855 g/cm³ (measured)  \( \xi = 0.950 \) (fixed)

Table II Typical Sheet Resistance Measurement Data at Room Temperature

| Sample No | L(cm) | V(mV) | I(A) | Sheet resistance (ohm/square) | Average (ohm/square) |
|-----------|-------|-------|------|-------------------------------|----------------------|
| 1         | 3     | 28.12 | 2.01 | 1.89E-02                      | 1.89E-02             |
|           |       | 25.44 | 1.82 | 1.89E-02                      |                      |
|           |       | 21.85 | 1.56 | 1.89E-02                      |                      |
|           |       | 17.66 | 1.26 | 1.89E-02                      |                      |
| 2         | 1.7   | 5.43  | 2.01 | 6.44E-03                      | 6.43E-03             |
|           |       | 4.73  | 1.75 | 6.44E-03                      |                      |
|           |       | 3.34  | 1.24 | 6.42E-03                      |                      |
|           |       | 2.32  | 0.86 | 6.43E-03                      |                      |
| 3         | 1.35  | 4.97  | 2.01 | 7.42E-03                      | 7.41E-03             |
|           |       | 4.30  | 1.74 | 7.41E-03                      |                      |
|           |       | 3.45  | 1.40 | 7.39E-03                      |                      |
|           |       | 2.92  | 1.18 | 7.42E-03                      |                      |

P.S. Circumference(C) for All Three Samples is 4.05cm.
Figure 1. Flow chart for the fabrication of the Ni-ZrO₂ cermet.
Figure 2. Schematic of the set-up for infiltrating zirconia solution.

Figure 3. Optical micrograph of a cermet having a porosity of 36.6 %. The white, grey and the dark areas represent the nickel, zirconia and the pore, respectively.
Sheet resistance (ohm/square, Ni wire)

Figure 4. Schematic of the set-up used for measuring the sheet resistance of the cermet electrodes.

Figure 5. Variation of the sheet resistance as a function of holding time at 1273K, 1373K and 1473K.

1* and 4 are outer terminals connected in series with a power supply and an amperemeter

2* and 3* are inner terminals connected to a voltmeter

Figure 4. Schematic of the set-up used for measuring the sheet resistance of the cermet electrodes.

Figure 5. Variation of the sheet resistance as a function of holding time at 1273K, 1373K and 1473K.
Figure 6. Optical micrographs of the cermet electrode before and after the 100 hour anneal at 1373K. The white, grey and the dark areas represent the nickel, zirconia and the pore, respectively.