Testing of Single Solid Oxide Fuel Cells
by DC and AC Techniques

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ABSTRACT

A test facility for 10 cm² single solid oxide fuel cells, established at Risø National Laboratory, is described. It enables a very careful characterization of cells by means of DC and AC techniques. The AC may be superimposed on the DC even at currents as high as 10 A. The maximum DC is 20 A. A model which is used for correction of an uneven radial current distribution is described. Usually the internal resistance of Risø 10 cm² cells is in the range of 25-35 mΩ at 1000°C.

1. INTRODUCTION

The national Danish SOFC programme (1) aims at the development of a bipolar flat plate stack design, at present with traditional materials for hydrogen conversion. Techniques have been established for production of 45x45x0.016 mm electrolyte platelets (ZrO₂, 8 mole% Y₂O₃ (YSZ)) by tape casting (2) and for production of La(Sr)MnO₃ and La(Ca)CrO₃ for cathodes and interconnect, respectively. Ni-cermets anodes with low Ni-content (40 vol% in reduced form (2)) and LSM based cathodes are mounted on sintered electrolyte plates by spray painting.

Development of material composition for electrodes and evaluation of fabrication process parameters require analysis of single cell performance. In order to focus on the defined objectives, the analysis is preferably conducted in an environment, which excludes stack related problems such as variations in local gas composition and chemical interaction with interconnect/sealing materials. Four test facilities have been established for analysis of single cell performance along these guidelines.
2. THE TEST FACILITY

The general layout of a test facility is shown in Fig. 1. A single solid oxide fuel cell is placed horizontally between two 40mm OD alumina tubes inside a split furnace. Sealing between the cell and the tubes is on both sides accomplished by a gold ring, which also acts as current collector. Usually the gold ring is made from ½mm gold wire, but larger dimensions have been used. Compression of the seals takes place at the operating temperature by applying an axial force in the range 100-500g. The diameter of the ring defines a test area of 10cm². Fuel gas and air are fed through central alumina tubes equipped with circular distribution plates. These plates, shaped with radial grooves, are placed ~1mm from the electrode surface during testing. Platinum wires contact the cell at the center for potential measurement (Vc). The potential at the cell rim (Vr) is measured at the current outlet from the gold seals. Cell temperature, usually 1000°C, is measured outside the test assembly at the rim of the electrolyte and inside the assembly at a distance of ~1mm from the center of the anode. The construction materials have been chosen to avoid cracking of hydrocarbons because of planned reforming tests. 9%H₂ in N₂ is usually used as a fuel gas to eliminate explosion hazards. The gas is saturated with water at room temperature to establish a difference in oxygen partial pressures corresponding to 930mV at open circuit voltage.

The resistance of the external circuit for current measurement has been minimized. 2 mm² gold wires connect each sealing ring to a 4mm² copper wire outside the furnace and an ammeter. This gives an overall resistance of 67 mΩ of the circuit connecting the electrode current pickup systems. The additional resistance of the current collecting system is discussed in section 3. Fig. 2 shows the electrical system setup, including a 20A galvanostat. The setup enables AC signals to be superimposed on the DC loads. The high resistance in series with the low impedance galvanostat ensures that the resulting cell impedance can be calculated accurately even at large variations in galvanostat impedance (0-100 Henry).

With respect to actual testing the main interest is attached to the cell resistance components in the direction orthogonal to the cell because the development aims at a bipolar design concept. In order to minimize the influence of in-plane resistance of the electrodes, current collector networks of platinum and/or gold are screen printed onto the electrode surfaces. Fig. 3 shows the current collector pattern, applied to both electrodes. The pattern consists of a circle, forming the contact basis to the gas sealing and current collecting gold ring. A number of ~1mm wide bars makes up the local current pick up system, the layout of the bars models the contact areas to interconnect plates.
and areas between the bars correspond to gas channels in the interconnect and thereby without direct contact to the interconnect. A painted porous Pt-layer covers the central 8% cell surface. A Pt layer thickness of ~10 μm is usual after one print and subsequent sintering. Several prints may be applied. A Pt print will always be required on the anode side to prevent reaction between gold and nickel at elevated temperature. Gold prints may be applied on top of the initial Pt print on the anode and directly to the cathode side.

3. THE MODEL

The presence of in-plane resistivity, be it in electrodes or in metallic current collection networks, will introduce an uneven radial current density distribution, i.e. the center of the circular test area will experience a lower current density than the rim area. The differences in current densities will be reflected in the measured local potential values \( V_c \) and \( V_r \). \( V_c \) > \( V_r \).

The measured \( V_r \) includes the voltage drop due to resistance in the current collecting gold seals. The ohmic resistance at 1000°C of the length of gold wire used for a complete ring has been measured to 71 mΩ. If the ring electronically is regarded as two parallel conductors of half the length of the circumference and the sum of current is taken to enter halfway between the ends, the resulting resistance of each ring amounts to 9 mΩ. 3 mΩ should be added to account for the terminal end (10 mm long, 2 wires), giving 12 mΩ/ring. Values of \( V_r \), corrected for the resulting voltage drop, are assumed to represent the rim potential of the cell.

Calculation of the area specific apparent cell resistance for measured current loads can be made from the cell area, OCV (Open Circuit Voltage) and \( V_c \) (giving \( R_c \)), as well as the corrected \( V_r \) (giving \( R_r \)). Fig. 4 shows E-I curves, measured for a good Risø cell. Calculation of the average slope of the two curves gives \( R_c = 0.25 \Omega \cdot cm^2 \) and \( R_r = 0.46 \Omega \cdot cm^2 \). OCV values were 913mV at the center and 900mV at the rim. The OCV values indicate a minor leak of air into the system, most probably beneath the gold ring seal through the porous anode. From these apparent resistances a computer model is used to find the true cell resistance.

The model divides the circular test area into five concentric rings, each having a width of 1/5 radius. The rings are numbered 1-5, starting from the rim. Each ring is ascribed a cross-plane (cell) resistance, \( W_r \), inversely proportional to the area of the ring.
and proportional to the true internal area specific cell resistance, \( R_x \ \Omega/cm^2 \), which is to be determined. Each ring is also ascribed an in-plane resistance, \( R_{P} \), taken to be inversely proportional to the length of the outer diameter of the ring and a factor \( K_r \). For ring 1 the length of the current path to the collecting gold ring is only half of that of the other rings. The in-plane resistance \( R_{P1} \) is therefore reduced accordingly. Fig. 5 shows an electrical equivalent circuit.

Given input values are: cell area, measured values for the total current \( I \), the potential of the center ring, \( V_c = E_5 \), and the potential at the rim \( V_r \) (corrected for the potential drop in the gold seals). Assuming linearity of \( E=F(I) \) across the interval \( OCV-V_r \), iterations with \( R_x \), beginning with \( R_t \) and decreasing towards \( R_c \) are carried out. In each iteration cycle the current through \( W_5 \) is determined from \( E_5 \). The potential drop between cell element 5 and 4 due to in-plane conduction \( \Delta E_5 = R_{P5} * i_5 \) determines \( E_4 = E_5 - \Delta E_5 \), which similarly for element 5 using \( W_4 \) provides \( I_4 \). In-plane current conduction of \( I_5 + I_4 \) through \( R_{P4} \) causes a potential drop \( \Delta E_4 = (I_5 + I_4) * R_{P4} \), which is used to determine \( E_3 = E_4 - \Delta E_4 \) and so on. Finally the potential drop by conduction of the sum of ring currents, \( \sum I_n \), across the outer half of ring 1 \( \Delta E_1 = \sum I_n * R_{P1} \) will provide the rim voltage \( E_1 - \Delta E_1 \), which may be compared to \( V_r \). Inside each iteration loop a value of \( K_i \) is sought by a secondary iteration to meet the criterium \( \sum \Delta E_n = V_c - V_r \). The iteration loops are stopped, when the calculated current distribution and \( K_i \) meet the criteria \( \sum I_n = I \) and \( \sum \Delta E_n = V_c - V_r \).

Fig. 6 illustrates the above evaluation of \( i_n \) for a cell. The resulting normalized current densities as function of radius are shown in Fig. 7 for the cell with 2 platinum current pickup prints on either side. A calculated distribution of current densities for a similar cell with one platinum print and one gold print on each side is also shown. The conductivity of gold at 1000°C is \(~4\) times higher than that of Pt, and the calculated radial current density variation is accordingly almost negligible.

4. AC-TESTING

AC impedence spectroscopy has been applied to the 10cm² cells with the setup, shown in Fig. 2. The measurements were carried out with 200mA sinusoidal AC in the frequency range 10kHz-0.1Hz, superimposed on different DC loads in the range 0-6A/10cm² in order to obtain the differential resistances at increasing load and in order to separate the polarisation resistances of the electrodes from the pure ohmic resistances. Spectra based upon phase and AC voltage at the rim were recorded (Fig. 8). The sum
of polarization resistances is seen to be reasonably well defined and a coarse separation of the electrode resistances seems possible. Subsequent analysis with Boukamp software (3) resulted in ohmic and non-ohmic resistances as given in Table 1 for comparison to DC values measured from the same cell. The agreement between AC and DC measurements is good.

Impedance measurements where AC is introduced at the rim, while phase and AC voltage is measured at the center were also carried out (Fig. 9). The sum of serial resistance and polarization resistances (66mΩ for as well 3A as 6 A loads) compares well to 63 and 61mΩ, measured by DC. Additionally the measurement appears to improve the possibility of separating the electrodes, possibly because more than 85% of the total resistance is related to the electrodes. For rim measurements only 50% of the total resistance is attributable to the electrodes, see Table 1. Application of both AC measurements in the model, described in section 3, gives close correspondence with current density distributions evaluated from DC measurements.

Further improvement of AC measurements is planned by introduction of reference electrodes on both cell surfaces. The reference electrodes will be mounted on the electrolyte outside the gold rings, and will as such refer to the Pt-air potential. It is anticipated that such a setup will enable a more direct study of the performance of each of the electrodes. However, the intention is not to make detailed electrode kinetic studies with such relatively large electrode areas. This is done with much higher accuracy on small areas (<0.5cm²). Such a setup, available at Risø National Laboratory, is described briefly elsewhere in these proceedings (4) for anodes and in (5) for the cathode.

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REFERENCES

1. M.Mogensen, C.Bagger, B.Kindl, F.W.Poulsen and P.Knudsen. "Results from the Danish SOFC Programme". 1992 Fuel Cell Seminar, Tucson, Az., Nov.29-Dec.2, 1992.

2. C.Bagger. "Improved production methods for YSZ electrolyte and Ni-YSZ Anode for SOFC". 1992 Fuel Cell Seminar, Tucson, Az., Nov.29-Dec.2, 1992.

3. B.A. Boukamp. "A nonlinear least squares fit procedure for analysis of immittance data of electrochemical systems". Solid State Ionics 20, 31-41, 1986.

4. M.Mogensen and T.Lindegaaard. "The kinetics of hydrogen oxidation on a Ni-YSZ SOFC electrode at 1000°C. These proceedings.

5. M.J.L.Østergård and M.Mogensen. "AC-impedance study of the oxygen reduction mechanism on La$_{1-x}$Sr$_x$MnO$_3$ is solid oxide fuel cells". To be published in Electrochimica Acta, 1993.

| Load A | Serial AC Resistance mΩ | Anode Resistance mΩ | Cathode Resistance mΩ | Sum AC Resistance mΩ | DC Resistance mΩ |
|--------|--------------------------|---------------------|------------------------|----------------------|------------------|
| 0      | 64                       | 39                  | 20                     | 122                  | N.A.             |
| 3      | 58                       | 31                  | 26                     | 115                  | 104              |
| 6      | 67                       | 20                  | 31                     | 117                  | 114              |
Fig. 1. Setup for testing of a single solid oxide fuel cell.

Fig. 2. Electronic circuits for testing of single cells. Combination of circuit 1 and 2 from top enables measurement of up to 7A/cell due to minimized resistance of $R_{wire}$ and $R_{Amp}$. Combination of circuit 1 and 3 from top allows current densities above 10A with superimposed AC.

Fig. 3. Screen print pattern for application of current collecting network (Pt/Au) on electrode surfaces.
Fig. 4. Curves for $V_c$, measured at the cell center, and $V_r$, measured at the cell rim, versus $I$ for a good Risø cell.

Fig. 5. Electronic circuit, corresponding to the computer model for calculation of current density distributions.
Fig. 6. Distribution of current and voltage drops between five cell rings. The apparent area specific cell resistance is 0.23Ω·cm² and 0.46Ω·cm² from the center potential and the rim potential, respectively. The calculated resistance is 0.37Ω·cm².

Fig. 7. Calculated current density distributions from center (left) to rim with one and three Pt current collector layers and with a combined layer of 1 Pt print and 1 Au print.
Fig. 8. Impedance plot for a relatively poor Risø cell. Phase and voltage was measured at the rim of the cell. The pure ohmic resistance therefore includes the resistance of the sealing rings and the resistance of the double printed Pt current collecting layer (compare to Fig. 9).

Fig. 9. Impedance plot for a relatively poor Risø cell. Phase and voltage was measured at the cell center, while AC was fed at the rim (compare to Fig. 8).