

A review of standardising SOFC measurement and quality assurance at FZJ

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Abstract

The need for standardisation/quality assurance (QA) is argued for citing extant problems with consistency, repeatability and reliability of data. A review of the cell testing procedure/QA system used at Forschungszentrum Jülich (FZJ) is given including an outline of how the FZJ system was developed. This is put in the context of more extensive QA systems following the outlines of the ISO 9000 series standards. Examples are used to illustrate how and why a number of standard cell test parameters was adopted. It was found that pre-normative research used to define testing parameters led to an improvement in cell performance generally. Therefore, it is recommended that other solid oxide fuel cells (SOFC) labs develop standardisation in testing and QA systems to maintain and improve their measurement processes.

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1. Introduction

Obtaining consistent, reliable and repeatable results in SOFC testing is no simple matter. The need for such is very evident and becomes increasingly important in making decisions as the technology approaches pre-commercial and commercial implementation, this being due to the need to make serious financial decisions regarding the best materials and designs to use.

There is a distinct difference between the majority “fundamental” development labs such as those typical of academic researchers and those (usually national) large research and development facilities that seek to bridge the gap between the fundamental research and commercial manufacturing. The bridging organisations have great difficulty in assessing the value of work from fundamental researchers in that there is no uniformity of testing conditions between labs, frequently no indication as to the repeatability of reported results and similarly no indication as to whether results reported for a potential material would be uniform over the medium time-scale even, etc. Whilst, as the abstracts and introductions invariably state, such results give indication of potential there is seldom the required amount

of information to attract larger scale developers. As a result one has to wonder how many materials with real potential stand little or no chance of ever being taken into consideration. Developers simply do not have the capacity to examine every possibility. This situation with national scale developers is mirrored exactly with commercial industrial organisations developing SOFCs and systems. This develops into a form of lethargy within the larger scale developers whereby it is easier to focus on existing materials that are known to work well generally and to concentrate on solving extant problems with said materials. Such a situation arises principally for political and financial reasons, these motivations are well understood by those involved and we cannot deal with those here.

In all branches of manufacturing and service industry management systems to ensure the quality of the output are seen as being necessary. As SOFC technology approaches that world it is necessary to think and behave more like that world to ensure effective communication and to present a professional image. Moreover, to adopt such systems provide marked advantages in all levels of SOFC development.

On closer analysis such systems represent a formalised means of ensuring good scientific and engineering practice. Looking to other fields of science and technology there exist similar systems ensuring the safety of pharmaceutical products, the integrity of evidence in forensic studies, the safety of pressure vessels

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and such like. In essence there is nothing new to scientists and engineers in such practices, merely it becomes more organised by adopting them.

There is a cost in adopting such systems, however this cost is principally one of time and effort rather than direct financial outlay. Experience dictates that once a system has been formulated and implemented however, there is little additional work (cost) required to maintain the system and its benefits more than exceed the initial and running costs.

FZJ has adopted such a system in relation to its SOFC testing activities. This presentation gives an outline of that system and offers examples explaining/illustrating the development of the FZJ standard system. It can be concluded that similar systems would be beneficial to other developers of all sizes.

To offer an example of how apparently minor details can strongly influence published data we will briefly discuss the case of pre-conditioning Ni-cermet anode cells prior to making general cell performance measurements, something which other labs either do not carry out or fail to report if they do. No personal criticism is intended of the labs concerned or their work as cited, however this published data makes the case in point and strongly suggests that we need to act to eliminate such difficulties.

2. Systems

The absence of any accepted SOFC standards does not imply that measurements cannot be standardised and closely controlled. Developing a process control system is a straightforward exercise:

1. Analyse what you want to do.
2. Analyse how you can do it best.
3. Therefrom define your critical process parameters.
4. Producing a written procedure detailing how the process should be carried out.
5. Documenting the results of each procedure.

As above there is nothing new to science/engineering in this, however in a formal quality system the emphasis is on control and thus the system is carefully described in the formal written procedure that is followed every time a measurement is made. This can be done without limiting scientific freedom if the system is properly designed.

Ideally the measurement will wherever possible be traceable to national or international standards—thus removing questions over the actual temperature or voltage perhaps. Thus, a comprehensive system will maintain records of calibrations and such like. It will also maintain records of equipment generally, personnel training, suppliers of consumables, etc. The reader can refer to ISO 9000 series generic Quality Assurance systems standards or guides to such to get details on what elements are required in a fully comprehensive QA system. FZJ has concentrated on the SOFC testing itself initially and are gradually incorporating other 9000 series elements into our system. External accreditation and ISO 9000 certification would be the final goal but this does not have to be done all at once, such may be completely

unsuitable for some labs. The present ethos however is anything but unsuitable.

Adopting the general approach of the ISO 9000 series QA standards and working towards that goal has several benefits. The main benefit is that this standard has been tried, tested and found good across the full range of manufacturing, service and research industries. Such a QA system would be compatible with other ISO, DIN, BS, etc., standards and should contain most of the required elements in any SOFC specific standards if/when such become available. Customers and potential financiers recognise and value such QA systems. Lots of material is available to guide one through implementing such a system.

Subsequent sections of this presentation illustrate elements in the process of developing the core SOFC testing procedure at FZJ, pre-normative research that allows defining critical test parameters and what the customer will receive resulting from the same. Whilst this is not a paper reporting scientific results or sample preparation per se, we begin with a general description of the type of cells we are referring to, a little on their manufacture and some description of the test facilities used here. We will not be too detailed as we are arguing for the idea and widespread introduction of formal control/QA systems generally and not asking that people necessarily adopt ours.

3. Experimental aspects

3.1. Preparation of cells

Developmental FZJ-type single cells (50 mm × 50 mm) are based on an anode substrate (thickness: ~1500 μm), an anode functional layer (AFL) (thickness: 5–10 μm) and an electrolyte (thickness: ~10 μm). The anode substrate, a porous composite consisting of NiO and zirconia stabilised with 8 mol% yttria (8YSZ) is produced in much larger sheets by warm pressing using a so-called Coat-Mix[®] material. The green-pressed anode substrate sheet is pre-sintered at 1230 °C. The anode functional layer (NiO/8YSZ) and the electrolyte (8YSZ) are then deposited by vacuum slip casting and the materials are co-fired at 1400 °C. Cell-sized pieces are laser cut to dimension from the parent sheet. Cathodes, as the LSM and LSCF mentioned above or other developmental compositions, are screen-printed (40 mm × 40 mm) with or without other functional layers such as CGO. Finally the completed cells are fired at ca. 1100 °C to sinter the cathode into place.

3.2. Cell housing

The furnace used in the single cell test facility at FZJ to heat up the cell and maintain operating temperature is a conventional furnace with a maximum temperature of 1000 °C. Heating is provided from three side walls. The working area in these types of furnaces is accessible from two sides. Modifications have been made to the furnace floor only to accommodate all gas and wiring feedthroughs. Refractory clay bricks are used for the feedthroughs and to level the single cell housing at approximately 10 cm above the normal floor of the furnace. The single cell measuring housing is placed directly on top of the refractory

clay bricks. For guiding the thermocouples and the Pt-wires used as potential probes/current carriers four-bore capillaries are mounted in the respective feedthroughs. The thermocouples and Pt-wires both have a diameter of 1.0 mm.

The single cell measuring housing is manufactured from inert and gas-tight Alsint® alumina which has been custom machined to dimension/for purpose. In the bottom plate of the measuring housing aluminium oxide tubes are cemented in place to provide the connections to the gas delivery system. The control thermocouple, used to measure and taken as the operating temperature of the cell is located in the cell housing itself, less than 10 mm from the cell. Small Faraday cages are available to surround the cell housing should such be necessary to reduce ambient electrical noise for EIS measurements.

In order to obtain sufficient electronic contact between the cell and the electronic devices, a Ni mesh is used on the anode side and a Pt mesh on the cathode side. On both sides, two meshes where used, a fine one and a coarser one, where the former is in direct contact with the electrodes and the current wires are attached to the coarser one. A mechanical load is applied of 20,000 Pa or higher (kgf per area of current collecting mesh) this ensure electrical contacting and cell sealing (see below). Current and potential sensing wires are made from heavy Pt-wire, the wiring is doubled for the current leads to accommodate large currents.

Sealing of the gas compartment is via a gold gasket (pressure applied as above). Cell dimensions are carefully and precisely controlled in manufacture. Some variation exists however in the cathode thickness (often intentionally). To accommodate this, our ceramics manufacturing/development institute who produce the cells, supply them with accurately measured cathode thicknesses. We manufacture and retain gold seals in varying thicknesses (at single micron tolerances). Experience and leak-testing experiments then allow us to choose from retained records the ideal gold seal thickness for each cell tested thus ensuring minimal gas leakage and maximal electrical contacting. Nevertheless systematic gas-leakage tests are carried out for every cell tested.

3.3. Pre-conditioning of the cell and performance tests

Heating the single cell (anode in its oxidized state) is carried out under air and argon, cathode and anode sides, respectively, with gas flow rates of 500 ml min⁻¹ both sides. The single cell is heated to 900 °C with a rate of 1 °C min⁻¹ (heating and colling rates are determined largely by the need to avoid the thermal shock of the alumina housing). Reduction is carried out at 900 °C by step wise increasing the amount of hydrogen on the anode side.

All measurements are performed with a fuel composition of 97% hydrogen and 3% water with a fuel flow (STP) of 1000 ml min⁻¹. This rate avoids the depletion of fuel influencing *IV* measurements at higher fuel utilisation rates. Water is introduced to the hydrogen in a two stage process; fuel is bubbled through water at ca. 28 °C to produce more than the 3% desired humidity; this is then fed into a condenser at 24 °C to remove the excess water and yield exactly 3% humidity. Experiment reveals

that this system is much more stable than simple bubbling (even temperature-controlled bubbling, despite theory suggesting that it should not). Further the greater pipe distance from the bubbler stage to the cell reduces transient pressure variations caused by the bubbling that can be measured electrochemically. All piping is insulated as appropriate. The oxidant composition is 21% oxygen and 79% nitrogen and the total flow (STP) is set at 1000 ml min⁻¹.

The electrochemical performance is generally measured between 600 and 900 °C. All electrochemical data are obtained by dc methods using one of a number of in-house constructed racks of equipment. Generally these comprise of a current-control power supply type Gossen 62N–SSP500-40 and a computer-controlled data acquisition system including a datalogger type NetDAQ 2640A (Fluke). The current–voltage characteristics are measured with increasing current load by a sequential step change of 0.0625 A cm⁻² starting from zero until the voltage drops below 0.6 V or until a maximum current load of 1.25 A cm⁻² was reached. The current densities at 0.7 V are calculated on interpolation or extrapolation (for $I > 1.25$ A cm⁻²). Calculations of the area-specific resistance are based on linear regression (dV/dj within the interval 0.65–0.75 V) or linear extrapolation of the current–voltage curves at 0.7 V. See later for choosing equilibration times for *IV* measurements.

Recording of the polarisation curves is under galvanostatic control, starting at the open circuit voltage using a fixed current step size of 0.0625 A cm⁻² and holding time of 30 s. The characteristic value of the cell voltage at each current density is taken as the average value over the last 5 s of each step. The cell temperature is monitored during the complete measurement. Polarisation measurements are performed at several operating temperatures with a difference of 50 °C. After completion of the first polarisation curve measurement at 900 °C the cell is brought to the nearest lower temperature, in this case 850 °C. The procedure of polarisation curve recording is repeated at the next 50 °C lower temperature, down to 650 °C.

4. Analysing the SOFC testing process and determining critical parameters

SOFC testing at FZJ is broken down into a number of consecutive events, activities, decisions and outputs, this is best visualised in the form of a flowchart (Fig. 1). This chart follows the usual conventions, describing the start of the process, references critical parameters, decisions that need to be made, feedback loops to deal with non-conformities and specifies what information is to be collected and how/where it is to be recorded.

Given the number of parameters that effect an SOFC performance measurement, it is impractical to detail how all of the critical measurement parameters are determined. Instead some selected examples will be illustrated. This determination could be described as pre-normative research, investigating the general behaviour of FZJ cells and testing system to determine the best procedure. Cells from different manufacturers can behave in very different manners, thus the actual values to be determined here may be of little use to other developers, however the key

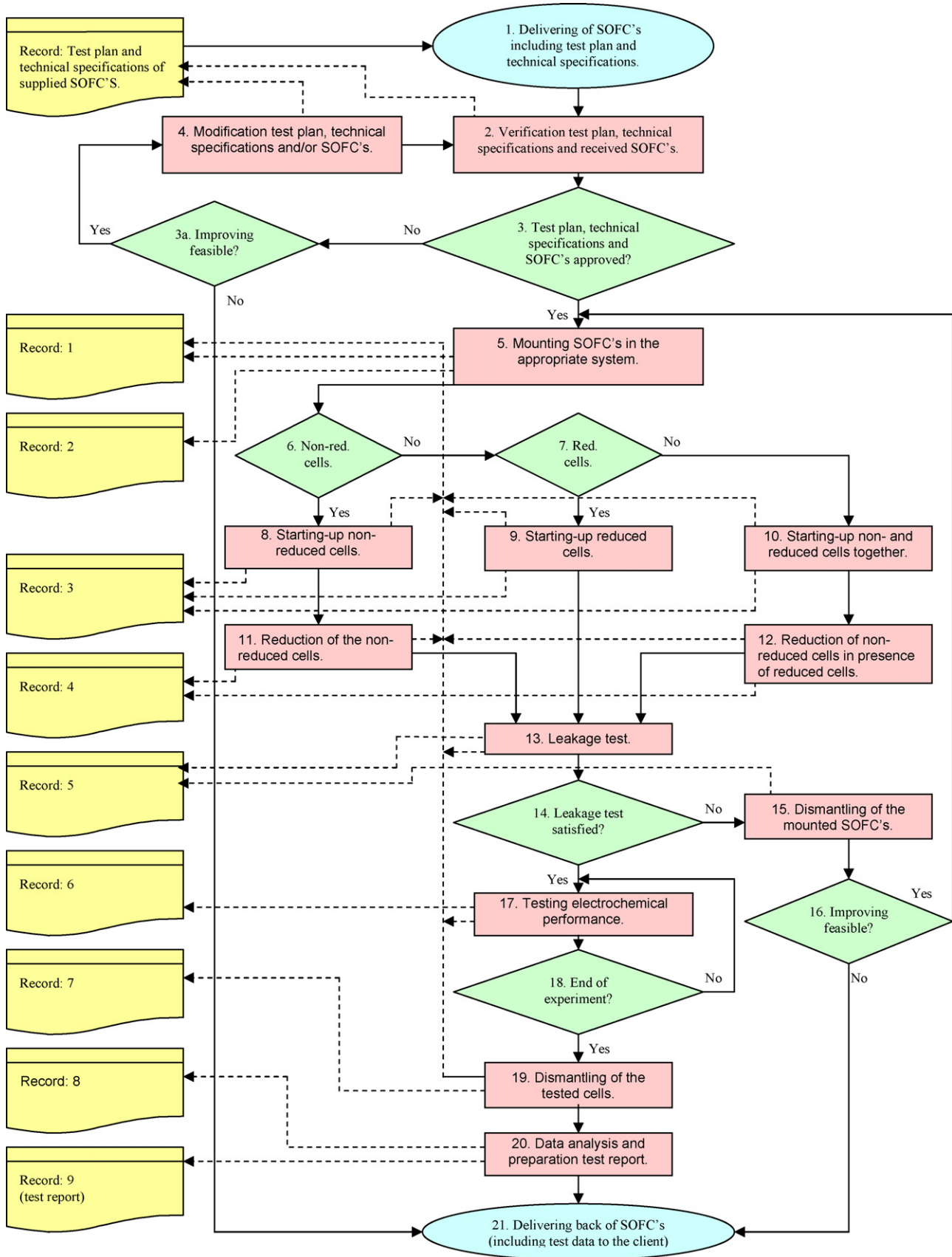


Fig. 1. Flow chart of testing procedure for single cells at FZJ.

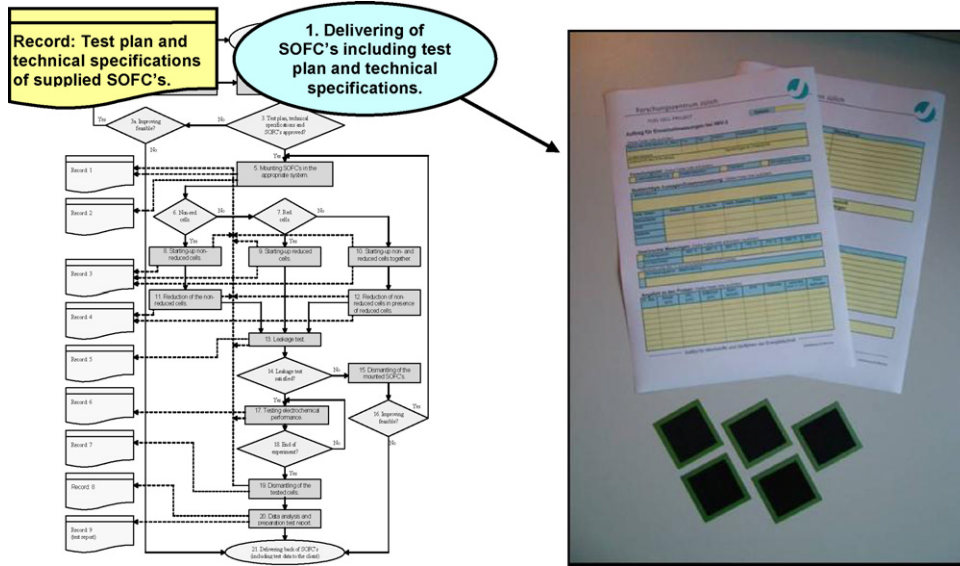


Fig. 2. Test plan and technical specifications of supplied SOFCs.

point here is not any specific values it is the general process of investigating the behaviour of the system.

4.1. Delivering SOFCs and test plan

Samples for testing are delivered to the process along with a standard form describing the cells and the work the customer wishes carried out (Fig. 2). The testing manager then checks the details of the cell and customer requirements to appraise whether the work can be carried out and what must be done to carry out the work effectively. The customer may have specified non-standard test conditions and a decision may be required as to whether to reject the work or to plan appropriate modifications to the standard procedure/equipment to accommodate this request. The form that arrives with the cells includes details such

as the cathode thickness—critical in determining the thickness of the gold gas seal; the chemical composition—to allow the manager to assess possible chemical interactions with the test-rig equipment; cell flatness—to estimate probability of good gas sealing.

4.2. Mounting SOFCs in the appropriate system

Chemical compatibility—the experimental set-up at FZJ has been developed mainly for measurements on LSM/YSZ/Ni-cermet SOFCs (see Fig. 3). The cell test-rigs are constructed from alumina components to minimise chemical reactions between cells and rig. For the current collection Pt current collection meshes are used on both anode and cathode sides, however on the anode side a second fine nickel mesh is placed between

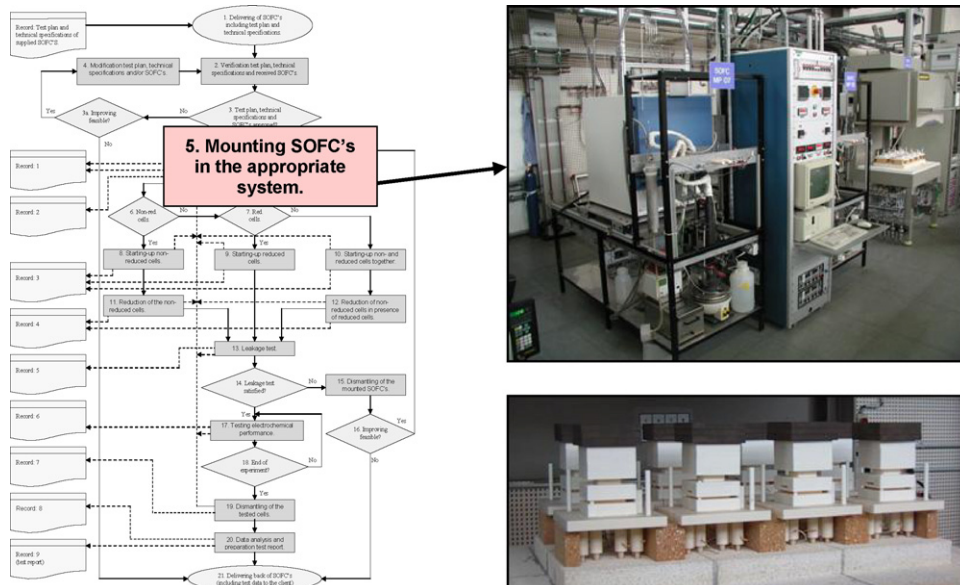


Fig. 3. Testing unit for single cell tests (cell dimensions: 5 cm × 5 cm).

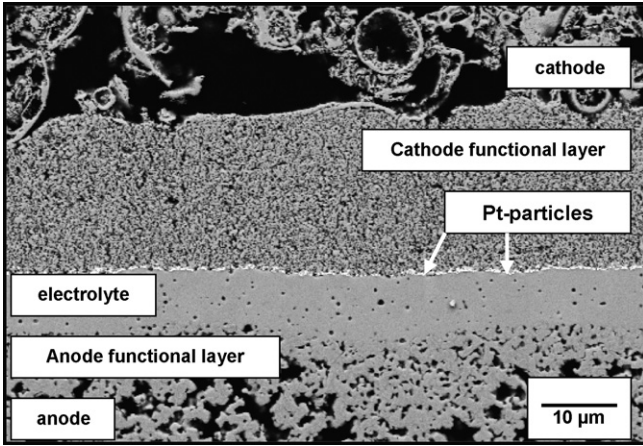


Fig. 4. Cross-section of an LSM-type single cell after 8000 h of exposure at 750 °C under a current load of 0.5 A cm⁻².

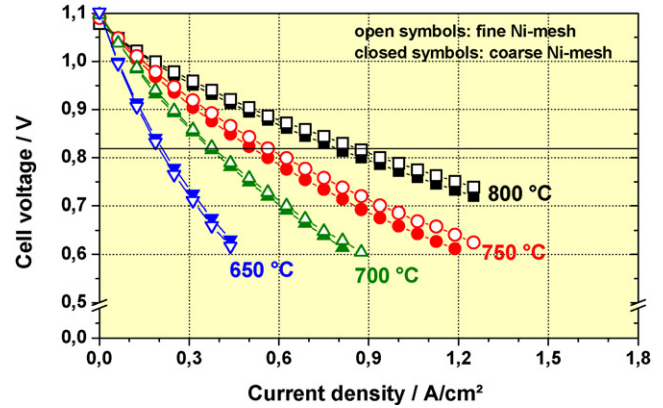


Fig. 5. Cell voltage curves for 5 cm × 5 cm anode-supported single cells with LSM cathode as function of the temperature and mesh size. Fuel gas: H₂ (3% H₂O) = 1000 ml min⁻¹, oxidant: air = 1000 ml min⁻¹.

the Pt and the Ni-cermet. It was found that Pt would slowly alloy into the nickel of the Ni-cermet without this additional mesh—this giving rise to reduced electrical contact between the cermet and Pt mesh in some cases. The additional Ni mesh is spot-welded to the Pt-mesh maintaining good electrical contact even if there is some migration of metals between both meshes.

It was also found that in very long term measurements Pt from the cathode mesh would tend to very gradually evaporate, become depleted and migrate to the electrolyte (where it was found using elemental mapping). Fig. 4 shows a micrograph of a cross-section of an anode-supported single cell with LSM cathode after 8000 h of exposure at 750 °C and 0.5 A cm⁻² with Pt deposition at the electrolyte–cathode functional layer interface. Two issues arise here, firstly the depletion possibly reducing electrical contact and secondly the electrochemical effect of Pt that has migrated to the heart of the triple phase boundary. This has not been fully investigated however clearly neither factor is good if we wish to measure the real cell performance—thus if a very long term measurement is to be made the Pt is replaced

by Au which does not appear to exhibit this problem at typical operating temperatures of ca. 800 °C.

Mesh size—contact between the cell electrodes and current collectors is always made with a fine mesh (Pt, Au or Ni as appropriate). To determine the most suitable mesh size we conducted a series of experiments, collecting a number of measurements on standard FZJ ASC cells using different anode mesh sizes. Fig. 5 illustrates the results of some such measurements using mesh sizes of 0.125 and 0.60 mm, respectively. It is seen that the finer anode mesh produces consistently better performance from the cell.

4.3. Ni-cermet anode reduction

The experience of the cell manufacture is key in determining suitable preliminary cell conditioning steps. Fig. 6 shows the Ni-cermet anode reduction procedure for FZJ-type single cells. Accepting cells from different manufacturers, it seems prudent to follow the manufacturer’s guides on initial cell conditioning and to treat measurements made during this phase as being

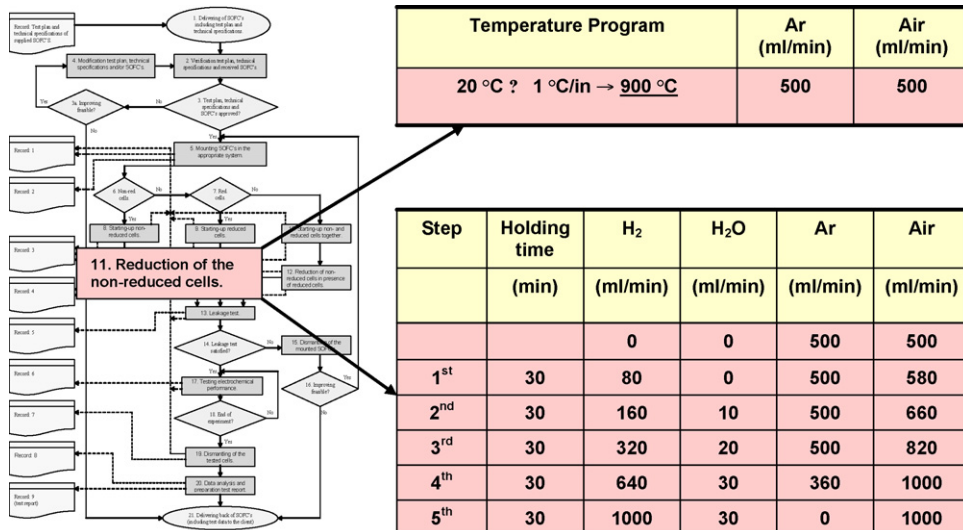


Fig. 6. Ni-cermet anode reduction procedure in single cell testing.

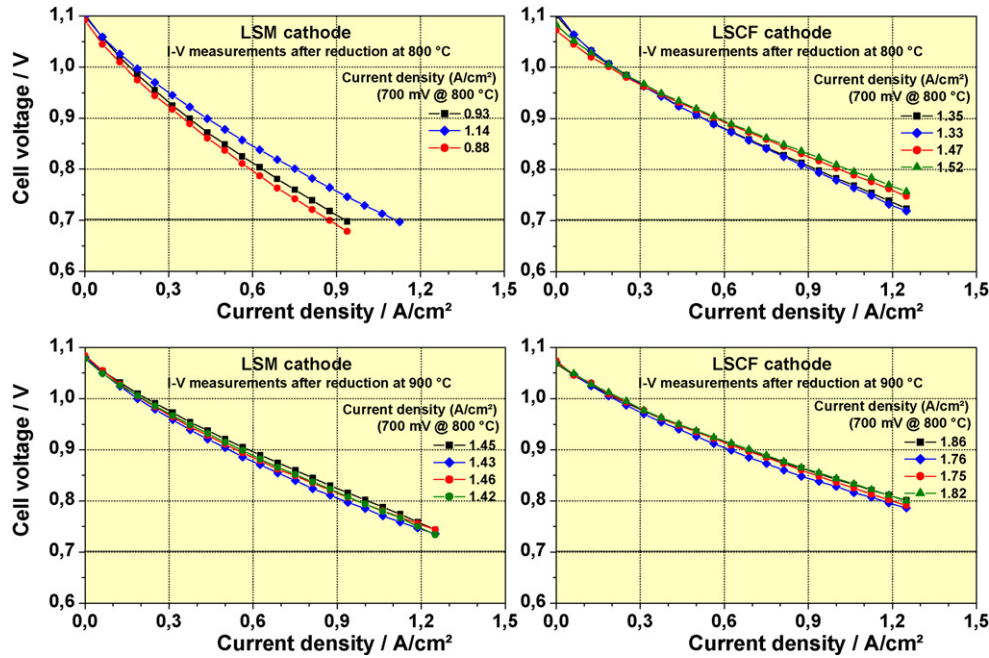
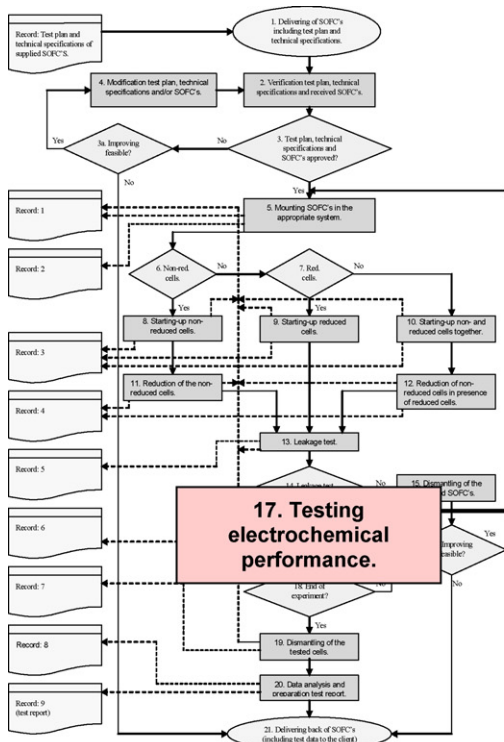


Fig. 7. Current–voltage plots for anode-supported cells with LSM- and LSCF cathode as function of temperature and reduction temperature.

non-typical and not indicative of the general performance of the cell. In the case of FZJ cells, an extensive study was performed to define the instructions for cell reduction. The influence of variations in the heating and reduction procedure on the electrochemical performance was systematically investigated [1]. Fig. 7 shows the current–voltage plots for anode-supported cells with LSM and LSCF cathode heated and reduced at 800 and at

900 °C. From this study it was concluded that either reduction at 900 °C or the application of a constant current to both type of cells (heated and reduced at 800 °C), resulted in a significant improvement in electrochemical performance. Cermets reduced at 800 °C resulted in a lower performance, a greater time to reach steady state performance, and less consistent performance (significant scatter between the individual data). Probably a slow



- Heating rate
- Gas composition and gas flow rates at the anode and cathode side during heating
- Gas composition and gas flow rates at the anode and cathode side during testing
- Cermet reduction method
- Leakage tests
- Measurement temperature
- Step size of the increase of the current density between each measurement points (I-V measurements)
- Hold-time between each measurement point (I-V measurements)
- Maximum current load or minimum cell output voltage
- Cooling/heating rate between consecutive I-V measurements

Fig. 8. Most important measurement/test parameters.

reduction at 900 °C influences the anode microstructure and stabilisation of electrochemical equilibrium in such extent that the measured electrochemical performance was maximised. Again, this may not apply to non-FZJ cells; however this example illustrates the type of pre-normative research and control that can improve your measuring process and thus the reliability and consistency of data.

4.4. Dwell-time between individual current–voltage points

Fig. 8 looks at a number of the most important factors during making the electrochemical measurement. We choose dwell-time between changing voltage/current and taking the next measurement as an example of pre-normative research/determining critical parameters. Fig. 9 shows the current–voltage plots collected at 800 °C leaving different time periods between changing the current density and measuring the voltage (current density steps 0.0625 A cm⁻¹ in all cases). From the figure it is clear that data points started to converge at around the 30 s dwell-time. Smaller time intervals resulted in

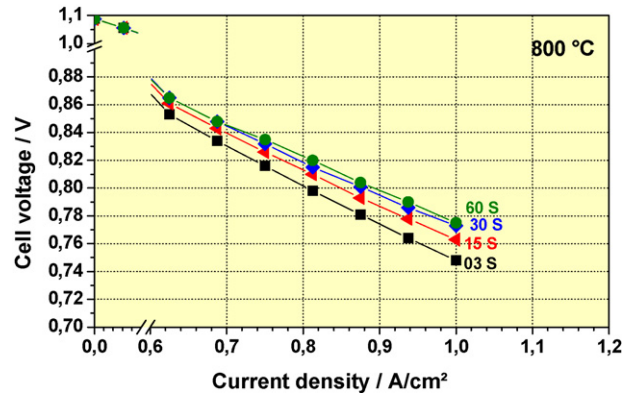


Fig. 9. Current–voltage plots as a function of the hold-time between individual points.

a measurable lower performance indicating the electrochemical equilibrium had not yet been reached. Based on this, we defined our dwell-time as 30 s. Also here, this is for FZJ cells, other cells may show faster or slower response time, however, finding out

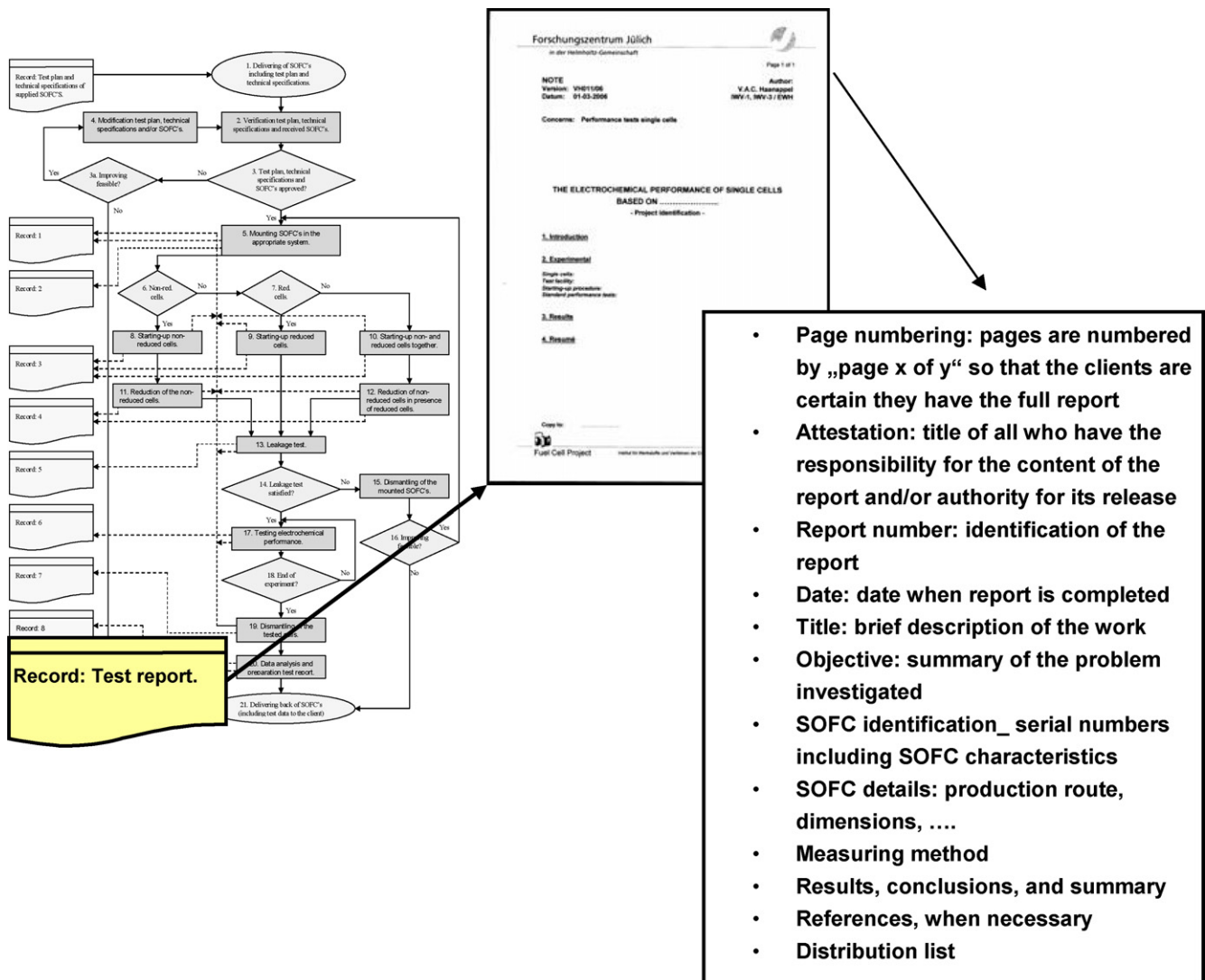


Fig. 10. Standard FZJ measurement report.

defining the parameter for each individual set-up and/or cells is the important point.

4.5. Standardised FZJ measurement reporting

The test report details all relevant information the customer has asked for, also comments from the operative carrying out the

work. In order to ensure that the customer also knows exactly what the results refer to, all of the relevant environmental and other test details are given. This includes specimen evaluation characteristics such as; findings from pre-test visual inspection, results from leakage tests, open circuit voltage under the given experimental conditions, the calculated area-specific resistance and current density at 700 mV and observations from post-test

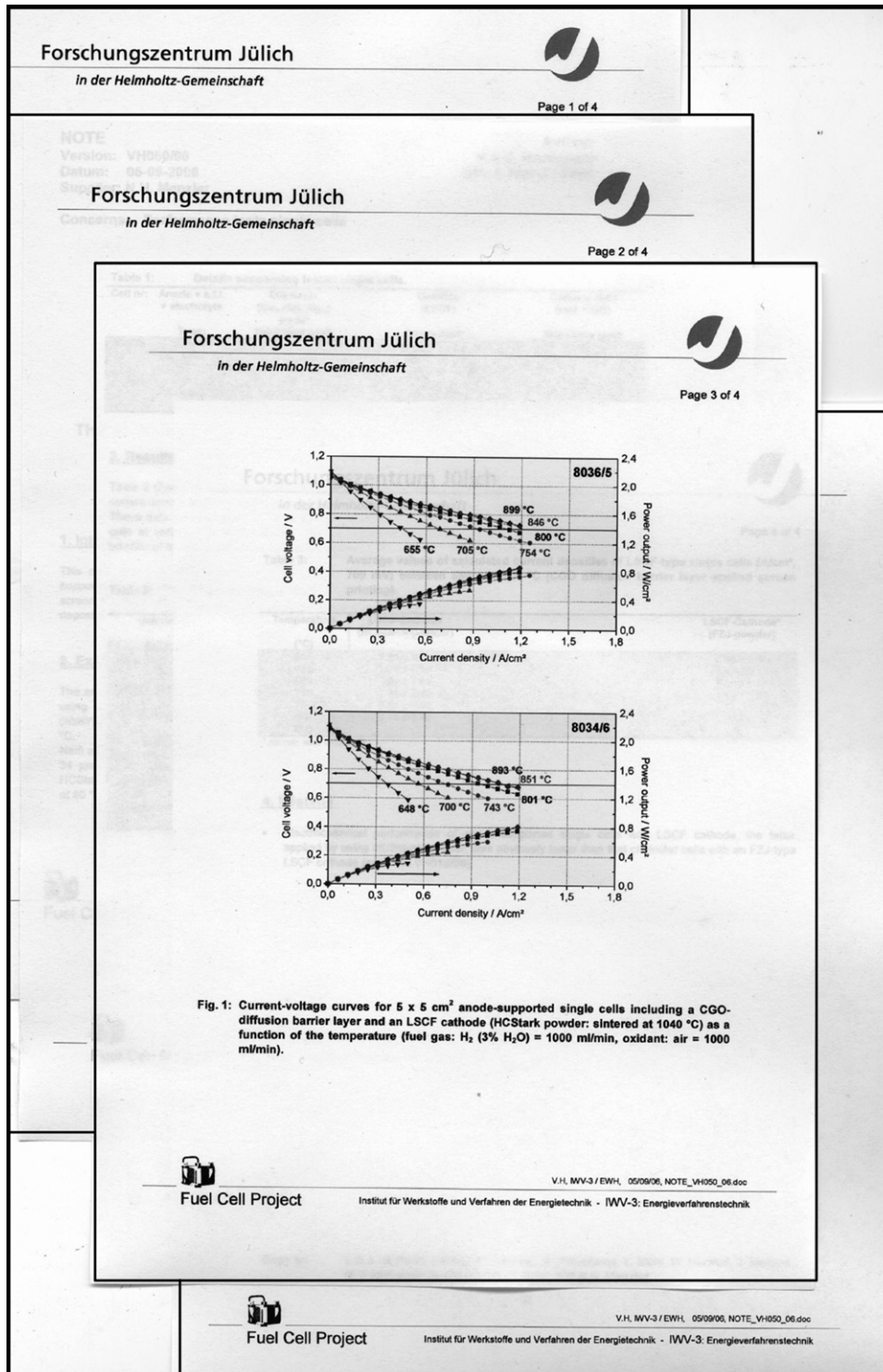


Fig. 11. Copy of a specific “example report” for tests on specific SOFCs.

visual inspection. The test report carries identification numbers that allow retrospective tracing of other details such as mass flow controller calibration, original test-data files et sim. The test operative has room to detail any relevant observations and make any comments he or she feels may be of interest for the customer. In particular, anything not conforming to the test specification is detailed and where possible explained.

Another important aspect is the uniformity in reporting, enhancing communication [2]; standardization of the report format is strongly recommended. Therefore, a format including 12 items based on the outline given by Taylor [2] is used for the FZJ test reports. A blank copy of the report format is given in Fig. 10. Evidently such standardised reporting makes comparison of cell performance using two or more such report sheets extremely easy. Each report contains all of the relevant information necessary for its interpretation—a lack of the availability of this information is often one of the greatest difficulties when trying to interpret data offered in reports or in the literature. By standardising the reporting and including all of the relevant information that difficulty will be largely eliminated—thus one can concentrate on the real science and engineering! Fig. 11 shows, as an example, a copy of a specific “example report” for tests on specific SOFCs.

5. Final remarks

Although many of the specifics in terms of the FZJ standard test parameters will not be directly relevant to other SOFC labs, the standardisation and honing of the measuring process surely is. Even for purely internal purposes such standardisation allows the lab manager to produce easily comparable and repeatable results. Much of the pre-normative research carried out in

standardising the FZJ process resulted in finding means of improving the performance of cells, so this work makes sense generally. It seems very likely that other labs that adopt such a system will find that they produce better performing cells/materials simply because they will have better optimised the measuring process. Performance optimisation is a normal part of developing any product. There are many aspects of this with respect to SOFCs. The system described above is only one of them, however, it is one that can be tackled successfully and (relatively) quickly, as opposed to the more complex questions and issues. It is the professional approach. Therefore, it is strongly urged that all SOFC labs who have not already done so to consider adopting such a system(s), they will all benefit from this, but the main beneficiary is the lab adopting the system itself. Our experience recommends this to all.

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