JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 970–976

Laboratory techniques for evaluating solid oxide fuel cells

J. VAN HERLE, K. RAVINDRANATHAN THAMPI

Institut de Chimie Physique II, Ecole Polytechnique Fédérale de Lausanne, CH 1015, Lausanne, Switzerland

Received 10 November 1993; revised 11 March 1994

The construction of a small solid oxide fuel cell laboratory is described in terms of required materials, measuring techniques and equipment design. Details of various electrode deposition techniques and ways of making contacts to the electrodes are also outlined.

1. Introduction

Research in the field of solid oxide fuel cells (SOFC) has been in progress for almost 30 years, with an increased interest during the last few years. The potential advantages of this energy conversion system are well known [1]: 'clean' energy (H_2 or CH_4 is used as a fuel; low NO_x emission), high efficiency, an all solid system (compact modules delivering high power densities) and recoverable heat as a byproduct (possibility of cogeneration). A number of problems, which formerly limited the use of fuel cells, have been solved by progress in materials science and electrochemistry; these involve chemical and thermal materials compatibility, and the fabrication of efficient electrodes and current collectors. This further explains the growing interest in SOFC development.

In most publications dealing with SOFC fundamentals, the experimental part gives a general description of the equipment setup, the techniques used and some materials handling, but frequently important details are omitted. This causes difficulty in reproducing results from other laboratories. Recently, the International Energy Agency (IEA), under their SOFC development programme, has highlighted important topics of relevance to SOFC development. Laboratory practices, ceramic powder characterization, micromodelling and SOFC system stack evaluation have already appeared in published form for the use of members [2–5].

This paper describes some designs and procedures acquired through hands-on experience, in addition to those published by the IEA. A good overview of routine and standard equipment for a SOFC laboratory has been published elsewhere [2].

2. General

The working principle of a SOFC is depicted in Fig. 1. Oxygen is reduced at the cathode to O^{2-} anions which are transported through the gas tight ceramic membrane (the solid oxide electrolyte), to the anode where they combine with fuel molecules (H_2 or CH_4) to give the combustion product(s) (H_2O and CO_2). The electrons are released and transported back to the cathode through the external circuit, thereby delivering electrical power. To indicate orders of magnitude, electrode thicknesses lie at around 5–50 μm, the electrolyte thickness at around 100–300 μm, and electrode areas may vary from a few to tens of square centimetres.

Since the solid electrolyte conducts the O^{2-} ions only at high temperatures, the cell is operated at 800 to 1000°C. As cathode materials, noble metals or conducting oxides of the perovskite family are used. As anode, metals serving as catalysts for hydrogenation reactions are used, or a matrix of these metals with solid electrolyte particles in the form of a cermet [1].

The essential requirements to operate a SOFC are the following (Fig. 1): control of temperature; gas handling and atmosphere control; a solid electrolyte sample; two electrodes (anode and cathode) – often the cell performance depends on the formulation and the procedure of electrode deposition; contacts to the electrodes in order to make electrochemical measurements; a cell holder suitably designed to manage the gas flow and separations.

Additionally, suitable measuring devices and techniques are also required to characterize the cell.

3. Practical aspects

3.1. *Gas handling and atmosphere control*

In the simplest case, the atmosphere is controlled by the direct supply of gas from a gas cylinder, e.g. air, O_2 or H_2. In this case, the system need not even be closed (see below). For precise partial pressures (of oxygen), a closed design with gas inlets and outlets becomes necessary. For many applications, an oxygen partial pressure range from 10^{-5} to 1 atm is sufficient; this can conveniently be achieved by mixing O_2 with N_2 or Ar, monitored by mass flow controllers. Instead of mixing pure oxygen, an already precalibrated O_2 in Ar or N_2 mixture, e.g. 1% oxygen allows more precise monitoring of low oxygen partial pressures.

Alternatively, the gases can be mixed less precisely using rotameters along with 'soap-bubble' meters, and the exact oxygen content measured by a commercially available or self-made zirconia based oxygen sensor.

For certain experiments, gases should be dried to

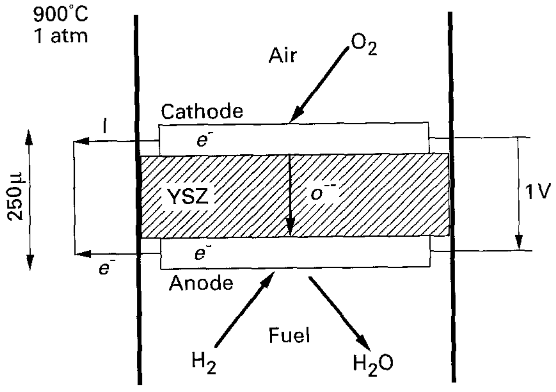

Fig. 1. Operating principle of a solid oxide fuel cell.

eliminate moisture. Water molecules will compete with oxygen molecules for the active sites on the electrodes and this is critical at low oxygen partial pressures [6]. As a drying agent, molecular sieve is used, contained in designed glass tubes (Fig. 2). The four-way stopcock allows the sieve to be bypassed, if required. A layer of blue silica-gel on top of the molecular sieve bed is useful to indicate the saturation of the molecular sieve with H_2O. The design has the advantage (besides being cheap) of easy regenerability: the whole unit can be disconnected and the tube inserted in an appropriate small, vertically arranged tubular oven, where the sieve is dried at 250°C under a stream of argon.

Hydrogen also can be used to set very low oxygen partial pressures in the system. Traces of oxygen are removed by passing through a deoxygenation catalyst. The gas is then passed through a water-bubbler. Both the deoxygenating and the water-bubbling unit are made of stainless steel but are otherwise similar in design to the molecular sieve unit (Fig. 3). Again the four-way glass stopcock allows bypassing of the unit. Connections between metallic tubing (6.3 mm) and glass tubing (o.d. 8 mm) are made by short tubes of PVC. The tightness is assured by Teflon tape wound around the plastic–metal or plastic–glass connection.

3.2. *Electrolyte preparation*

The solid ion conductor material used was always yttria-stabilized zirconia (YSZ), varying from 6 to 8 mol% of yttria dopant concentration (6YSZ-8YSZ). Sample shape and size varied from thin tape cast plates (50 mm × 50 mm × 0.1–0.3 mm) to thick pressed pellets or squares (diameter or edge 25 mm, thickness 1–2 mm). 'Green films' of tape cast samples were sintered in our laboratory. An example of a sintering curve is given in Fig. 4.

For sintering the films, the underlying substrate was a flat, mirror-polished pure alumina (99.8%) plate (material KER 710 after DIN), to which the YSZ green film will not stick. The film was loaded with a weight (alumina or zirconia) of 0.5–2 g cm^{-2} on top. Between the weight and the YSZ film a 0.3 mm thick pure alumina paper was placed as a separator.

In contrast to the procedure practiced in other

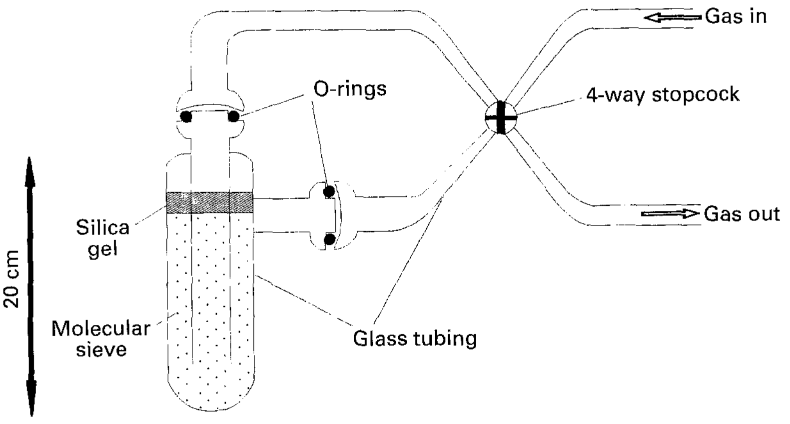

Fig. 2. Molecular sieve unit for the drying of gases.

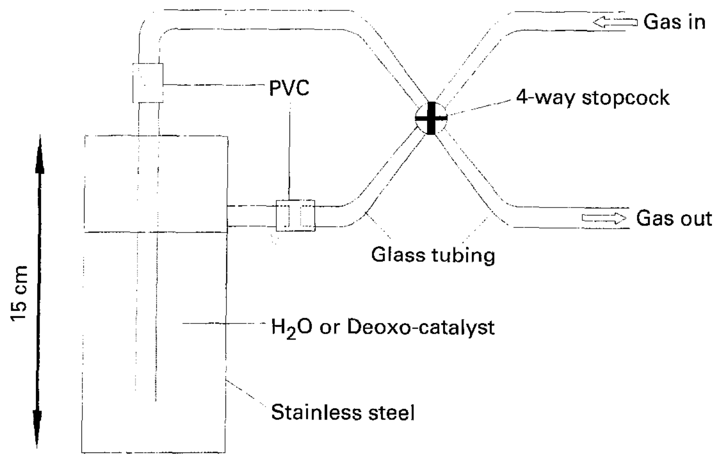

Fig. 3. Water bubbling unit or deoxygenating unit for hydrogen gas.

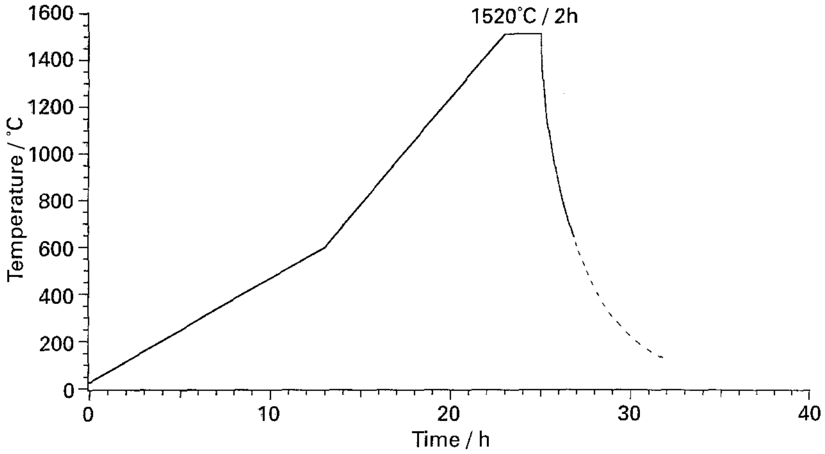

Fig. 4. Sintering curve for a 200 μm thin 'green' YSZ tape.

laboratories [e.g. 6, 7] electrolyte surfaces were not further polished in our experiments. In fact, it was hoped to achieve the opposite, namely a rough electrolyte surface (by etching with HF [8]), since this improved the adherence of the electrode when it was attached to the YSZ surface. The electrode impedance was also lowered.

Conductivity of electrolyte samples can be measured with a variety of techniques [2], of which the most common is the four point method. Usually, a rod of electrolyte material of 2 mm × 2 mm, several centimetres long, was cut from a *thick* sample with a diamond saw for this purpose.

To cut strips, rather than rods, without damage from *thin* samples (< 300 μm), the following method was used. The plate to be cut was glued with an acetone-soluble wax, which liquefies upon heating, onto a graphite support block. The sides of the block were provided with threads to allow fixing onto a screw of the diamond saw unit (Fig. 5). Graphite was chosen because (i) it is a heat conductor (for the wax to melt and detach) and (ii) it is soft for the cutting blade. With this technique, a series of e.g. 2 mm wide strips could easily and quickly be cut from a plate of 100 to 300 μm thickness.

The diamond saw may also be used for cutting electrolyte test samples of specific size, e.g. four squares of 20 mm × 20 mm out of a 40 mm × 40 mm plate. This is however time-consuming. A much quicker method, which in most cases was sufficiently accurate, made use of the thermal shock effect on ceramic material [9]. A heating wire (Kanthal, diameter 0.6 mm) tensioned with springs between two fixing points was electrically heated to redness. On placing a YSZ plate (< 300 μm) on the hot wire, the thermal shock caused the plate to break sharply along the line of its contact to the wire.

Another device for measuring the conductivity of the electrolyte samples, made use of the van der Pauw technique [10]. According to van der Pauw, any four contacts connected to a conducting sample of known and constant thickness allows direct determination of the resistivity of that sample through application of the van der Pauw formula [10]. The simple device consisted of a small block (15 mm × 15 mm × 4 mm) containing four holes (diam 0.7 mm) arranged in a square of 10 mm × 10 mm. The block was made of stumatite, a mineral (60% SiO_2, 35% Al_2O_3, 3% TiO_2, 1% Fe_2O_3) which is cheap, light, insulating, very easily machinable and temperature resistant (up to 1200°C). Silver or platinum wires were fed through the holes and fixed at the other side with a silver metal binder paste (RS Components Ltd, UK). The device is pressed down with a weight onto the test sample. Retained onto yet another stumatite support with a ceramic rope binding, the whole setup is easily slid into the oven for measurement. The same technique is also used for measuring resistivities of 'real' (i.e. usually porous) electrodes, deposited on a non-conducting substrate (alumina).

3.3. *Electrode preparation*

The standard electrodes for SOFC applications are lanthanum strontium manganite (LSM) for the cathode, and nickel-cermet for the anode [1]. These were usually prepared by mixing the electrode powders with a suitable binder (in the approximate ratio 2 : 1 by weight) to form a paste. The paste was then screen printed or slurry coated onto a YSZ plate and fired. A

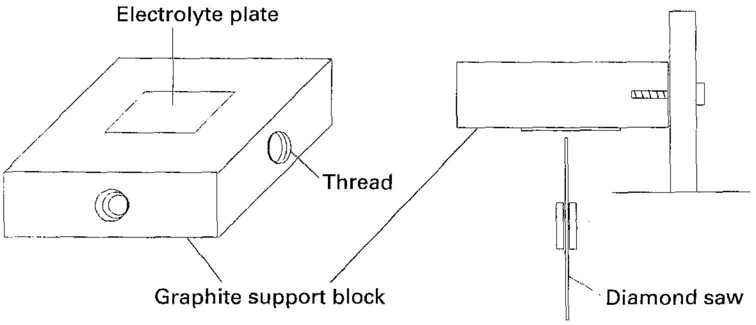

Fig. 5. Mounting of a thin electrolyte plate on a graphite support block for cutting strips with a diamond saw.

good binder was prepared by dissolving 8 wt% ethylcellulose in terpineol, under magnetic stirring, on a heating plate.

For testing purposes, commercial metal pastes or lacquers can be used. Platinum was often sufficient as a test anode, and silver was a good test cathode. The metal pastes were applied directly onto the electrolyte surface by a brush and fired. In particular, the Degussa platinum paste was preferred over other commercial pastes because of its better adhesion property.

To make electrodes that show low overpotential, other deposition techniques than brushing pastes were necessary. As a rule, the electrolyte surface was first chemically etched [8]. Application of electrodes in the subsequent step, that adhere well to the electrolyte, was achieved by electroless deposition [8, 11] (for metals), slurry coating or a solution impregnation method, followed by a sintering step (for oxide electrodes). With the last technique, especially active sites or domains could be established at the electrode/electrolyte interface [12].

Generally, the electrodes are characterized by their morphology, thickness and porosity. All these properties may be qualitatively evaluated through scanning electron microscopy. A quantitative estimate for *porosity* was achieved by the following. The weight of the deposit, together with the geometrical electrode area and the known density of the electrode material, allowed calculation of the theoretically expected thickness, d_{th}, of the electrode if it were assumed to be a dense layer. On a microstylus apparatus the real thickness, d_{rl}, was measured. The volume porosity was then estimated as $(1 - d_{\mathrm{th}}/d_{\mathrm{rl}})$.

Other than by the microstylus, electrode *thicknesses* could also be accurately measured under the electron microscope by viewing a crossection. The disadvantage obviously lies in the necessity to break the sample.

In some cases, the *effective surface area* of electrodes could be estimated by simple cyclic voltammetry in contact with an aqueous electrolyte, as for instance for porous platinum paste electrodes in 0.5 M H_2SO_4. From the charge under a distinct peak of the cyclic voltammogram, the effective surface of a 10 μm thick electrode was calculated to about 20 cm^2, a factor of 10 times the geometrical area of 2 cm^2. This agreed well with other measurements from the literature [13]. It shows that because of its open three-dimensional network, a porous electrode can have many more potentially active sites than expected.

3.4. *Electrode contact*

3.4.1. Materials. As contacting wires pure noble metal material is generally used (Pt, Au, Ag, diameter 0.25 to 0.5 mm).

Alternatively, an alloy of Ag–Ti can be used. This alloy is less volatile and more rigid than pure silver at high temperatures. For high currents (several A), the use of > 1 mm diameter Haynes alloy (No. 214 or 230) lead wires is recommended. Thick noble metal wires (Pt, Au) are too expensive, and were found, for the case of gold, to easily melt at high temperature and under high current load.

As current collectors, commercial platinum mesh (cathode side) or nickel mesh (anode side) cut to the desired size was pressed on the electrodes. To each mesh two lead wires were spotwelded. A gold mesh was fabricated in the following way. A piece of commercial graphite sponge was cut to an appropriate size, e.g. 10 mm × 10 mm. Graphite being conductive, the piece was directly goldplated from a gold bath, and subsequently baked in an oven at 900°C for several hours to completely burn off the graphite, to give a spongy goldmesh with many contact points and crosslinks. The advantage of gold as a material is its softness, excellent conductivity at high temperatures, inertness towards chemical reaction with the electrodes, and easy reusability.

3.4.2. Methods. In some cases, a metal binder paste could be used directly as a contacting aid for connecting a wire to an electrode, e.g. binding a platinum wire to a platinum electrode with a platinum paste. However, this frequently gave weak mechanical contacts. One good paste was the previously mentioned silver epoxy. Its two components were thoroughly mixed in equal quantities at room temperature, and immediately applied. By blowing hot air on the contact, the paste set to a mechanically strong, highly reliable contact within 3 min.

A way of making 'neat' contacts, i.e. without any paste, is through thermo-compression. Pt, Au or Ag wires, about 3 cm in length, were hammered flat at one edge and then pressed under a weight onto any electrode. A 0.3 mm thin alumina paper inserted between the weight and the wire prevented them from bonding together. The bonding was achieved by heating from one to several hours at an appropriate temperature, e.g. at 930° for gold or at 850°C for silver. The 3 cm long wire tails were spotwelded to longer Ag–Ti wires; the spotwelded contact was subsequently reinforced by application of the silver epoxy paste. An alternative to electrical spotwelding was flame welding.

3.5. *Equipment design and tools*

Electrochemical testing on undivided cells (the so-called 'oxygen pump mode' [2]) was conducted in a tubular oven under controlled atmosphere. A long open ended mullite tube (o.d. 60 mm) with at least 15 cm protruding outside of the furnace on both sides was useful. Both sides of the tube were closed by stainless steel flanges: through a 45 degree angle inner construction, the flanges, which need not be cooled, pressed a regular rubber O-ring onto the mullite tube to give a gas tight connection. The gas stream passed from one side to the other. The wires contacted to the cell, which was placed in the middle of the oven, were guided through four-hole mullite tubelets (o.d. 9 mm), which at the same time served as iso-

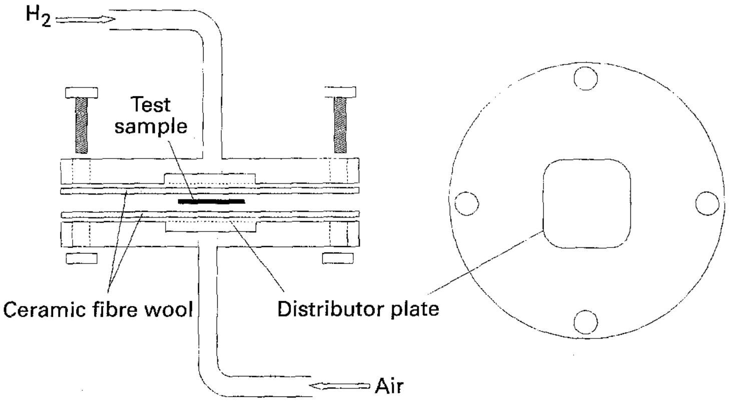

Fig. 6. Flange design for holding a SOFC test sample.

lation, towards an electrical feedthrough in one of the flanges. The feedthrough was fixed on the flange by a simple O-ring and had a single cable connection to the outside with eight inner wires. These corresponded to eight gold pin contacts on the inside of the feedthrough. To the contacting wires of the cell, small metal 'feet' were soldered which were then easily and firmly inserted into the hollow gold pins.

An extra 3 mm o.d. tube outlet in one flange was provided for the thermocouple placed close to the cell. This thermocouple feedthrough was hermetically sealed with a fast drying silicon glue. The thermocouple could not be connected through the gold pin contacts of the electrical feedthrough, which became hot during measurement, since it needed a proper reference point.

Divided cells, i.e. with fuel and oxidant atmospheres separated by the electrolyte membrane as in Fig. 1 ('fuel cell mode'), were tested in two ways. Using the more tedious method, the cell was a thick pellet ($> 500\,\mu$m) that was glued onto a pure alumina or zirconia tube (o.d. 20 to 25 mm) with a ceramic binder (Feuerfestkitte 1500, Firag, Switzerland) and allowed to dry so that the binder set. This tube was then positioned in the tubular oven. Hydrogen was passed into the tube (anode side), whereas the cathode (outside) was exposed to the air atmosphere.

This design was useful for doing impedance spectroscopy and current-overvoltage measurements on electrodes. In particular, electrical noise from within the oven was minimized by keeping a grounded Inconel tube (500 mm long, o.d. 54 mm) in the oven which shielded the cell. The Inconel Faraday cage was periodically sandblasted to remove its oxide layer.

Ceramic binder pastes were checked for tightness with the same tube setup. Via the inlet an overpressure was exerted in the tube, closed at the opposite end by the pellet glued to the tube with the ceramic binder under test. The pressure was recorded by a transducer and its decay with time followed on an X–Y-recorder.

The much quicker way of testing a solid oxide fuel cell consisted of the design depicted in Fig. 6. The cell was pressed between two alumina paper cushions (2 mm thick) and high temperature inox steel flanges (Inconel 600) each with one inlet. Humidified hydrogen was passed on the anode side and air on the cathode side. At the edges of the test sample, hydrogen diffused to the atmosphere where it spontaneously burned. Using pure hydrogen gas was acceptable on safety grounds, because of the rapid and complete combustion of exhaust hydrogen. Current collector meshes had been put over the electrodes with tape to hold them in place during mounting of the sample. Under the pressure of the flanges and the high temperature exposure during heat up, the meshes bound well in situ to the electrodes, whereas the tape burned off. The flanges were secured with screws and nuts, held in place by ceramic washers, and the assembly was inserted into a chamber furnace, with only the gas inlets protruding. At operating conditions an overpressure of only ~ 20 mbar was exerted on both sides of the test membrane.

The major advantage of this design is the speed of installing and demounting a sample, which can be recovered for reuse.

3.6. *Electrochemical measurements*

Current–voltage curves of fuel cells in operation can be recorded in a number of ways. The simplest methods involved use of a standard resistance box or electronic load. The more precise and usual method made use of a potentiostat.

For impedance spectroscopy measurements, care had to be taken in determining the electrolyte resistance from the high frequency intercept with the real axis in a Nyquist plot. The upper frequency limit of the frequency response analyzer (Solartron FRA 1253, Schlumberger Ltd, UK), 20 kHz, was often insufficient to close the electrode arc to intersect the real axis at the higher frequency part, especially at high temperatures ($> 800°$C), and the electrolyte resistance could only be derived by extrapolation to an intercept. Therefore, an equivalent electrical circuit model was necessary to fit the experimental data and extrapolate them to the real axis intercept at high frequency. The electrodes used for the impedance measurements must possess a well known and reproducible electrochemical behaviour for which appropriate equivalent models are available. Platinum paste (Degussa 308A) or silver lacquer (Degussa L200) electrodes were studied in detail [14, 15] and found to give an electrode impedance response that could be fitted by simple circuit models.

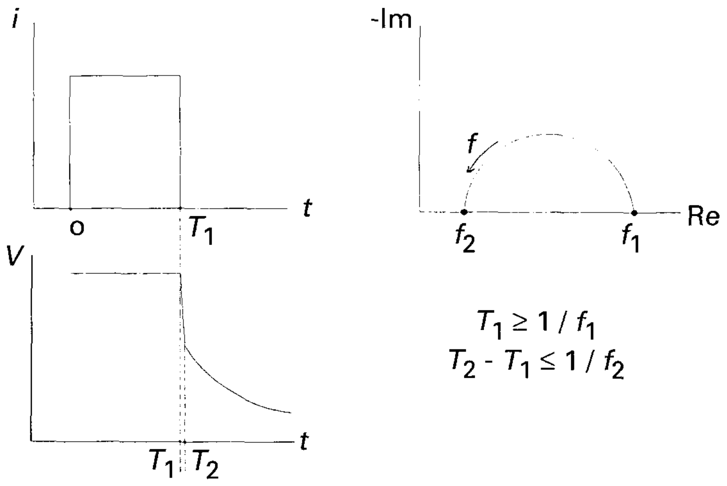

Fig. 7. Correspondence between impedance spectroscopy and the current interruption method. See text.

Another method used for determining the ohmic resistance part of a fuel cell in operation, was the current interruption technique. With this technique, a constant current pulse of known duration was applied between both electrodes of a SOFC. Following the sudden current interruption at the end of the pulse, the voltage between both electrodes dropped back to zero (for an oxygen pump measurement) or to the open circuit value (for a fuel cell measurement), at first abruptly, then followed by an exponential tail. The vertical drop was considered to be purely ohmic and ascribed to the electrolyte resistance, whereas the exponential drop corresponded to the polarization of the electrodes [7]. The voltage drop was recorded on the millisecond scale on a fast digital storage oscilloscope. The minimum duration of the constant current pulse was determined by the time necessary for the cell to reach steady state conditions. This time, T_1, corresponded to the inverse of the frequency, f_1, in an impedance measurement at which the electrode impedance response arc intersected the real axis at the low frequency end (Fig. 7). Equally, the vertical ohmic drop on the oscilloscope had to be read within a timescale, $T_2 - T_1$, that corresponded to the inverse of the frequency f_2, the high frequency intercept of the impedance arc on the real axis, where it approached the electrolyte resistance value. This correspondence between impedance spectroscopy and current interruption is represented in Fig. 7.

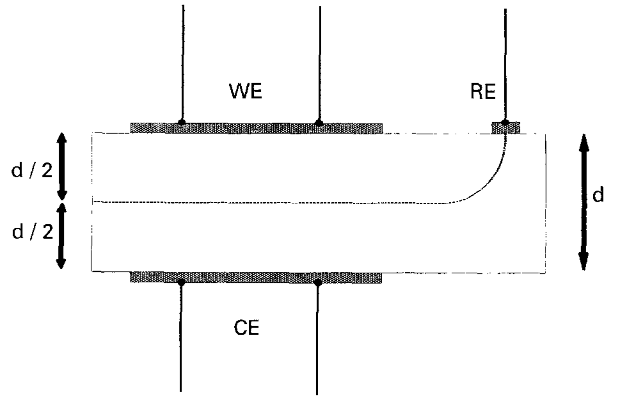

Fig. 8. Electrode geometry for an SOFC test sample with reference electrode (scale exaggerated). The reference electrode equipotential line is drawn here halfway the electrolyte thickness (RE: reference electrode, WE: working electrode, CE: counter electrode).

Therefore, to correctly apply the current interruption technique, a preliminary impedance measurement was advisable. This made the current interruption measurement virtually redundant, since the impedance measurement already supplied the required data. Furthermore, the distinction between the abrupt drop and the lagging tail was not always sharp, due to fast electrode kinetics at high temperatures. This was compounded by the electrical noise on the cell, for example coming from the heating elements of the oven, especially at high temperatures and low resistance values (large electrode area and thin electrolyte membrane), where the voltage drop was very small. This could in part be overcome by shielding the cell with a grounded Inconel tube and by averaging the signal on the oscilloscope over a number of interrupt cycles.

The use of a reference electrode in solid state electrochemistry is straightforward. In general, a platinum or silver wire was fixed with a metal paste onto the electrolyte test sample, a few mm away from one of the electrodes (on the cathode side in the case of divided cells), which were arranged symmetrically on opposite faces of the electrolyte membrane (Fig. 8). It must, however, be stressed that the ohmic drop between this reference point and either of the electrodes always needed to be specifically determined for every sample (e.g. by impedance spectroscopy). It cannot be assumed that the reference electrode will naturally lie on the equipotential line that ‘cuts’ the electrolyte ‘in half’ (Fig. 8), so that both ohmic drops (between reference and cathode on one hand, and between reference and anode on the other hand) will add equally to give the total ohmic drop between anode and cathode. This is of the utmost importance when constructing current-overvoltage curves.

Acknowledgements

Many thanks to H. Middleton (Imperial College, London) for various helpful discussions regarding the current interruption technique, also for demonstrating the flame welding technique. To J. Castano (Labo de Céramique, EPF Lausanne) for use of the laboratory facilities. To A. J. McEvoy, for comments on the manuscript. The continued financial and moral support from L. Dubal, Swiss Federal Energy Office, is greatly appreciated.

References

[1] K. Kinoshita, F. R. MacLarnon and E. J. Cairns, 'Fuel Cell Handbook', US DoE Pub. 644, Sept. (1988).

[2] 'Recommended Practices for SOFC Products and Systems Evaluation, an IEA SOFC Task Report', Swiss Federal Office of Energy, Bern, Switzerland, Aug. (1992).

[3] U. Bossel, 'Facts and Figures, an IEA SOFC Task Report', Swiss Federal Office of Energy, Bern, Switzerland, Apr. (1992).

[4] 'SOFC Micromodelling, an IEA SOFC Task Report', Swiss Federal Office of Energy, Bern, Switzerland, May (1992).

[5] 'SOFC Stack Design Tool, an IEA SOFC Task Report', Swiss Federal Office of Energy, Bern, Switzerland, Nov. (1992).

[6] T. Gür, R. Raistrick, A. Huggins, *J. Electrochem. Soc.* **127** (1980) 2620–2628.

[7] D. Wang, A. Nowick, *ibid.* **126** (1979) 1155–1165.

[8] J. Van Herle, K. R. Thampi, A. J. McEvoy, *in* 'Fundamental Barriers to SOFC Performance'. Proceedings of the 4th IEA SOFC Workshop, Lausanne, Switzerland, Aug. (1992), Swiss Federal Office of Energy, Bern, Switzerland, p. 21–28.

[9] U. Bossel, Fuel Cell consultant, Baden (Switz.), private communication.

[10] L. J. van der Pauw, *Philips Research Reports* **13** (1958) 1–9.

[11] M. M. Murphy, J. Van Herle, A. J. McEvoy, K. R. Thampi, J. Electrochem. Soc. (in press).

[12] K. R. Thampi, J. Van Herle, A. J. McEvoy, *in* 'Fundamental Barriers to SOFC Performance', Proceedings of the IEA Workshop, Lausanne, Switzerland, Aug. (1992), Swiss Federal Office of Energy, Bern, Switzerland, p. 35–42.

[13] T. Kenjo, S. Osawa, K. Fujikawa, *J. Electrochem. Soc.* **138** (1991) 349–355.

[14] J. Van Herle, A. J. McEvoy, *Ber. Bunsenges. Phys. Chem.* **97** (1993) 470–474.

[15] *Idem, J. Phys. Chem. Sol.*, **55** (1994) 339–347.