INTERNATIONAL ENERGY AGENCY

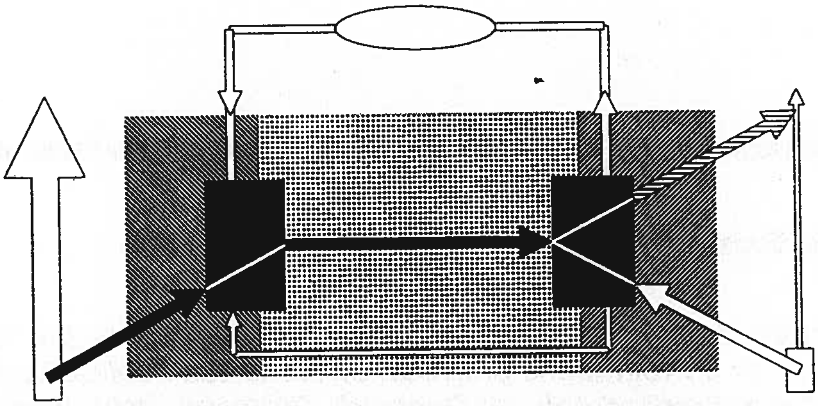
Programme of R, D & D on Advanced Fuel Cells
Annex II : Modelling & Evaluation of Advanced SOFC

EF Nr. 192852

Final report :

RECOMMENDED PRACTICES FOR SOFC PRODUCTS & SYSTEMS EVALUATION

(exploratory phase)



Swiss Federal Office of Energy, Operating Agent Task II

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RECOMMENDED PRACTICES FOR SOFC PRODUCTS & SYSTEMS EVALUATION

(exploratory phase)

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PREFACE:

THE IEA PROGRAMME OF R, D& D ON ADVANCED FUEL CELLS

International Energy Agency

The International Energy Agency was formed in November 1974 to establish cooperation among a number of industrialized countries in the vital area of energy policy. It is an autonomous body within the framework of the Organization of Economic Cooperation and Development (OECD). Twenty-two countries are presently members, with the Commission of the European Communities also participating in the work of the IEA under a special arrangement.

Programme of R,D&D on Advanced Fuel Cells

The IEA Implementing Agreement for a Programme of R,D&D on Advanced Fuel Cells was established in April 1990. There are now ten signatories to the agreement: Denmark (DEA), Germany (KFA-Jülich on behalf of BMFT), Italy (ENEA), Japan (NEDO), the Netherlands (NOVEM), Norway (NCSIR), Spain (Hidroeléctrica Española), Sweden (NEA), Switzerland (OFEN), United Kingdom (DOE). The overall programme is managed by an Executive Committee while the management of the individual tasks is the responsability of the Operating Agents. The first of the two tasks of the IEA Advanced Fuel Cells Programme deals with the analysis of the Balance-of-Plant of Molten Carbonate Fuel Cells and the other with the Modelling and Evaluation of Advanced Solid Oxide Fuel Cells. Five new annexes are in preparation.

Annex II: Modelling and Evaluation of Advanced Solid Oxide Fuel Cells

The collaborative effort was scheduled for an initial two year term of Annex II, with Switzerland acting as Operating Agent. The targeted objective was to advance natural gas-fuelled solid oxide fuel cells technologies through:

i) the numerical modelling of innovative concepts which have the potential for low-cost mass production and higher conversion efficiency; the establishment of the necessary experimental data base and the model validation;

ii) the elaboration of recommended practices for SOFC products evaluation and their application to available SOFCs in order to assist the development taking place in industry, strengthen confidence and prevent confusion in the market.

The original signatories were Italy, Japan, the Netherlands, Norway, and Switzerland. They have been joined by the United Kingdom, Denmark and Germany.

The task-sharing work has been divided into seven *activities*, each with an appointed *activity leader*:

i) Stack Design Tool (Norway)
ii) Micromodelling (Switzerland)
iii) SOFC Data (Denmark)
iv) Recommended Practices for Electrochemical Evaluation (United Kingdom)
v) Recommended Practices for Thermomechanical Evaluation (Italy)
vi) Recommended Practices for Powder Characterisation (The Netherlands)
vii) Recommended Practices for Stack Evaluation (Japan)

Augustin McEvoy, from the Federal Institute of Technology, in Lausanne, acted as Operating Agent on behalf of the Swiss Federal Office of Energy.

Executive Summary

The evaluation of "SOFC Products" must encompass all aspects of Solid Oxide Fuel Cell Systems, ranging from power conversion, quality of power, controls, reliability and safety, materials, thermal cycling and aging rate, through to cost effectiveness and impact on the environment.

The development of internationally agreed upon evaluation procedures for each of these areas as well as procedures for preventive maintenance, failure analysis, diagnostics and economic analysis is needed now to assist the development taking place in the industry while strengthening confidence and preventing confusion in the market.

It is the purpose of the "Recommended Practices for SOFC Products & Systems Evaluation" activities to adress the development of such test procedures. Experts groups have been set up within the IEA SOFC-Task to launch the necessary research activities toward this goal.

During Phase I of the SOFC Task, it has been possible to complete an exploratory approach, whose results are presented in this final report. A first set of four topics have been scrutinized, i.e.:

1. **Electrical / Electrochemical Characterisation of SOFC Components & Cells**, under the leadership of **Hugh Middleton** (United Kingdom), in collaboration with Denmark, Italy, Japan, the Netherlands, Norway, Switzerland
2. **Mechanical / Thermomechanical Characterisation of SOFC Materials & Components**, under the leadership of **Marco Brocco** (Italy), in collaboration with Switzerland, Japan, Netherlands and Denmark
3. **SOFC Powder Characterisation**, under the leadership of **Fred van Heuveln** and **Joep Huijsmans** (Netherlands), in collaboration with Italy, Japan, Norway, Switzerland and the United Kingdom
4. **SOFC Stack Evaluation**, under the leadership of **NEDO** (Japan), in collaboration with Switzerland and the United Kingdom.

In the area of *Electrical / Electrochemical Characterisation*, the basic material for solid oxide fuel cells - the ceramic electrolyte together with the electrodes and their mutual interface which go to make up a PEN (Positive - Electrolyte - Negative) structure (integrating sometimes the current collectors) were the object of intensive R&D throughout the period of this report. The objective of Recommended Practices in this area was to recognise those parameters and laboratory procedures significant for characterising the electrical and electrochemical behaviour of cell components or PEN structures, so that by a common understanding of problems and methodology the IEA partners could establish mutual credibility and intercomparability of performance data.

In the *Mechanical and Thermomechanical* area, on the other hand, where characterisation of structural ceramics is established practice and nationally and internationally recognised standards (ASTM, DIN, BS, etc), are readily available, the task was their transfer to the electroceramic case. In consequence, the Recommended Practices are in a more advanced state of formulation, although the task itself is laborious and cannot be fully terminated within Phase I of the IEA SOFC Task.

Characterisation of *Ceramic Powder* is equally a well established laboratory procedure. This topic was selected because of the anticipated consequences of variations of precursor powder characteristics on the electrical and electrochemical behaviour of the subsequently fabricated electroceramics and cermets, and because of indications of uncontrolled variability in some commercially available precursor powders, giving problems of reproducibility and quality control for SOFC ceramics products. In this case, the intercomparability of results from IEA partners carrying out a preselected array of testing procedures, was validated by a "Round Robin" test.

SOFC Stacks exist only in prototype form among the partners involved in this IEA Task. As development tools at the present state of advancement, the imposition of recommended evaluation procedures would be unnecessarily restrictive. The work in this area, therefore, limited itself to an evaluation of the principles of stack assessment, so that a common operating philosophy could be established in anticipation of future collaborative effort in which systematic comparison of the consequences of stack morphology, materials, fuel and oxidant formulations and operational procedures can be expected.

The formulation of the Recommended Practices as presented in this Final Report reflects the very considerable efforts of the respective activity leaders and their working groups, which each group carried out autonomously. The Recommended Practices, therefore, follow the state-of-the-art and the perspective of experts in each activity. To become the acknowledged recommended practices which are required, this exploratory phase will have to be extended in a comprehensive way including the exercise of the recomendations. We believe indeed that such an important activity should find place in the work programme of the Phase II of the SOFC-Task.

Augustin McEvoy
Operating Agent

August 1992

Electrical / Electrochemical Characterisation of SOFC Components & Cells

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Introduction

The present report describes the state-of-the-art electrical and electrochemical characterisation techniques for SOFC components and cells$^{(1)}$.

It is assumed that the SOFC components or cells have been fabricated by proprietary methods, and so accordingly only outline reference is given to these processes. The purpose behind this report is to cover those aspects which specifically relate to the application of the methods to SOFC testing and to point out some of their caveats.

In order to structure the recommendations, the subject matter has been broken down into 6 basic sections starting with test gases and finishing with the complete cell. The first section on standard gases has been included to promote reproducibility and facilitate meaningful comparisons between repeated measurements from any given test procedure. The second section is aimed at those who are interested in conductivity measurements of individual cell components, while the remaining sections focus on electrochemical testing. The concepts of half cells and complete cells are described, where the former are used to provide more fundamental information, and the latter to provide performance data.

1. Standard Test Gases

The recommendation and definition of standard gases arises mainly from the need to control oxygen and water vapour pressures reproducibly, while restricting the permutations to a manageable number of mixtures. The most widely used, and convenient unit to express gas mixtures in is volume%.

1.1 Inert Gases

Inert gases are used as the ballast in making up the standard gas mixtures discussed below. Apart from true inert gases such as helium and argon, satisfactory gas mixtures for SOFC applications can also be made with nitrogen or carbon dioxide. Carbon dioxide would normally be used in mixtures for PO_2 control. Helium is used in tests where gas chromatography is used to analyse the composition.

1.2 Wetting and Drying Gases

The standard level of water in a 'wet' gas is 3% by volume, which can be made by bubbling the test gas through a container of water at 25°C, but if the temperature of the surrounding apparatus is below the dew point then condensation can be a problem. However, this can be overcome by lowering the water vapour level to 2% by bubbling through a solution of ammonium sulphate.

Drying gases is relatively straight forward and normally involves passing the gas through a tube or column packed with a drying agent such as molecular sieve, or phosphorous pentoxide. Caution should be observed with CO cylinders as it has been known for iron carbonyl to build up over long periods of storage. This contaminant could cause problems with the measurements, but can be readily removed by passing the gas over heated activated alumina.

1.3 Flow Rates

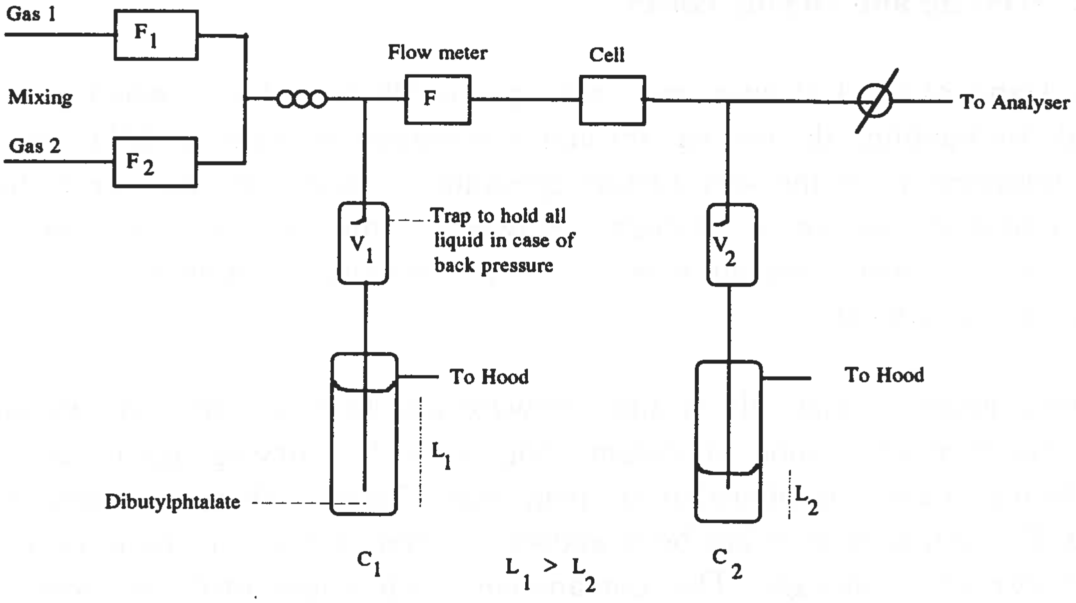
Since gas flow rates exert a significant effect in some measurements, particularly when performance testing PEN structures, flow rates should be stated. The effects of flow rate are again touched upon in the relevant subsections. Consideration should also be given to the effects of cooling, leakage, and space velocity or residence time. Flow rates should be stated in units of $dm^3\ s^{-1}$.

1.4 Gas Analysis

The composition of gas mixtures can be measured accurately using gas chromatography, provided reference or calibration gases are available. Care should be taken to avoid ingress of air in the sampling procedure. The analysis of water vapour by this method is troublesome.

1.5 Pressure Control

There are several sources of pressure build up due to restricted outlets in the cell; for instance, water condensation, carbon deposition and GC sample loops. These may break membranes or seals or give errors in total pressure estimates. A pressure control should thus be added to cells. For instance, the following simple devices control flow and pressures, provide over pressure protection and give a visible impression of total pressure drop and flow in the cells.



Cell gas normally let out via C_2, portions may be taken to analyser (without changing pressure). Unused mixture goes through C_1. Since C_1 and C_2 maintain relatively stable pressures, F may be a rotameter. Gas blockage in the cell forces all of gas out of C_1 instead of creating a high over pressure.

1.6 Standard Hydrogen Mixture

The use of dry hydrogen is not recommended since it imposes unrealistically low oxygen partial pressures in the system. Moreover, the PO_2 value of dry H_2 is also very susceptible to the ingress of moisture or oxygen from parts of the system such as leaks in the seals. However, such effects could be swamped by the introduction of water vapour in a controlled manner. These 'wet' gas mixtures also emulate more realistically the gases likely to be encountered in the fuel supply in commercial SOFC systems and stacks. In the testing of half cells, a hydrogen/water mixture diluted in an inert carrier gas should be used, since this constitutes less of an explosive risk. Thus, two standard mixtures are recommended, to be selected according to the specific test in question:

1. H_2 saturated with water vapour (3%) at 25°C
2. H_2 saturated with water vapour (3%) at 25°C, balance inert gas

1.7 Standard Reformed Mixture

Reformed methane is simulated by mixing carbon monoxide and hydrogen in the ratio 1 to 3, but in the absence of moisture this ratio would lead to carbon deposition at high temperatures. To overcome the problem, the gas mixture should also contain water vapour, preferably in the ratios:

$$CO:H_2:H_2O = 1:3:2$$

The actual composition for a mixture saturated in water vapour at 25°C is:

1.4% CO, 4.5% H_2, 3% H_2O, 91% inert gas.

The handling of mixtures containing larger amounts of water (steam) would necessitate heated pipework etc., to prevent condensation.

1.8 Standard Methane Mixtures

For direct oxidation of methane, pure and diluted gas mixtures saturated with water should be used.

1. $CH_4 + 3\%H_2O$
2. $10\%CH_4 + 3\%H_2O$ + balance inert gas

1.9 Standard Internal Reforming Mixtures

For internal reforming studies, a mixture containing largely water should be used: $CH_4:H_2O = 1:3$, but this mixture can only satisfactorily be made with a steam generator (humidifier).

1.10 Standard 'Poison' Mixtures

The effect of sulphur poisoning should be studied using controlled amounts of H_2S in the fuel gas stream. This can be achieved by taking one of the standard gas mixtures given above and blending it with H_2S. The nominal concentration of S supplied in natural gas is approximately 10 ppm and it is recommended that tests should be carried out with S levels above and below this value. The suggested compositions are 2 and 20 ppm.

1.11 Standard Cathode Gas Compositions

For most applications dry air is recommended ($21\%O_2+79\%N_2$), but some studies may require water vapour, while others may require oxygen. The three compositions are listed below:

1. Dry air
2. Wet air (3% water)
3. Dry oxygen

1.12 Standard Mixtures for PO_2 Control

Such mixtures should be used primarily for conductivity measurements where the material is subjected to a controlled oxygen partial pressure. The range of log PO_2 from 0 to -20 (atm) can conveniently be covered by the following gas mixtures:

1. O_2 + inert gas (CO_2 can be used here as an inert gas)
2. H_2 + H_2O + inert gas
3. H_2 + CO_2
4. CO + CO_2

These can be achieved by using mass flow controllers which, due to their low drift, allow measurements to be made over an indefinite period. The use of rotameters (without pressure control) is not recommended since there is no provision for maintaining the flow rates accurately over long periods of time.

2. Temperature and Duration

The most important temperature range is 800 to 1000°C and it is suggested that all tests be carried out within this range. Before measurements start, the sample should be stabilised at or above the highest measurement temperature for a stated period of time. Measurements should then be carried out at decreasing temperatures.

The duration of tests should be stated in hours, together with decay in measured response (ageing effects) and the ability to withstand thermal cycling.

3. Conductivity Measurements

Conductivity measurements are required for component materials such as cathode (P), electrolyte (E) and anode (N), which may exist initially as precursor powders. In order to make conductivity measurements, it is necessary to produce suitable samples, which may be either pellets or films, depending on the intended application. The details of sample preparation will not be discussed, but is assumed pellets will be made by the use of hydraulic presses followed by high temperature sintering; electrode films could for instance be made by tape casting, screen printing or CVD processes onto suitable substrates.

The relative density or the porosity of the sample material must be specified, as well as the average grain size. It must be specified whether or not the value is corrected for porosity, and, in that case, the method of correction.

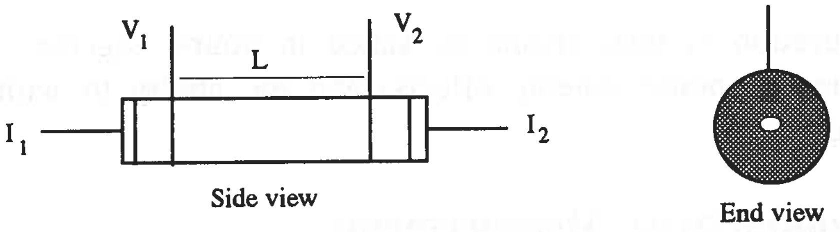
The conductivity must be accompanied by oxygen activity and temperature measurement.

3.1 Total Conductivity

The materials encountered in SOFC technology may in general be classified as conductors. The recommended practice for measuring the conductivity of such materials comprises the use of 4-point contacts (2 for current and 2 for voltage), This eliminates the impedance of contacts (electrodes) as well as connecting leads. Both AC and DC measurements are acceptable.

Measured values of resistance less than 1 ohm should still be consolidated by measurements on a known standard with a resistance in the same order of magnitude as the sample. Eventually, the value obtained for a true short circuit should be used for correcting measured values.

4-point methods comprise the bar geometry and the van der Pauw geometry. The bar geometry is shown schematically below:

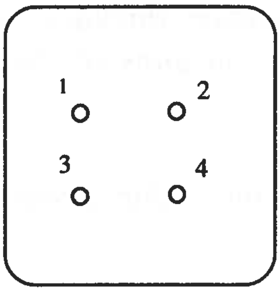


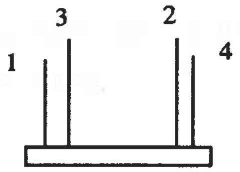
Independent of the conductivity, the accuracy of this method is limited by the accuracies in the:

1. measurement of the distance between the voltage probes and the sample cross section in this region of the bar.

2. Current uniformity between the voltage probes. This can be assured by a long, thin bar, and by current distributing electrodes at the bar ends.

The van der Pauw geometry$^{(3)}$ comprises 4 point contacts in a rectangular arrangement of relatively arbitrary dimensions on a sample surface as shown overleaf.





The distance between neighbouring points must be as order of magnitude larger than the thickness of the film.

2-electrode measurements (for disc-shaped samples) can replace 4-point measurements, provided the measured conductance is moderate and the necessary precautions are taken. High frequency AC or impedance spectroscopy measurements should be used to eliminate electrode impedances. The ohmic resistance of the electrodes can usually not be eliminated by AC techniques and must thus be known or negligible. The lead resistance may be eliminated by still using 4 leads for the two electrodes.

Grain boundaries may be relatively more conductive than bulk and thus increase the material's conductivity. This can not be detected by impedance spectroscopy. This case is mostly encountered in moderately and poorly conducting materials, and is not too important in SOFC technology.

In more conductive materials, on the other hand, grain boundaries may be relatively resistive. They then contribute to the material's resistance, which may be seen in impedance spectroscopy at temperatures up to 700°C. Determination of grain boundary resistance is particularly important in zirconia electrolyte materials. Values for grain boundary resistivity (or its corresponding conductivity), can be given in various ways:

1. Simply using the sample geometry; this gives a value with units of, for instance, ohm cm. This value is practical to compare with the bulk resistivity for the user of the actual material, but says nothing about the volume resistivity of the grain boundary phase.

2. Using the known microstructure of the material to estimate the product of the grain boundary resistivity and the grain boundary thickness (which is known), in units of, for instance, ohm cm^2.

3. Using an estimate of the grain boundary thickness to calculate the true resistivity of the grain boundary phase, in units of, for instance ohm cm.

It is thus important that the meaning of the value given for the grain boundary resistivity is explained.

3.2 Determination of Transport Number and Minor Transport Contributions.

Ionic transport numbers down to 0.001 may be determined by using the EMF method. Values an order of magnitude may be determined under good conditions, but due to semipermeability and polarisation of electrodes, the ionic transport numbers obtained should always be considered as minimum values. The relative error in the measurements can typically range from 10% when t is 0.5 to an order of magnitude when t is 0.001.

The possible contribution of protonic conductivity can be checked by employing the EMF methods using a water vapour pressure gradient and no oxygen pressure gradient, but a simpler experiment is to compare conductivities in dry and wet atmospheres.

A more elaborate approach using $^{18}O/^{16}O$ exchange, coupled with dynamic SIMS analysis enables oxygen diffusivity and exchange coefficients to be determined directly.

Finally, a number of techniques based on the use of blocking electrodes and other means of eliminating either the ionic or the electronic currents have been described, but should be treated with caution.

As most methods dealing with minority transport contributions have many possible sources of error, it is recommended that values claimed should be measured by at least two different techniques.

4. Half Cell Measurements

Half cell measurements are the work horse in developing new electrodes. They are generally fabricated and tested before progressing on to complete PEN structures. The half cell essentially allows the investigator to concentrate studies on one particular aspect of development. For the sake of clarity in reporting results, investigators are advised to adopt the following terms in describing their cell geometry and gas control:

Divided and Undivided Cells

A cell interposed between two different gas atmospheres is referred to as a divided cell, whereas a cell surrounded by a single gas environment is referred to as an undivided cell:

Divided

Undivided

Simplified divided and undivided cell configurations

Symmetric and Asymmetric Cells

A symmetric cell has identical electrodes on both sides of the electrolyte membrane, whereas an asymmetric cell has different electrode materials. The most common type of asymmetrical cell has 3 electrodes comprising 'working', 'counter' and 'reference' electrodes. The terminology here is taken in the usual electrochemical sense, so the working electrode corresponds to the electrode whose performance or characteristics are under study. The counter electrode corresponds to the other current carrying electrode positioned on the opposite side of the electrolyte membrane. The reference electrode is used as the common point for controlling and measuring the potential of the working electrode, and does not carry any appreciable current. (In the case where a potentiostat or galvanostat is used the reference electrode lead is a very high impedance, and should therefore be protected by screening).

4.1 Thermal Cycling

The ability of the half cell to withstand thermal cycling should be noted, and it is recommended that at least 3, but preferably 10 cycles from room temperature to the operating temperature should be carried out. The reported figures should include heating and cooling rates, maximum and minimum temperatures and dwell times. A typical heating rate would be 100°C hour^{-1}. A practical point should be noted here that divided cells do not withstand thermal cycling particularly well because of the problems with sealing. It is recommended therefore that thermal cycling studies are carried out on undivided cells.

4.2 Ageing

This is related to thermal cycling and refers to the decay in performance over long periods of time e.g., 1000 hours. Ageing studies should be carried out after thermal cycling.

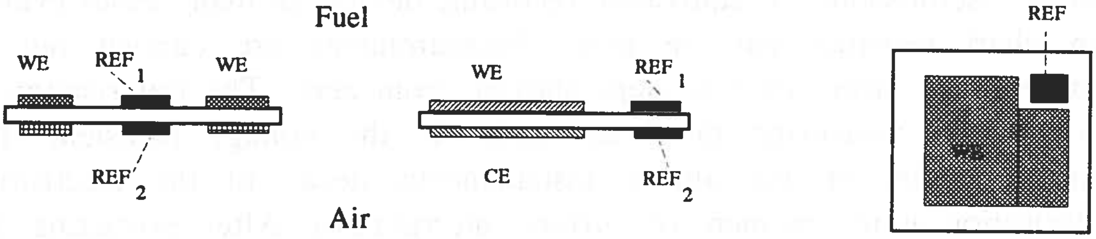
4.3 Contacts

Contacts to the outside world present a particular problem because in practice they may involve the use of long thin wires of a noble metal such as platinum, which can introduce very significant ohmic voltage losses when currents are passed. The solution therefore, is to use separate leads for current and voltage measurements, so that in a typical cell arrangement there should be two contacts to the working electrode - one to carry the current and one to measure the voltage (with respect to the reference). In general there should be provision to make separate voltage measurements from all current carrying electrodes of interest to the investigator. This may for instance result in a total of 4 contact wires.

Another aspect of considerable importance is the concept of spreading resistance, which occurs when currents are forced to flow in the plane of the electrode outwards from the point of contact to the interface with the electrolyte. This can be minimised by using metal grids (or mesh) for providing multiple contacts, and can be either incorporated in the electrode film during the sintering process, or alternatively mechanically pressed onto the electrode surface during cell assembly. The grids should provide contacts points without impeding the flow of gas to the reaction zones. If grids are used, then the mesh size should be reported. Moreover, the degree of contact between the mesh and the electrode should be stated or illustrated by micrograph cross section.

4.4 Reference Electrodes

The separation or gap between the reference electrode and the adjacent current carrying electrode should be large when compared with the thickness of the electrolyte membrane. In the case of thicknesses in the range 10 to 250 µm these do not present a problem, but for thicker electrolyte sheets the latter consideration is of the utmost importance. In practice, the separation should be at least ten times the electrolyte thickness. Ideally, no lines of equipotential should enter the reference electrode, so in this respect it should be placed as far away from the current carrying electrodes as possible. Examples are illustrated below:



Examples of reference electrode arrangements.

A true reference electrode should follow the Nernst equation if it is to be considered electrochemically reversible, and in practice this requires fast electrode kinetics. The generally accepted reference possessing this property is Pt exposed to air. Thus, it is recommended that the reference electrode be positioned on the cathode side of the cell (if it is divided). If it is deemed necessary to have the reference electrode on the fuel side of the cell, then a second reference should also be included on the air side thus enabling the offset due to the low PO_2 to be measured. Experiments carried out in undivided cells operating in environments other than air will require some knowledge of the true PO_2 in order to compare measured voltages with other experiments, and this could for example be done by measuring the PO_2 with a zirconia probe.

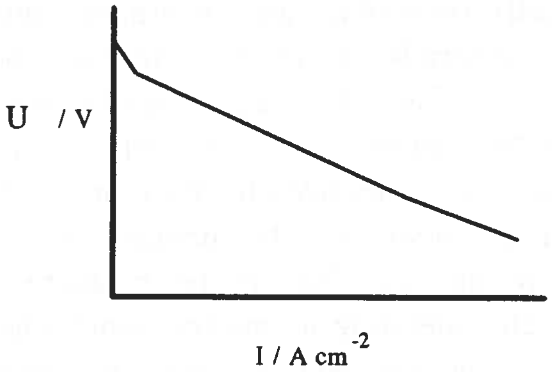
Where the reference electrode is used in a potentiostatic control circuit then allowance for the ohmic resistive drop between the working and reference electrodes should be made if accurate electrode kinetic information is required. In some commercial instrumentation this measurement can be made automatically by the use of optional 'I*R compensation ', but care should be taken not to over or under compensate. For a direct measurement of this resistive component, AC impedance spectroscopy is recommended.

5.0 Methods

The primary goal is to obtain the overpotential (U) versus current (I) characteristics of the cell or PEN structure.

5.1 Current Interruption Method

The current interruption method enables the purely ohmic contribution to the cell voltage to be subtracted. The method requires a constant but adjustable current source which provides a current step or pulse of sufficient duration to allow monitoring of the voltage transient on a digital storage oscilloscope, or equivalent recording device. In many cases even a pen chart recorder can be used. Measurements are carried out at progressively larger current steps starting from zero. The polarisation is obtained by measuring the break point in the voltage transient (the principle relies on the almost instantaneous decay of the electrolyte polarisation at the moment of current interruption). After extracting the overpotential from the voltage transient, the characteristics of the cell can be plotted. The conventional practice is to display current on the abscissa and voltage on the ordinate of the plot as shown in the diagram below.



I–U characteristic response

5.2 AC impedance Spectroscopy (IS)

In half-cell studies. IS allows delineation of the electrolyte impedance from the electrode impedance. Studies of the electrode impedance should be done using a small perturbing ac signal, typically 10 mV over the electrode studied (larger signals allowed over the whole sample). Larger amplitudes may affect the impedance, and the linearity should in those cases be verified (whether or not the impedances obtained vary with the amplitude).

As even small potentials applied at low frequencies may change the performance of electrodes irreversibly, it is recommended that the frequency sweep is made from high to lower frequencies, and that the reproducibility is checked by reversing or repeating the sweep.

The electrode impedance may in some cases be further deconvoluted into, for instance, double layer capacitance, charge transfer resistance and mass transport impedance. It recommended that curve-fitting software is used for this purpose, and that the program and the equivalent circuit used are specified, and the goodness of fit is reported or illustrated.

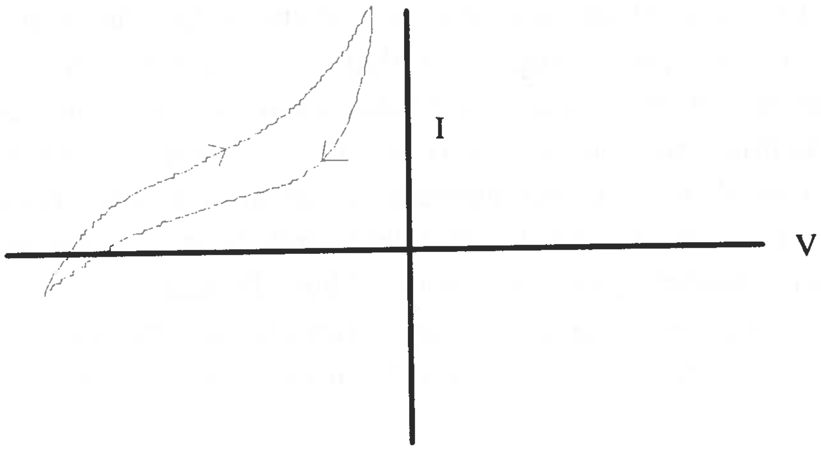
During IS analysis, a dc (bias) potential or current on the electrode may be superimposed on the perturbing ac voltage or current. An electrode impedance obtained from IS under dc bias conditions may be calculated into an overpotential from ohms law once the dc current is known. The current is obtained directly in galvanostatic (constant current) mode, while it may be obtained from the total dc resistance and the dc voltage applied in the potentiostatic (contact potential) mode. Thus, IS analysis over a range of bias potentials may give current-voltage relations as obtained from other methods. The possibility of Joule heating under forced bias conditions should be noted.

5.3 Cyclic Voltammetry (CV)

Cyclic voltammetry is a technique used for probing electrode reactions and kinetic behaviour. This is a non-steady state method which can reveal significant transient phenomena such as adsorbed moisture, oxygen or other intermediate reaction products. The technique requires the use of a triangular voltage generator and a potentiostat, and the output is most conveniently displayed on an XY pen plotter as current versus voltage. The convention is to plot voltage on the ordinate and current on the abscissa. Some computer based systems are available. Irreversible changes in the cell can be investigated by carrying out multiple scans. Steady state behaviour can be conveniently plotted on the same scales by either using a very slow sweep rate (e.g., 1mV min^{-1}) or point by point at pre-selected potentials.

This is done in practice by sweeping to the next potential and then holding until the current has decayed to a constant value. Ohmic losses can be compensated for by electronic methods using positive feedback in the potentiostatic circuit. In some more sophisticated units, cyclic voltammetry can be combined with current interruption measurements.

In reporting results, all control parameters must be stated i.e., sweep rate (mVs^{-1}) sweep reversal potentials (V), starting potential (V), number of scans. It is very convenient to mark the direction of potential sweep with arrows, as shown below:



Cyclic voltammogram

5.4 Continuous Monitoring

Monitoring the cell performance over a long period of time can be done using an external resistive load, but this entails recording both the current and the cell voltage. Although this is adequate for PEN and complete cell testing, it does not impart the level of control required for half cell testing. In this latter case, it is more appropriate to use potentiostatic or galvanostatic control.

The performance over a period of time should be observed and presented graphically. The duration of the tests should not be more than 1000 hours. In order to consider the mass balance in the system, it is necessary to measure the yield of products and any unreacted fuel gas. This can be done by periodic sampling with gas chromatography or mass spectrometry.

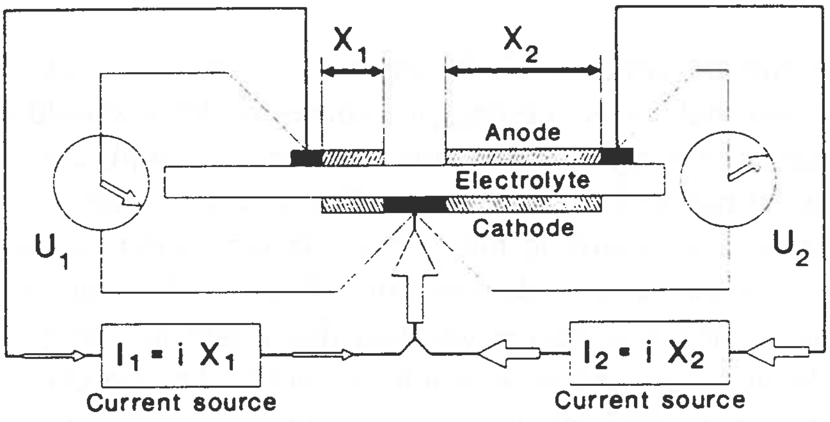
6.0 PEN Testing

The PEN structure contains all the elements of the fuel cell, and may be regarded as two half cells. Testing procedures on PEN should be restricted to performance testing, and should not try to duplicate the detailed complexities of half cell measurements. The effects of redox-cycling of the anode (alternative exposure to fuel and air) is very important and should be carried out at least once. Likewise, the effect of thermal cycling should also be studied, but it is recognised that this might not be practical. Leak testing of the structure and seals would be useful. The standard gas mixture on both sides of the PEN should be noted when reporting results. The cell and connection geometries should also be stated. Attention should be paid to the operating temperature of the PEN and also the point at which the temperature is actually measured. Coupled with this is the time taken to heat the PEN structure up to the operating temperature and the time elapsed before recording the first I-U measurement.

Defining the start time enables operating time and decay rate to be calculated. Studies should be limited to obtaining I-U characteristics, preferably repeated at regular intervals during the performance testing. The total length of the test is an obviously important quantity to be stated. AC impedance may, however, reveal changes in bulk, grain boundary and electrode resistances which appear under use in a PEN. Current densities should be reported in units of A cm^{-2}.

6.1 Parametric Characterisation

Complete characterisation of PEN requires an estimate of the total in-plane and cross-plane resistance between the current collectors in contact with the electrodes. The values obtained depend on the geometry of the current collection, so it is necessary to specify exactly the geometry used, in order to achieve reproducibility between different samples. The problem has been treated theoretically(2), and can be simplified with just two parameters which describe the PEN completely, namely the characteristic length (L) and a term called the resistance area (C). Several limiting cases have been considered and one specifically recommended for practical implementation. The geometry is of the asymmetric cell category, in which two electrode strips of different sizes are required as shown in the example overleaf.



Measure voltages for identical current densities
at the same time
under identical experimental conditions

Twin cell specimen for PEN characterization

The strips are made by removing part of the electrode films on both sides of the PEN, and making pairs of contacts (I and U) to each strip as shown. In order to obtain L and C, it is necessary to obtain the I-U curve for both the strips, under identical conditions. The exact details are given in the cited reference.

A simplified non-destructive version of the method may also be possible, obviating the need to remove sections of the PEN. In this case, wires are fixed to the surface of each electrode. (3 on one side and 1 on the other), at measured distances from the centre line of the PEN.

6.2 Direct Measurement of In-Plane Resistance

The in-plane resistance of both electrode layers can be measured by the van der Pauw methods described previously, but measurements made at elevated temperatures may require removal of one of the electrodes, in order to obtain accurate results on the other electrode. The removal of electrodes may become unnecessary though if the temperature is reduced to the range of say 300 to 500°C.

6.3 Performance Testing

Performance testing on a routine basis of 'as received' PEN plates should employ a reproducible current collection system, which minimises the effects of in-plane resistance. Ideally this can be achieved by the use of conducting plates in contact with the entire area of each electrode, but this would create too great an obstruction to gas flow. A practical solution then is the use of metal mesh or grids, which have multiple contact points with the electrode, but avoid obstructing the gas flow. The position of the current and voltage leads on the mesh are also important and it is recommended that the current lead be placed in the centre of the mesh, and the voltage lead mid way between the centre and the edge. This then minimises ohmic losses in the lead contacts. In cases where solid current collecting plates are used e.g., channelled bi-polar plates, then the lead contacts should also be made in the same way.

In reporting data, it is important to give information about the current collector, including the material (e.g., Pt), mesh size (e.g., 1mm), diameter of the wire used in making the mesh (e.g., 0.25 mm), and in the case of bi-polar plates, the channel dimensions (e.g., 1mm).

Should it be considered necessary to test the PEN with reference electrodes, then the configuration outlined in section 4 on the subject of half cells should be adopted.

Performance data should be obtained at steady state, to eliminates initial activation phenomena, and may for example be presented as I-U curves, or power density-U curves. In either case it is recommended that an external power supply (potentiostat) be used to control the test, rather than a restive load.

The effect of flow rate on the performance should also be observed, since flow rates can change the current response very significantly. The effects of water and 'poisons' should also be studied, using the recommended gas mixtures.

Mechanical / Thermomechanical Characterisation of SOFC Materials & Components,

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contents

INTRODUCTION

This report describes the proposed methods and techniques for measuring and testing characteristics and physical properties of SOFC materials & components.

The proposed procedures are the results of the review by an adhoc group of experts of the existing standards. They represent the state-of-the-art for characterising geometrical, mechanical and thermal properties of SOFC materials and components and are therefore not yet definitive.

This document is not comprehensive and is not specifically structured but presents a list of parameters considered as relevant and for which Recommended Practices are described. These parameters are presented in Table I.

Given the present status of R&D, it has been decided to limit the work to planar SOFC components and moreover to focus attention on final product rather than materials at intermediate processing steps (e.g. green tapes).

This report substantially adopts industrial type standards, procedures and practices.

Of the 15 relevant thermomechanical parameters listed in table I, detailed recommended practices only for four of them appear in this report : thickness, porosity, apparent density and biaxial flexural strength. A short description of the other parameters is presented, pending development of full recommendations.

TABLE I - LIST OF RELEVANT PARAMETERS FOR SOFC SINTERED MATERIALS/COMPONENTS

- THICKNESS
- WARPAGE
- ROUGHNESS

- ELASTIC PROPERTIES
    - Young's modulus
    - Shear modulus
    - Poisson's ratio

- BIAXIAL FLEXURE STRENGTH

- TOUGHNESS

- POROSITY
- APPARENT /BULK DENSITY
- GRAIN SIZE

- GAS TIGHTNESS

- THERMAL CYCLING
- THERMAL EXPANSION
- THERMAL DIFFUSIVITY/CONDUCTIVITY
- SPECIFIC HEAT

THICKNESS

1. Scope

1.1 This test method covers the determination of the thickness of single cell components (anode, cathode, electrolyte and interconnect material).

2. Applicable documents

2.1 *Calibration block specifications*

2.2 *LVDT Specifications*

2.3 *Recommendations from manufacturers*

3. Apparatus

3.1 *Dial indicators* reading in 1 µm divisions and accurate to ±1 µm shall be used.

3.2 *LVDT (Linear Variable Differential Transformer)* equipped measuring devices having resolution equal to or better than 0,25 µm shall be used.

3.3 *Opto-mechanical autofocusing devices* using a laser stylus with a focus of 1 µm in diameter capable of responding up to 3 nm in the focused plane deviation. The apparatus will be used in differential mode for thickness measurement.

Note1: for the scope of this test method devices 3.2 e 3.3 are recommended for more accurate measurement provided by the 3.1 device.

3.4 Calibration blocks

3.5 For holding the specimen under evaluation special jigs shall be provided in order to make measurements tip versus tip.

4. Test specimens

4.1 Specimens under test shall be anode, cathode, electrolyte and interconnect material, selected at random from the lot to be tested. The number of specimens required by this test method cannot be established presently, but it should be selected with the intent of determining reasonable confidence limits based on stack best performance from the electrochemical standpoint.

4.2 Test specimens shall have lateral dimensions not exceeding 200 by 200 mm.

4.3 For rectangular geometries or facial dimensions larger than 200 by 200 mm, refer to the procedure described in 5.3.

5. Procedure

5.1 For square-shaped samples measure the thickness at each of the four corners and at the center point. Points of measurement shall be at least at 12% and no more than than 25% of the maximum lateral dimension.

5.1.1 In case of using dial indicators the thickness should be measured to the nearest 1 µm.

5.1.2 In case of using LVDTs or Laser devices the thickness should be measured to the nearest 0.1 µm.

5.2 In case of using dial indicators or LVDT three different readings are recommended for each of the five points of measure.

5.3 For different geometries and/or samples having lateral dimensions greater than 200 by 200 mm, the number of test points shall be calculated by assuring a surface coverage with a density of about 0.0125 measured points per square centimeter. Points shall be located in a regular array according to 5.1.

6. Calculations

6.1 For each square shaped specimen of the batch, the average thickness, T_k, is calculated as follows:

$$T_k = T_{av} = \Sigma T_i / 5 \qquad i = 1,2,3,4,5$$

where T_i = thickness at point i
$k = 1 \div n$
n = number of specimens

When dial indicators or LVDTs are used T_i is the average value of the three readings at each point of measure:

$$T_i = \Sigma T_j / 3 \qquad j = 1,2,3$$

7. Report

7.1 The test report should include the following:

7.1.1 Test configuration and specimen lateral dimensions;

7.1.2 Number of tested specimens;

7.2 For each specimen report:

7.2.1 average value of the thickness, T_{av};

7.2.2 maximum measured thickness, T_{max}, and minimum measured thickness T_{min}.

7.3 For the whole batch report:

7.3.1 mean value of the thickness:

$$T_M = \Sigma T_k / n;$$

7.3.2 standard deviation:

$$\sigma = \sqrt{\frac{\sum_{1}^{n} (T_K - T_M)^2}{n-1}}$$

8. Precision and Bias

8.1 Bias depends almost entirely on the accuracy of the measuring devices and care taken to set up the equipment.

No interlaboratory data are available presently to estimate bias.

Note: Round Robin tests should be performed in order to assess bias sources by using a reference specimen which could be a silicon single crystal electronic grade wafer about 300 µm thick.

POROSITY

Open porosity is the most important parameter to be evaluated characteristic should be considered for anode, cathode, electrolyte and interconnect material.

Several standards are available in literature; those ASTM test methods that have been evaluated, cover the determination of apparent porosity in ceramic materials through the calculation of a specimen volume V, dry weight D, weight in water W and saturated weight S. Substantially they refer to the determination of apparent porosity, bulk density, water absorption and apparent specific gravity by the means of Archimedes' principle.

According to ASTM C 373 standard method, specimens under test should weigh at least 50 g, which is a strong limiting factor for immediate applicability to SOFC components. Besides the above standard considers the boiling of specimens for 5 hours and 24 hours soaking to allow water impregnation; the inherent difficulty in handling and in avoiding possible breaking of specimens prevents a safe applicability of this procedure; therefore experimental verification is needed before any direct assumption of the results obtained as correct.

1. Apparatus

1.1 Currently the determination of apparent porosity is worldwide accomplished by the mercury intrusion method which allows also the evaluation of pore size distribution.

Mercury intrusion method

Determination of total apparent porosity and pore size distribution by the mercury penetration technique is based on the behaviour of non-wetting liquids in capillaries. A liquid which has a wetting angle of more than 90 degrees cannot spontaneously enter a small pore because of the surface tension, however this resistance may be overcome by exerting a certain external pressure.

The volume of the intruded pores is determined by measuring the volume of mercury that is forced into them at various pressures. A single pore size distribution determination involves increasing the pressure, either continuosly or step-wise, and recording the measured intruded volume.

a) *Total apparent porosity* (under evaluation)

b) *Pore size distribution*

According to the assumption of the pores to be cylindrical, the most common mercury intrusion devices make use of the Washburn equation. The espression is obtained from the following considerations:

- the force tending to push the liquid out of the capillary is $-2\pi r\sigma\cos\theta$
- the force exerted by the external pressure over the area within the contact circumference is $\pi r^2 p$.

when the equilibrium is reached

$r\,p = -2\,\sigma\cos\theta$ which is the Washburn equation

where:

r = pore radius;
p = absolute pressure;
σ = surface tension;
θ = wetting angle.

Although in any porous material there are no cylindrical pores, the above equation is generally used to calculate a pore size distribution from mercury porosimetry data.

Beside it must be added that when using mercury the surface tension should be considered as a variable value; at 25°C it is $482.2\ 10^{-3}$N/m, while at 50°C it is $472\ 10^{-3}$N/m.

The wetting angle is also a variable depending on the nature of specimen; values between 125° e 152° have been found for a large number of materials.

Taking the average values of $480\ 10^{-3}$N/m and 140° for the surface tension and the wetting angle respectively, the equation transforms into:

$r = 7500 / p$ where r is in nm and p is in kg/cm^2

or $d = 1500 / p$ where d is the pore diameter in nm and p is in MPa

which still keeps its validity for the pore radius distribution, while if the pores are not cylindrical but have an irregular shape, the expression will give lower values for the calculated radii. SEM analysis is recommended in order to evaluate the appropriate pore shape .

2. Test specimens

2.1 At least five representative test specimens for each determination shall be selected from anode, cathode, electrolyte and interconnect material. The specimens shall be shaped and sintered. Major facial dimensions shall be 50 by 10 mm.

3. Procedure

3.1 This method involves hazardous materials, operations and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

3.2 Dry the test specimens to constant mass by heating in an oven at 150°C, followed by cooling in a desiccator.

3.3 Place the specimens in the measuring device - dilatometer or sample cell - in such a manner as to fill most of the cell volume, while keeping the specimens separated with glass spacers or equivalent method.

3.4 Make the measurements applying carefully instrument precautions and following its instructions.

4. Report

4.1 The report should include:

4.1.1 specimens preparation, number and dimensions;
4.1.2 total open porosity;
4.1.3 pore size distribution;
4.1.4 SEM micrographs or the assumed shape of pores;
4.1.5 pore average diameter value for the batch tested;
4.1.6 standard deviation.

APPARENT DENSITY

1. Scope

1.1 This test method covers the determination of density close to apparent density for ceramic materials almost free of open pores, at ambient temperature (23 °C) by buoyancy.

This test method is applicable for determining apparent density of electrolyte and interconnect materials; for anode and cathode materials this test method provides density values close to bulk density.

1.2 This method may involve hazardous materials, operations and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 ASTM Standard E12: Definitions of terms relating to density and specific gravity of solids, liquids and gases.

2.2 ASTM Standard C693-84: Standard Test Method for Density of Glass by Buoyancy.

3. Definition

3.1 Density of solids: the mass of a unit volume of a material at a specified temperature. The units shall be stated as grams per cubic centimetre.

4. Apparatus

4.1 *Digital Analytical Balance*, sensitive to 0.1 mg or better, equipped with pan and suitable device for suspending basket and specimen.

4.2 *Beaker*, of convenient capacity to fit inside the balance chamber and allow immersion of the basket or wire loop specimen holder in distilled water.

4.3 *Thermometers*, calibrated (18 to 28°C), sensitive to 0.1 °C for determining air and water temperatures.

4.4 *Nickel-Chromium-Iron or Platinum-alloy wire*, less than 0.2 mm diameter for suspending the specimen either in a basket or a loop made of the same wire. The suspension wire shall be cleaned by degreasing or heating in a vacuum.

An acceptable alternative method of cleaning the platinum-alloy wire is to heat in an oxidizing gas flame until there is no longer any color emitted from the gases passing around the wire.

5. Reagent

5.1 *Distilled water*, fresh, boiled and used within 24h, allowed to stabilize at balance air temperature for at least 2h in the beaker.

6. Test Specimens

6.1 Specimens weighing about 1.5 g shall be shaped and sintered with facial dimensions measuring 50 by 50 mm.

6.2 Dry the test specimens to constant mass by heating in an oven at 150°C, followed by cooling in a desiccator.

7. Procedure

7.1 Hold the specimens and covered beaker of boiled distilled water near the laboratory balance until the water has cooled to ambient temperature before weighing.

7.2 Adjust the balance assembly (modified pan, supporting platform, basket, thermometer and beaker) and reset the balance display.

7.3 Weigh the specimen in air to the nearest 0.1 mg and record as W_A.

7.4 Place the specimen in the immersed basket or loop holder. The suspended assembly should be agitated slightly with a vertical motion to wet the suspension wire above the meniscus at the reference position and to ensure that no air bubbles are adhering to the specimen or holder.

7.5 Weigh the specimen in the distilled water to the nearest 0.1 mg and record as W_W.

7.6 Read the distilled water temperature to the nearest 0.1°C and determine the water density from Table I. Record this as ρ_W.

8. Calculation

8.1 Calculate the specimen density, ρ, at the water temperature as follows:

$$\rho = \frac{W_A - W_w f_c}{W_A - W_w} \rho_w$$

where f_c is the air to water density ratio, ρ_A/ρ_w, and ρ_A is the air density at 23°C and 760 mmHg, which is 0.001193 g/cm^3.

9. Report

9.1 Report the following:

9.1.1 identification of test sample as from the production process;

9.1.2 density of specimen, ρ, in grams per cubic centimetre;

9.1.3 temperature T_w for which the specimen density is reported.

10. Accuracy

10.1 The accuracy of this method is to be evaluated by measuring the density of a reference specimen. A reference specimen could be a silicon single crystal electronic grade wafer about 300 μm thick.

11. Precision

11.1 To assess the precision of this method interlaboratory comparison of apparent density values is needed through Round Robins using reference standard materials like electronic grade silicon.

TABLE I - Density of Air-Free Water, g/cm^3

Temp. ℃	0,0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0.8	0,9
18	0,99859	857	856	854	852	850	848	846	844	842
19	840	838	836	834	832	830	828	826	824	822
20	820	818	816	814	812	810	808	806	804	801
21	799	797	795	793	791	788	786	784	782	779
22	777	775	773	770	768	766	763	761	759	756
23	754	752	749	747	744	742	740	737	735	732
24	730	727	725	722	720	717	715	712	710	707
25	705	702	700	697	694	692	689	687	684	681
26	679	676	673	671	668	665	662	660	657	654
27	652	649	646	643	640	638	635	632	629	626
28	624	621	618	615	612	609	606	603	600	598

BIAXIAL FLEXURE STRENGTH

1. Scope

1.1 This test method covers the determination of the biaxial flexure strength (Modulus of rupture(1)) of thin ceramic substrates and, specifically, of the materials making up the PEN structure of SOFC.

This method is applicable to specimens in the as-fired or as-sintered condition; it may be used with specimens having warpage. Limits imposed on warpage are those required by a proper cell working performance.

1.2 Current procedure refers directly to ASTM standard F394-78 (reapproved 1991), and it is rewritten, with modifications, for the applicability to the materials under study.

1.3 Ceramic substrate materials are considered to be brittle or perfectly elastic, that is, fracture normally occurs at the surface under tensile stress caused by flexure.

A more appropriate definition for the biaxial flexure strength, σ, is the following: the maximum stress in a biaxial mode of flexure that a specimen develops at rupture. This stress will normally be the calculated maximum radial stress at the center of the convex surface. This mode of flexure is a cupping of the circular plate caused by central loading and supporting near the rim.

2. Summary

2.1 The test specimen, a circular disk, rests on three ball bearings symmetrically spaced near its periphery. It is bent in a cupping fashion by the application of force to the center of the specimen through an upper flat end right cylinder, at a prescribed constant rate in a compression test machine until the specimen breaks. The breaking load, the dimensions and elastic constants of the specimen, and the radii of the support and load are used to compute the maximum tensile stress which is at the center of the tension (convex) surface. This is usually the point of origin of the fracture. The computed or center stress then is the breaking stress (biaxial flexure strength). This configuration eliminates premature fracture from an edge defect or anomaly.

---

(1) This expression is passing out of usage

3. Referenced Documents

3.1 ASTM F 394 - Standard Test Method for Biaxial Flexure Strength (Modulus of Rupture) of Ceramic Substrates.

3.2 A.F. Kirstein, W.H. Pell, R.M. Woolley, L.J. Davis "Deflection of centrally loaded thin circular elastic plates on equally spaced point supports", Journal of Research, U.S. National Bureau of Standards, JNBAA, Vol. 70C (1966) 227.

3.3 A.F. Kirstein, R.M.Woolley "Symmetrical bending of thin circular elastic plates on equally spaced supports", Journal of Research, U.S. National Bureau of Standards, JNBAA, Vol. 71C (1967) 1.

3.4 ASTM E4 - Standard Practices for Load Verification of Testing Machines.

4. Apparatus

4.1 *Testing machine* - Any compression-type testing machine capable of providing a uniform crosshead travel rate such that the stress rate be 20 MPa/s and containing a load-measuring cell having a resolution of 0.2% of full scale or better on a scale appropriate to the material under test.

4.2 *Test fixture for supporting and loading specimens* - Since the biaxial flexure strength is not dependent on the number of support points it is suggested to use three ball bearings 1.5 mm in diameter, positioned 120° apart on a circle having a diameter of 8 ± 0,025 mm. The load is applied to the specimen center by a right circular cylinder of hardened steel having a diameter of 0,8 ± 0,02 mm, with the end flat and perpendicular to the axis. The cylinder must apply the load perpendicularly to the plane containing the supporting balls, and the cylinder axis must be within 0.4 mm of the center of the support circle.

4.3 *A pad of nonrigid material* should be used between the cylinder and specimen to distribute the load uniformly over the 0,8 mm diameter cylinder end; this pad material may be 0.05 mm thick polyethylene sheet.

4.4 *Measuring devices* for measuring the specimen thickness to the nearest 0.001mm as from the proposed method described in this document, and the specimen diameter to the nearest 0.01 mm.

4.5 *Desiccator* for specimen storage prior to testing

4.6 *Hygrometer* for measuring ambient-test relative humidity to an accuracy of ±5% of the reading.

4.7 *Thermometer* for measuring ambient-test room temperature.

4.8 *Timer* to time the loading period to the nearest 1s in order to verify the stress rate.

5. Test specimens

5.1 Specimens (anode, cathode, electrolyte and interconnect material) shall be those available from the fabrication process provided that they are in accordance with the requirements for planarity and other geometrical characteristics. Specimens shall be 15 ÷ 20 mm in diameter.

5.2 *Specimen defects* - no cracks or scratches shall be visible within the support circle of the tension surface of the specimen.

5.3 *Specimen conditioning* - the specimens shall be dried in an oven at 150°C to 200°C for at least 1 hour and cooled at room temperature in a desiccator.

6. Procedure

6.1 Prepare and condition at least ten specimens according to section 5.

6.2 Record room temperature and relative humidity before stressing the first specimen and at 4 hours interval during the test to an accuracy of 1°C and 5%, respectively.

6.3 Remove a specimen from the desiccator. Measure and record the diameter at three location about 60°C apart to the nearest 0.01 mm.

6.4 Measure and record the thickness of a specimen to the nearest 0.001 mm at three support points and at the center.

6.5 Center the specimen in the test fixture on the three supports.

6.6 Place the polyethylene film over the specimen center.

6.7 Lower the loading plunger carefully onto the specimen.

6.8 Insert the fixture into the test machine.

6.9 Start the timer and simultaneously apply the load at a uniform rate perpendicularly (90 ±1°) to the specimen surface at its center until the specimen breaks. The crosshead travel rate shall be such that the center stressing rate is 20 MPa/s. Record the elapsed time at fracture.

6.10 After fracture occurs, record the following data:

6.10.1 Load, P, at fracture to 0.2% of full-scale value or better, including the ram weight.

6.10.2 Specimen thickness to the nearest 0.001 mm at the fracture origin if it is not at the specimen center.

6.10.3 Time in seconds to fracture.

7. Calculations

7.1 Calculate the biaxial flexure strength for each specimen from the following equation:

$$\sigma = -\frac{3}{4\pi}\frac{P}{t^2}(X-Y)$$

where:

σ = maximum center tensile stress (MPa)

P = total load causing fracture (N)

$$X = (1+v)\ln\frac{b^2}{c^2} + \frac{1-v}{2}\,\frac{b^2}{c^2}$$

$$Y = (1+v)\left(1+\ln\frac{a^2}{c^2}\right) + (1-v)\frac{a^2}{c^2}$$

v = Poissons' ratio

a = radius of support circle (mm)

b = radius of loaded area (mm)

c = radius of specimen (mm)

t = specimen thickness at fracture origin (mm)

7.2 Calculate the mean value of biaxial flexure strength (in MPa) for the test lot from following equation:

$$\bar{\sigma} = \frac{\sum_1^n \sigma_i}{n}$$

where: σ_i= individual specimen strength value (MPa)

n = number of specimens

7.3 Calculate the estimated standard deviation $\Delta\sigma$ for the test lot from the equation:

$$\Delta\sigma = \sqrt{\frac{\sum_1^n (\sigma_i - \bar{\sigma})^2}{n-1}}$$

8. Report

8.1 Report the following:

8.1.1 identification of the specimens tested;

8.1.2 ambient room temperature and relative humidity as required in 6.2;

8.1.3 mean, minimum and maximum thickness as from 6.4 and 6.10.2;

8.1.4 rate of increase of load, or rate of crosshead travel, or rate of stressing calculated from measured time to fracture or from loading rate;

8.1.5 the values of Young's modulus of elasticity and of Poisson's ratio used for the material;

8.1.6 the calculated biaxial flexure strength of each specimen;

8.1.7 the mean biaxial flexure strength of the test lot.

8.1.8 the estimated standard deviation for the lot.

9. Precision and Bias

9.1 No interlaboratory data are available; to assess the precision and bias of this method Round Robin tests should be performed by using reference standard materials.

ELASTIC CONSTANTS (E, G, υ)

Test specimen
- anode, cathode, electrolyte

Measurement method/technique
- Resonance frequency method (Dynamic elastic modulus)
  according to: Test Method ASTM C623 | modified *
  JIS R1602 and JIS R1605 |

* Test pieces are excited by an electrostatic alternating field (Bordoni technique).

- Measurement of elastic deformation/ Three /four point bending (Static elastic modulus)
  according to: JIS R1602 , T_{room} only

GAS TIGHTNESS

Test specimen
Electrolyte only

The leak rate (L_r) is determined in accordance with:

$$L_r = V (p_1 - p_2) / \Delta t A$$

where:

p_1, p_2 = He initial and final partial pressures
V = He volume
Δt = test time
A = test surface

Proposal

Measurement still under study to evaluate a correct procedure and the usefulness of knowing D, diffusion coefficient

THERMAL CYCLING

Test specimen

- individual components (anode, cathode, electrolyte , interconnect)

Measurement method/technique

- specimens should be subjected to thermal cycling from room temperatur up to 1000°C min
- minimum cycling should be 15 complete (back and forth) cycles
- heating and cooling rates should be 100°C/h
- thermal cycling resistance should be evaluated through flexural test in accordance with the methods addressed in this same document.

THERMAL EXPANSION, α

Test specimen

- individual components (anode, cathode, electrolyte, interconnect)

Definitions

Mean coefficient of linear thermal expansion: $\bar{\alpha} = (L_2-L_1)/(T_2-T_1) L_o$

(where: $L_2 = L(T_2)$, $L_1 = L(T_1)$, $L_0 = L(T_0)$ with $T_0 = 293K$)

Instantaneous coefficient of linear thermal expansion: $\alpha_i = 1/L_o(dL/dT)$

Proposed measurement method

ASTM C372-88

Push rod method - ASTM E228-85

under examination

Interferometric methods

Method proposed to CEN n. BS 7134 section 4.1/90 - Method for determinatio of thermal expansion

THERMAL CONDUCTIVITY

Test specimen

- individual components (anode, cathode, electrolyte , interconnect)

Measurement method

Laser flash method

Calculation

Thermal diffusivity α will be determined as follows:

$$\alpha = \omega L^2/t_{1/2} \ [cm^2/s]$$

where:

L = thickness

$t_{1/2}$ = time for rear surface temperature to rise to one half of its maximum value

ω = parameter that is a function of the heat loss

For the ideal case of zero heat loss $[\Delta T(10\, t_{1/2})/\Delta T(t_{1/2}) > 1.98]$ and sufficiently small pulse width $(\tau/t_{1/2} < 0.02)$, $\omega \approx 0.139$.

Thermal conductivity k will be determined as follows:

$$k = C_p \alpha B$$

where:

C_p = specific heat, still under evaluation

B = bulk density, as determined in accordance with the method addressed in this same document

THERMAL CAPACITY

Test specimen

- individual components (anode, cathode, electrolyte , interconnect)

Calculations

Thermal capacity C is determined as follows:

$$C = c\,W$$

where:

c = specific heat (still under evaluation)

W = mass of specimen as determined from the weight of specimen W=D (D = dry weight of specimen*)

* see ASTM C373-88

SOFC Powder Characterisation

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contents

SCOPE

Powders, or precursors of powders, for the fabrication of SOFC anode-, cathode-, electrolyte- and ceramic interconnect structures are the relevant products to be evaluated. The aim is to provide a standard set of powder properties which have to be measured according to recommended methods and measurement conditions.

The set is based on the results of a "round-robin" test for electrolyte powder between 5 laboratories. Of course, this is a too small basis for recommended practices, but at the moment is the best procedure for a standard method. Exercising of the recommended practices is neccessary for further refinement.

It is assumed that the powders have been fabricated by proprietary methods. Specific powder requirements will not be discussed or defined, due to the custom-tailored demand from end-users in relation to proprietary forming techniques. In addition, the finer details of the instrumental techniques for the characterization are not discussed, since these aspects are covered elsewhere.

DATA RECORDING

In the following paragraphs, selected powder properties with the recommended measurement methods will be described. The selected powder properties and recommended measurement methods for SOFC powders were defined during the IEA workshop in Oslo in 1991 (1). After the workshop, the proposed properties and methods were evaluated through a round robin test between 5 laboratories (see Appendix A), i.e. Cookson Group (CG) from the United Kingdom, Eniricerche (ENI) from Italy, Senter for Industriforskning (SI) from Norway, Alusuisse/Lonza (A–L) from Switzerland and The Netherlands Energy Research Foundation (ECN). The powder used for the test was delivered by TOSOH Corporation (Grade: TZ–8Y; Lot. No.: Z800929P). In the near future, more laboratories need to be involved in the test, and also other SOFC powders need to be tested.

The selected powder properties to be measured are:

1 Chemical composition
2 Phase composition
3 Specific surface
4 Particle size distribution
5 Particle shape
6 Sinterability
7 Powder density
8 Flowability

In the following paragraphs the recommended measurement methods for each selected property will be given. If appropriate recommended measurement conditions and recommended measurement output will also be given.

State–of–the–art SOFC powders are:

* Electrolyte : 3 or 8 mol.% Y_2O_3 stabilized ZrO_2 (3– or 8YSZ)
* Cathode : Doped (e.g. Sr or Ca) $LaMnO_3$ or $LaCoO_3$
* Anode : Ni–YSZ cermet (most often NiO–YSZ precursor)
* Interconnect : Doped (e.g. Mg, Ca, or Sr) $LaCrO_3$, if not metal

An international list of SOFC powder manufacturers is given in Appendix B (2).

1 CHEMICAL COMPOSITION

Recommended method:

*	X-ray fluorescence (XRF)	Main components
*	Emission Spectroscopy based on an Inductively Coupled Plasma Source (ICP)	Impurities
*	Thermogravimetric analysis (TGA)	Moisture
or		
*	Drying to constant weight at 120°C and determination of loss on ignition at 1050°C	

If XRF is not available, one should also use ICP for the major elements.

Alternative methods:

*	Atomic absorption spectroscopy (AAS)	Main components
*	Electron microprobe analysis (EMA)	Impurities

Recommended measurement conditions:

XRF:

Standard sample preparation and measurement conditions for the above mentioned methods are difficult to establish. This is related to the particular instrument and the "in-house" standard procedure which is used in a laboratory for a given method. Recommended is to make glass beads for main component analyses, by fusing the powder sample in lithium tetraborate at a temperature of 1200°C.

ICP:

Possible destruction methods for preparing the ICP solution are: 1/ acid destruction or 2/ melt destruction followed by dissolution. A recommended destruction method for cathode- and interconnect materials is dissolution of the powder in a mixture of 9 grams of HNO_3 and 3 grams of $HClO_4$ in teflon bombs for 10 hours at 190°C. For anode-cermet powders and electrolyte powders, dissolution in HF or fusion of the powder in potassium pyrosulphate at about 200°C is recommended. Two problems with HF dissolution are the volatility of Si-fluorides, which can be an important impurity of zirconia-based materials and the insolubility of Y, Ca and Mg-fluorites, all of which can be important in zirconia based materials.

TGA:

It is recommended to determine moisture between room temperature and 120°C at a heating rate of 5°C/min.

It is recommended to determine loss on ignition between 120 and 1700°C (or at least 1500°C) at a heating rate of 10°C/min.

Recommended output from measurements:

- Dissolution/destruction method
- Instrumental specifications
- Standard reference materials used
- Weight percentages of the oxides of the main components.
- Parts per million (ppm) for the impurities.
- Standard deviations of the measurements

2 PHASE COMPOSITION

Recommended method:

X-ray diffraction

Alternative methods:

*	Differential Scanning Calorimetry (DSC)	Phase changes as a function of temperature
*	EMA	Elemental mapping or quantitative analysis

Recommended output from measurements:

- Instrumental specifications
- Standard reference material used
- Measurement conditions
- Crystallographic phases detected with indication of quantities (main component, traces)
- Crystallite size from line broadening
- Unit cell parameter (optional)

3 SPECIFIC SURFACE

Recommended method:

- Nitrogen adsorption (single point BET model)

Recommended measurement conditions:

Nitrogen adsorption can be used as a 1-point or as a multi-point method. For the 1-point method the lower detection limit is 5 m^2/g; for the multi-point method the lower detection limit is about 1 m^2/g. With the multi-point method additional information on the pore size of the powder particles (only in the 2 - 40 nm or meso-pore range) can be obtained. It is recommended to heat the powder to 200°C and to evacuate to about $5x10^{-2}$ torr. For accuracy reasons the amount of powder used should correspond to a total surface of about 20 - 50 m^2.

Recommended output of measurements:

- Instrumental specifications
- Measurement method (1- or multi-point)
- Pre-heating temperature and time and evacuation pressure
- Total sample mass measured
- Specific surface in m^2/g
- Statistics of the measurement
- Specific pore volume (cm^3/g) and pore size distribution (optional)

4 PARTICLE SIZE DISTRIBUTION

Recommended method:

- Dynamic and static light scattering techniques

Alternative methods:

- Sedimentation

Recommended measurement conditions:

For zirconia powders, the recommended practice for powder dispersion has been described in a paper by H. Raeder (3). In short, the sample is dispersed in distilled water using sodium polyphosphate as dispersant. An ultrasonic "finger" probe with a

600W generator (Cole–Parmer 4710) is used for de–agglomeration. In a contribution from the Cookson Group to the round robin test it was mentioned that a single ultrasonic de–agglomeration treatment may give unreliable results, due to variabilities in agglomerate strength between zirconia samples (even from the same manufacturer). Therefore, it is recommended that measurements are repeated under conditions of increasing ultrasonic power and sonication time until no further reduction in particle size is observed. The dispersion is measured with the recommended method.

For other SOFC powders, this method still has to be tested. If the method is insufficient for these powders, a recommended practice for the measurement is: 2 minutes vibrating in ethanol in an ultrasonic bath.

Recommended output of measurements:

- Instrumental specifications
- De–agglomeration procedure
- The complete particle size distribution curve with indications for particle sizes (µm) for which resp. 10–, 50– and 90 vol. % of the total particle population is smaller (D_{10}–, D_{50}– and D_{90} values)
- Statistics of the measurement

5 PARTICLE SHAPE

Recommended method:

* Scanning Electron Microscopy (SEM)

Recommended measurement conditions:

Powder should be sprinkled on double sided adhesive tape to show complete agglomerates. In addition, the sample may be given a sonication treatment in alcohol, in order to break up the agglomerates and to show the primary particles

SEM pictures should be made with different magnification factors. The set of pictures should at least contain magnifications of 200, 5000, 10.000, 20.000 and 40.000x.

Recommended output of measurements:

- Instrumental specification
- Sample preparation treatment
- Scale bar and magnification on the photograph

- Prints (preferentially 10 x 13 cm^2) of the above given magnifications

6 SINTERABILITY

Recommended method:

- * Dilatometer analysis
- * Thermo-mechanical analyzer (TMA)

Alternative methods:

- * Determination of the green-forming and sintering conditions, in order to obtain a density of 97%
- * Application of sintering experiment/model of Sasaki et al. (4).

Recommended measurement conditions:

Green pellet fabrication:

– total height of pellet(s):	10 mm
– diameter of pellet:	10 mm
– applied pressure:	200 MPa

Heating rate: 10°C/min.

Final temperature:

– electrolyte powders :	1600°C
– cathode powders :	1400°C
– anode powders :	1400°C
– interconnect powders :	1700°C

Gas atmosphere: air

Recommended output of measurements:

- Instrumental specifications
- Pellet preparation specifications (including addition of pressure additives)
- A dilatogram
- The temperature at maximum sintering rate
- The density of the fired body (g/cm^3 and expressed as percentage of the theoretical density) determined by a pycnometer (Archimedes method)

Note: theoretical density of 8 mol% YSZ should include the extra atomic mass of HfO_2. E.g. when this is done for an additional atomic mass of 1.4 wt% HfO_2 in the cubic unit cell (lattice parameter = 0.514 nm), the theoretical density of the round robin zirconia is calculated as 6.0 g/cm^3, instead of 5.9 g/cm^3 for hafnia-free 8 mol% YSZ.

7 POWDER DENSITY

Recommended method:

* Tap density

Recommended measurement conditions:

Recommended practice is the method described by the British Standard Institution (BS 5600: Part 2: Section 2.3) (5).

Recommended output of measurements:

- Instrumental specifications
- Amount of powder tapped
- Geometry of tapping cylinder
- Times and method of tapping
- Density before tapping (g/cm^3)
- Density after tapping (g/cm^3)

8 FLOWABILITY

Recommended method:

* Flowmeter

Recommended measurement conditions:

Recommended practice is the method described by the British Standard Institution (BS 5600: Part 2: Section 2.6) (6).

Recommended output of measurements:

- Instrumental specifications
- Geometry and material of the filling funnel
- Amount of powder tested (preferably 100 g)
- The flow-time (flow-time in seconds / 100 g of powder)

DATA ANALYSIS

Using the measured data it is possible to characterize and to compare SOFC powders. In a first approach, a round robin test was carried out with an 8 mol% Y_2O_3-stabilized ZrO_2 (8YSZ) powder from Tosoh. A summary of the results of the round robin test is given in Appendix A. Detailed results from the round robin test are available on request from F.H. van Heuveln (ECN).

The best response in the round robin test was obtained for: 1/ chemical composition, 2/ phase composition, 3/ specific surface, 4/ particle size distribution, 5/ particle shape, 6/ sinterability and 7/ powder density. In general the data could be well compared, except for the chemical composition (especially the impurity levels) and the particle size distribution.

The determination of the chemical composition shows the difficulties of recommending comprehensive measurement procedures. It is clear that many more powders and laboratories need to be involved and, particularly for silica in zirconia, more development work on analytical methods is needed. There is a need for a set of certified standard SOFC powders to which all analyses can be referenced.

The determination of the particle size distribution requires a standard pre-treatment of the powder (de-agglomeration), for which recommendations are given.

The recommended property "flowability" was only determined by 1 out of 5 laboratories. For particular applications (e.g. plasma spraying) this is an important parameter and, therefore this still is a recommended property.

With respect to earlier proposals, two recommended properties have not been included any longer, i.e. pore size distribution of the powder and surface chemistry. The former property was only determined by 1 out of 5 laboratories and it is questionable if the determination of this parameter is meaningful. The latter property is only meaningful for specific forming techniques (e.g. tape casting) and the required characterization technique (e.g. Zeta-meter) is not standard available at many laboratories (response from 1 out of 5 laboratories).

REPORTING FORMAT

A reporting format for the characterization of SOFC powders has been designed by the Italian partner (7) and was presented during the Oslo workshop. It is recommended to update this format periodically.

A powder characterization format shall include, at least the items listed below:

1/ A powder identification code.

2/ A listing of the powder properties.

3/ A description of a possible powder pre–treatment (e.g. de–agglomeration procedure, dissolution procedure)

4/ A description of the measurement method.

5/ A description of the measurement conditions.

6/ A description of standard reference materials used.

7/ An indication of the accuracy and the precision of the measurement.

For each of the properties, the recommended output which was described earlier should be included in the above described items.

REFERENCES

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3. H. Raeder (1991): Powder dispersion for particle size measurements.

4. K. Sasaki, P. Bohac, H. Hofmann and J. Gauckler (1991). Modelling: Sintering of ultrafine ZrO_2 powders.

5. British Standards Institution (1985). Powder metallurgical materials and products. Part 2: Methods of sampling and testing metallic powders. Section 2.3: Determination of tap density. BS 5600: Part 2: Section 2.3: 1985.

6. British Standards Institution (1985). Powder metallurgical materials and products. Part 2: Methods of sampling and testing metallic powders. Section 2.6: Determination of flowability by means of a calibrated funnel (Hall flowmeter). BS 5600: Part 2: Section 2.6: 1985.

7 M. Chindemi and R. Millini (1991). SOFC powder cards.

8. R. Millini (1990). Characterization of powders for SOFC application in Eniricerche, Presentation at the IEA expert meeting, Lausanne, 5-6 November, 1990.

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Appendix A

SUMMARY OF RESULTS OF ROUND ROBIN TEST

The proposed properties and methods were evaluated through a round robin test between 5 laboratories. Cookson Group (CG) from the United Kingdom, Eniricerche (ENI) from Italy, Senter for Industriforskning (SI) from Norway, Alusuisse/Lonza (A–L) from Switzerland and The Netherlands Energy Research Foundation (ECN). The powder used for the test was delivered by TOSOH Corporation (Grade: TZ–8Y; Lot. No.: Z800929P). In the following tables the above described abbreviations for the laboratories will be used.

A summary of the results of the round robin test is given below. A more detailed description may be obtained from F.H. van Heuveln on request[1].

In Table 1 the powder properties, which had to be determined in the round robin test, are listed as a function of the response from the different contributing laboratories. In Table 2 the response on the recommended methods is given. Note, that two powder properties (i.e. pore size distribution of the powder and surface chemistry) are no longer incorporated in the list of recommended properties, for reasons given earlier.

Table 3 gives the properties of the test sample. In Tables 4 – 7 the results for chemical composition, specific surface area and particle size distribution from the different laboratories are summarized. With respect to the chemical composition, the recommended methods were agreed during the workshop in Oslo in 1991. The round robin test has made clear that this item needs more attention, i.e. the recommended methods are only a "starting point" for a comprehensive measurement procedure, which also has to be tested for other SOFC powders. Especially, CG has done a lot of work on the analytical methods for the determination of the chemical composition of YSZ (main components and impurities). The following results were reported: 1/ CG agrees with an XRF fused disk method for the main components; 2/ ICP can be used for Ti, Al and Ca; 3/ AAS can be used for Na, K, Mg and Fe; 4/ XRF pressed disk can be used for Ti, Al, Fe and Si and probably Cl. Especially, problems were experienced with Si, because they were unable to obtain a satisfactory zirconia

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[1] F.H. van Heuveln , ECN, Westerduinweg 3, P.O.Box 1, 1755 ZG Petten, The Netherlands.

standard. They conclude, that what is really needed is a set of standards for all elements to be measured, with agreed values.
For the phase composition, all laboratories reported a 100% cubic ZrO_2 without the presence of detectable amounts of free Y_2O_3. It is suggested by ENI to combine the use of XRD with standard chemical analysis. For single phase materials it is possible that a small fraction of an amorphous phase is present. This amorphous phase, not necessarily has to have the same composition as the crystalline matrix. The YSZ stoichiometry would then be different from that derived from chemical analysis. The procedure of combining XRD and chemical analysis is based on the accurate determination of the unit cell parameter of the cubic unit cell (8). The usefulness of this method as a recommended method needs to be investigated by another round robin test.

For the particle shape, all supplied pictures showed spheroidal agglomerates with a wide range of dimensions (up to 70 μm). The surface of the agglomerates is covered with submicron particles. Except for the spheres, many parts of broken spheres can be detected.

For the sinterability three laboratories reported that pressed pellets could be sintered to 96–98% of the theoretical density at 1500°C with a soaking time of 2 – 3 hours. One laboratory reported that the maximum sintering rate was observed at 1335°C. Note, that theoretical density of 8 mol% YSZ should include the extra atomic mass of HfO_2. E.g. when this is done for an additional atomic mass of 1.4 wt% HfO_2 in the cubic unit cell (lattice parameter = 0.5134 nm), the theoretical density of the round robin zirconia is calculated as 6.00 g/cm^3, instead of 5.9 g/cm^3 for hafnia-free 8 mol% YSZ.

The tap density of the powder was 1.5 g/cm^3 (determined with: 1/ a JEL Stampfvolumeter; 2000 taps or 2/ with a Quantachrome instrument; 3000 taps) or 1.35 g/cm^3 (tapping by hand; 1100 taps).

The flowability of the powder was only determined by one laboratory (Alusuisse-Lonza). The flowtime was given by the time for 100 g of a sample to flow out of a funnel. The apparatus consisted of a flow regulating funnel, a filling funnel and a beaker. The flow regulating funnel was made of aluminium and the upper edge diameter was 72 mm. Overall height of the funnel was 67 mm and the diameter of the outlet was 4 mm. Note, that these dimensions are not in correspondence with those described in reference 5. The resulting flowtime was 103 sec/100 g of powder (average of 3 measurements).

Table 1

Response on "Powder properties"

Company	Chemical composition	Phase composition	Specific surface	Particle size distribution	Pore size distribution	Particle shape	Sinterability	Surface chemistry	Powder density	Flowability
CG	+	+	+	+	−	+	+	−	+	−
ENI	+	+	+	+	+	+	+	−	+	−
SI	+	+	+	+	−	−	−	−	−	−
A-L	+	+	+	+	−	+	+	−	−	+
ECN	+	+	+	+	−	+	−	+	+	−

Table 2

Response on "Recommended methods"

Company	ICP (impurities)	XRF (main components)	XRD	Nitrogen absorption (BET)	Light scattering techn.	Mercury porosimetry	SEM	Tap density	Flowmeter
CG	+	+	+	+	+	−	+	+	−
ENI	+	−	+	+	+	−	+	+	−
SI	+	+	+	+	−	−	−	−	−
A-L	+	−	+	+	+	−	+	−	+
ECN	+	−	+	+	+	−	+	+	−

Table 3

Properties of TZ–8Y lot no. Z800929P supplied by TOSOH

1. Chemical analysis

	Y_2O_3	Al_2O_3	SiO_2	Fe_2O_3	Na_2O
wt %	13.30	<0.005	<0.002	<0.002	0.077

2. Ignition loss: 0.82 wt %.

3. Specific surface area: 15.8 m^2/g

Table 4

Chemical composition of the main elements of 8YSZ powder.

	ZrO_2 % W/W	HfO_2 % W/W	Y_2O_3 % W/W	Y_2O_3 % mole	method
CG	84.0	1.47	13.95	8.2	XRF
ENI	84.0	1.39	14.6	8.6	ICP
A–L	83.6	1.64	14.2	8.5	ICP–OES
SI	86.65	...	13.40	7.8	XRF
ECN	81.8	1.35	14.2	8.7	ICP
TOSOH	?	...	13.3		?

Table 5

Chemical composition of the impurities of 8YSZ powder, all units in ppm.

	Al_2O_3	Na_2O	CaO	SiO_2	TiO_2	Fe_2O_3	K_2O	MgO	S	Cl	C
CG[1]	<100	...	...	<100	200	<100	...	...	...	...	...
CG[2]	30	...	...	70,(35*)	20	10					
CG[3]	...	850	36	...	...	...	6	...	...	...	...
CG[4]	...	770	...	<43*	...	20	...	<20	...	...	...
CG[5]	10	...	30	...	20	...	...	...	<10	...	450
CG[6]	...	...	...	58*,86	...	...	...	...	...	1100	...
ENI[7]	4800	717	...	...	...	...	...	...	...	...	...
A-L[7]	<100	800	100	100	<100	<100	...	<100	...	700	...
SI[7]	<950	≈540	≈1400	<2150	67	<21	<6025	<330	...	...	...
SI[8]	<38	470	420	<20	≈167	<21	120	<33	50	1200	...
ECN[9]	<20	770	...	...	...	...	...	...	...	...	...
TOSOH	<50	770	...	<20	...	<20	...	...	...	...	...

[1] XRF fused glass bead (average of two measurements)
[2] XRF pressed disc (average of two measurements)
[3] Flame Atomic Emission (no reference possible in this technique)
[4] Flame Atomic Absorption
[5] ICP; S & C by LECO
[6] SiO_2 by colorimetry with standard addition & against aqueous standards; Cl by titration
[7] ICP, chlorine and sodium are normally determined by other techniques
[8] XRF pressed disc
[9] ICP, chlorine and sodium are determined by AAS

Table 6

Specific surface of 8YSZ powder.

	Specific surface area m^2/g		sample pretreatment temperature °C	time minutes
CG	13.5	1st	110	120
		2nd	150	20
ENI[1]	16.2		250	240
A-L[2]	13		150	120
SI	15.7		130	60
ECN	16.8		200	180
TOSOH	15.8		?	?

[1] Specific pore volume 0.17 cm^3/g, pore size distribution presented.

[2] Average of four determinations, 13.3, 13.3, 12.4, and 12.2.

Table 7

Particle size distribution of 8YSZ powder. Given are the cumulative values of the particle size in μm, at 10%, 50% and 90% of the distribution.

	D[0.1]	D[0.5]	D[0.9]	
CG-1	0.20	0.31	0.49	light scattering technique (Malvern Mastersizer), sample treated as described in the paper by H. Raeder (350 W ultrasonic probe).
CG-2	0.20	0.72	2.90	CG-2 and CG-3 are identical repeat measure-ments and shows a clear variation in the results
CG-3	0.23	0.84	3.74	
CG-4	24.95	51.03	84.00	no sonication, but Dispex A40 dispersant added
ENI-1	1.3	2.2	3.2	light scattering technique (Malvern Mastersizer), values derived from figure
ENI-2	12.52	35.49	54.26	laser scattering, powder as received
ENI-3	0.15	0.49	2.72	laser scattering, sample treated as described in the paper by H. Raeder
ENI-4	0.16	0.62	3.94	laser scattering, powder after milling, see section 7.2 for details
A-L	0.23	0.86	5.41	sample treated as described in the paper by H. Raeder
A-L	0.25	1.17	6.78	sample preparation according to own internal procedure
SI		0.15		after deagglomeration, according to treatment described by H. Raeder
ECN	0.39	2.54	9.49	light scattering technique (Malvern Mastersizer)

Note.
For the reporting format it is recommended that the total particle size distribution curve is reported, because the above quoted numbers can be misleading in the case of e.g. a bimodal distribution.

LIST OF SOFC POWDER MANUFACTURERS

Y_2O_3-stabilized ZrO_2 electrolyte powders

JAPAN

TOSOH Co.
1-7-7 Akasaka Minato-ku
Tokyo 107
Tel. : 03-3585-6734
Fax : 03-3585-4289

OSAKA CEMENT
1-4-4 Dojimafama Kita-ku
Osaka 530
Tel. : 06-556-2233
Fax : 06-556-2199

DOWA MINING Co., Ltd
1-8-2 Marunouchi Chiyoda-ku
Tokyo 100
Tel. : 03-3201-1086
Fax : 03-3201-1097

KYORITSU CERAMIC MATERIALS Co., Ltd
2-41 Tsukisan-cho Minato-ku
Nagoya 455-91
Tel. : 052-661-3182
Fax : 052-654-1639

NISSAN CHEMICAL INDUSTRIES
3-7-1 Kandanishiki-cho Chiyoda-ku
Tokyo 101
Tel. : 03-3296-8391
Fax : 03-3296-8210

DAIICHI KIGENSO KAGAKU KOC
14-4-4 Koraibashi Chuo-ku
Osaka 541
Tel. : 06-231-3835
Fax : 06-231-2922

SHOWA DENKO K.K.
1-13-9 Shiba Daimon Minato-ku
Tokyo 105
Tel. : 03-5470-3291
Fax : 03-3431-3142

NIKKATO Co., Ltd
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Tokyo 141
Tel. : 03-3494-0471
Fax : 03-3493-7881

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VIKING CHEMICALS
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Tel. : 53-468555
Fax : 53-468466

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Telex : 8811765

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SOFC Stack Evaluation

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contents

1. Standard Testing Conditions

The following testing conditions should be specified as standard by stack manufacture before operating.

① Stack temperature (℃)

② Operating pressure (Pa)

③ Fuel composition (recommended: H_2 saturated with water vapour at 25℃)

④ Oxidant composition (recommended: air)

⑤ Fuel utilization (%) (recommended: $Uf>50\%$)

⑥ Oxygen utilization (%)

⑦ Standard current density (A/㎠)

2. Testing Items

2-1 Pre-test Check

(1) Electric isolation check

After setting up and before heat up, check cell resistance and cell to earth resistance.

(2) Leak check with inert gas

After heat up to standard temperature, flow N_2 or CO_2 into anode and cathode sides. Measure the flow rate of inlet and exit gases. Check the difference between them.

(3) Leak check with reactant gas

Flow standard fuel and oxidant into anode and cathode sides. Sample gas from anode and cathode exit lines through drier. Analyze gas composition with gas chromatograph.

(4) Open circuit voltage (OCV) check

Read OCV of stack and proper cells.

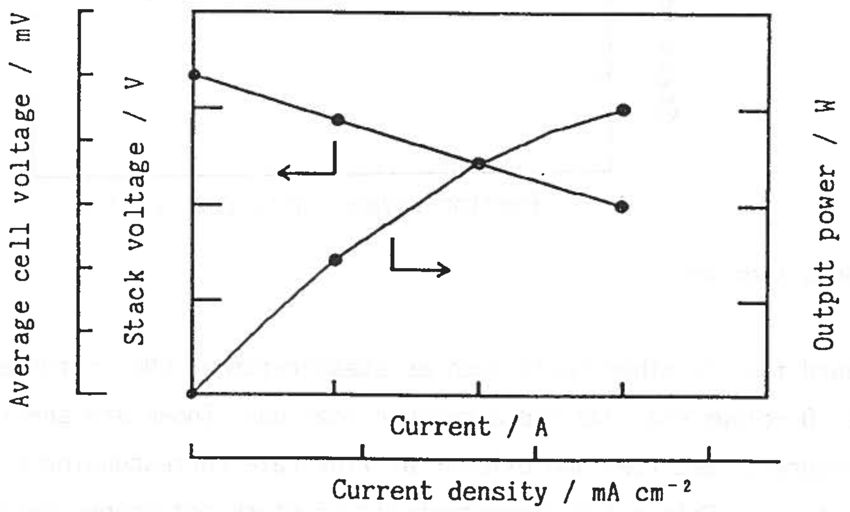
2-2.Initial Performance Test

(1) I-V characterictic at constant flow rate
Set fuel and oxidant at flow rate corresponding to standard utilization at maximum current i_{max} (i_{max} is specified by stack manufacturer). Obtain I-V characteristic of stack and proper cells in the range of $0 \sim i_{max}$.

(2) Internal resistance check
Keep stack at open circuit. Measure internal resistance of stack and proper cells.

(3) I-V characteristic with pure O_2
Flow O_2 instead of standard oxidant. Set fuel and O_2 at flow rate corresponding to standard utilization at i_{max} . Obtain I-V characteristic of stack and proper cells.

I-V characteristic at constant flow rate



(4) I-V characteristic at constant gas utilization (If possible)
Set fuel and oxidant at flow rate corresponding to standard utilization at each current density. Obtain I-V characteristic of stack and proper cells.

(5) Temperature distribution in stack (If possible)
Set stack at standard operating conditions and standard current density. Measure temperature of several cells at proper points. Also measure temperature at several proper points within a cell.

2.3 Gas Utilization Test

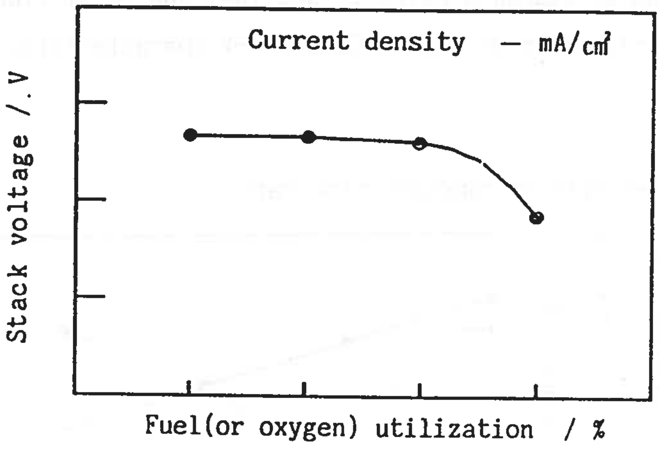
(1) Effect of fuel utilization

Leave oxygen utilization at standard. Set current density at standard. Record voltage of stack and proper cells for changing fuel flow in certain range (recommended: from 30% to 80% of fuel utilization).

(2) Effect of oxygen utilization

Leave fuel utilization at standard. Set current density at standard. Record voltage of stack and proper cells for changing oxidant flow in certain range (recommended: from 15% to 30% of oxygen utilization).

Effect of fuel (or oxygen) utilization



2-4 Fuel Composition Test

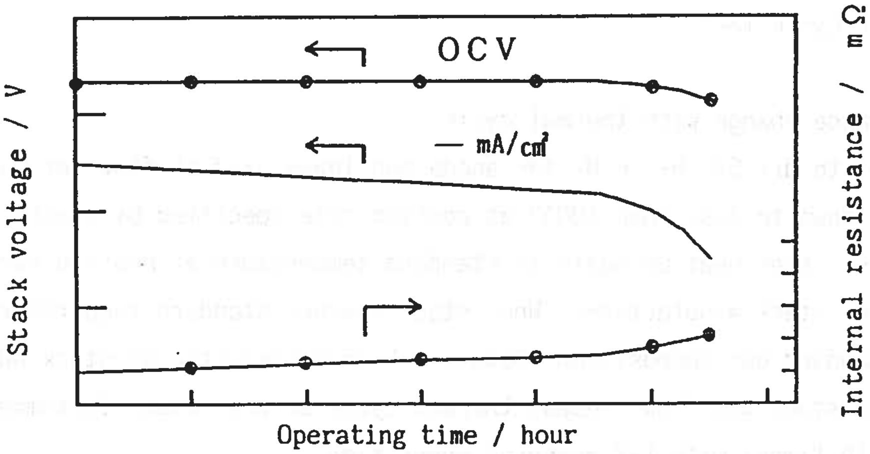
Change standard fuel to other fuels such as steam-reformed LNG, reformed methanol gas, O_2-blown coal gas and air-blown coal gas (Those are specified by stack manufacturer). Set fuel and oxidant at flow rate corresponding to standard utilization at i_{max}. Obtain I-V characteristic of stack and proper cells in the range of 0～ i_{max}.

2-5 Long-term Operation Test

(1) Voltage degradation with time at constant current

Operate stack in succession (recommended: more than 1,000 hours) under standard operating conditions at standard current density. Record voltage of stack and proper cells while operating. Also obtain OCV and I-V characteristic of stack and proper cells at regular intervals (recommended: about every 100 hours) at constant flow rate.

Long-term operation



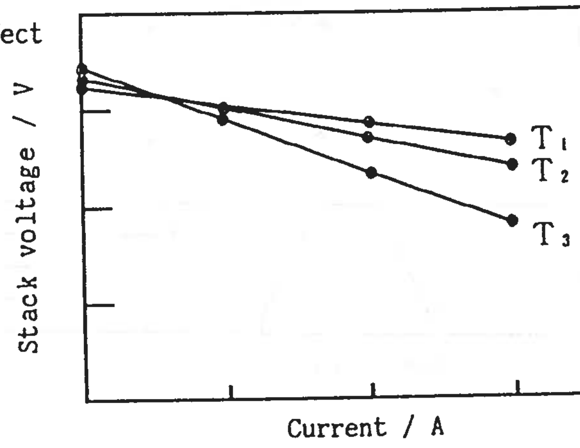
(2) Internal resistance change with time

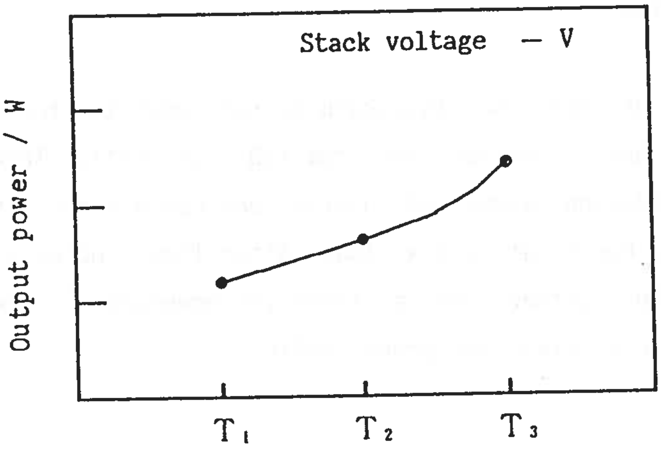
Read internal resistance of stack and proper cells at regular intervals (recommended: about every 100 hours) under open circuit.

2-6 Temperature Effect Test

Set cell temperature at T_1, T_2, T_3 ($T_1 < T_2 < T_3$; T_2 usually means standard temperature). Obtain I-V characteristic of stack and proper cells at constant flow rate at each temperature.

Temperature effect





2-7 Thermal Cycle Test

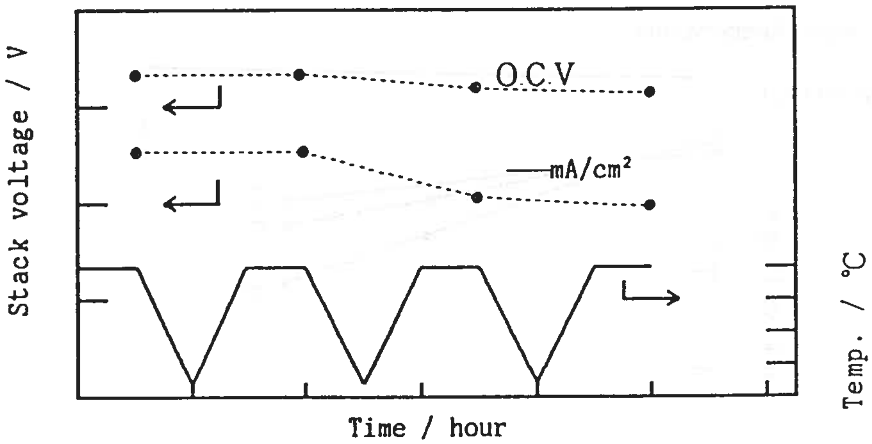
(1) Performance change with thermal cycle

Switch fuel to dry 5% H_2 in N_2 for anode and leave oxidant flow for cathode. Cool stack down to less than 100℃ at cooling rate specified by stack manufacturer, then heat up again to standard temperature at heating rate specified by stack manufacturer. When stack reaches standard temperature, switch fuel to standard gas composition. Obtain I-V characteristic of stack and proper cells at constant gas flow. Repeat thermal cycle several times (recommended: more than 10 times) with I-V measured every time.

(2) Cross-leak check with thermal cycle

After stack reaches standard temperature, flow standard fuel and oxidant at standard flow rate into anode and cathode sides. Sample gas from anode and cathode exit lines through drier. Analyze gas composition with gas chromatogragh.

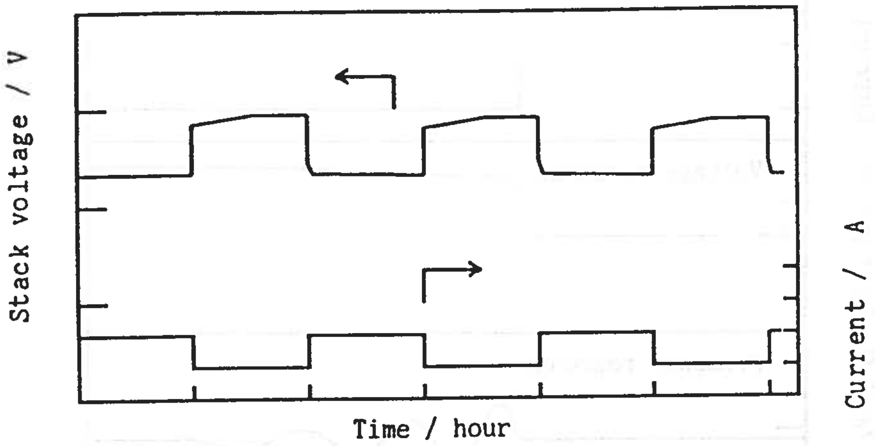
Thermal cycle test



2-8 Load Cycle Test

After operating at 100% load (standard current density) for several hours (recommended: 8 hours), switch load from 100% to partial load (recommended: 20%) with utilization maintained constant and operate for several hours (recommended: 16 hours) at partial load. After that, increase load again to 100 %. Repeat this pattern several times (recommended: 7 times) while recording voltage of stack and proper cells.

Load cycle test



2-9 Heavy Load Test

Set load more than 100% (recommended: 200%) while adjusting gas utilization constant. Operate in succession (recommended: more than 100 hours) at that load. Record voltage of stack and proper cells during operation.

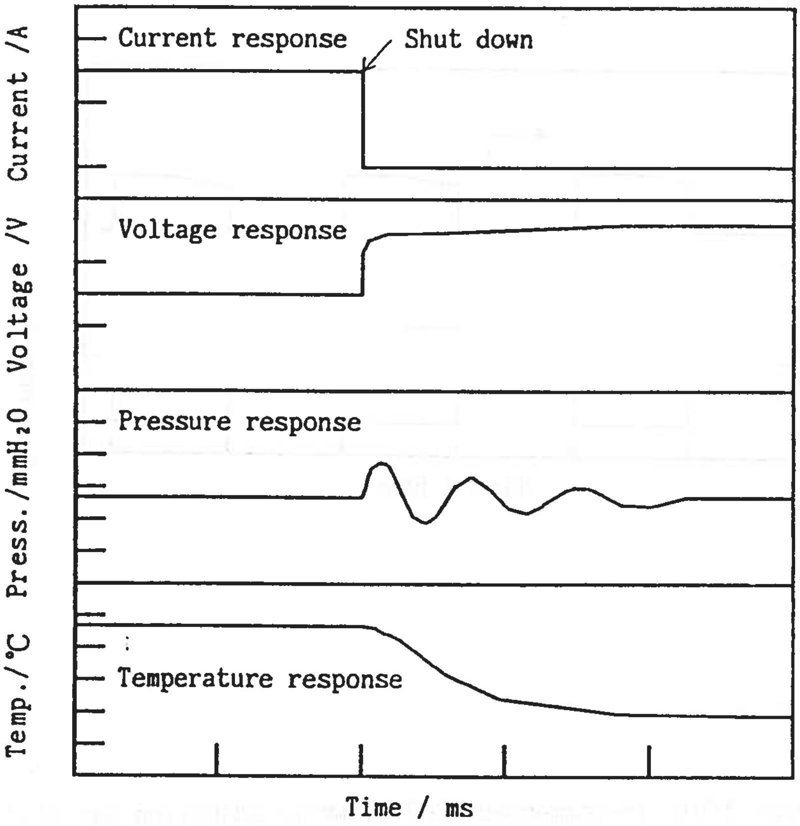
2-10 Emergency Shut-down Test

(1) Voltage response on shut-down
Switch stack from 100% load to open circuit. Record transitional voltage change of stack and proper cells accompanied with shut-down with high-speed recorder.

(2) Pressure response on shut-down
Switch stack from 100% load to open circuit. Record transitional pressure change accompanied with shut-down with high-speed recorder.

(3) Temperature response on shut-down
Switch stack from 100% load to open circuit. Record transitional temperature change accompanied with shut-down with high-speed recorder.

Shut-down test



2-11 Differential Pressure Test

Switch stack to open circuit. First, keep fuel inlet pressure higher than oxidant inlet pressure (recommended: by 9.8 $\times 10^3$Pa). Record OCV change due to gas cross-leakage which may occur. Also sample gas from anode and cathode exit lines through drier. Analyze gas composition with gas chromatogragh in order to determine whether cross-leakage occured or not. Next, keep oxidant inlet pressure higher than fuel inlet pressure (recommended: by 9.8 $\times 10^3$Pa), then repeat the same method described above.

3. Description of Stack Structure

It is to be recommended that the following items are added in the test data.

(1) Active electrode area (㎠)

(2) Number of cells

(3) Gas manifold structure

(4) Cooling system

(5) Power density (power/volume: W/ℓ)

(6) Gas seal method