

Measurement Note

DEPC (MN) 049

Guide to durability testing of PEMFC electrocatalysts

This Measurement Note provides a guide to the key parameters which need to be controlled in durability testing of polymer electrolyte membrane fuel cell (PEMFC) electrocatalysts. The use of electrochemical test methods to characterise degradation of catalyst performance in single cell fuel cells is described. Comparison is made between durability testing at constant load and dynamic testing.

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Introduction

Durability of PEMFCs is one of the major barriers to commercialisation of the technology for stationary power generation and automotive applications. The most common degradation modes of PEMFC stacks are membrane failure, decay of electrocatalyst performance, corrosion of the carbon support, poisoning, flooding of reaction sites, fuel crossover and corrosion of conductive components. Degradation is most severe when the membrane electrode assembly (MEA) is highly stressed, e.g. by rapid fluctuations in potential or when non-uniform distribution of reactants, temperature or humidity occurs. While membrane failure is the major lifetime constraint, the other degradation modes cause a gradual decrease in the output voltage of the stack. The 2002 DTI Sustainable Energy Route Map for fuel cells set a performance degradation target of <1% over 1000 hours operation. In the long term, fuel cell stacks for stationary applications need to reach 40,000 h operation, while those for more demanding automotive applications will require 4000 h, without unacceptable loss of performance. The physical mechanisms of fuel cell degradation are not well understood in detail but qualitatively are a result of irreversible changes in the kinetic and/or transport properties of the cell. Useful reviews of the subject have been published by Gottesfeld and Zawodzinski [1] and Fowler et al [2].

When conducting durability tests on any system, there are generally two approaches. The first is to carry out an exposure test in conditions that are as representative of those in service as possible. The timescale of such tests should be long enough that meaningful data regarding degradation rates and mechanisms can be extrapolated, which is often not practical. The second approach is to carry out an accelerated test; here the issue is whether the methods used to accelerate the test will modify the degradation mechanisms under study. The first approach is generally preferable but such tests are time consuming

as they can last for thousands of hours. However, the development of reliable accelerated ageing tests for PEMFC catalysts has yet to occur but should follow from better understanding of degradation mechanisms.

Care should always be taken in laboratory testing to ensure that service conditions are reproduced as accurately as possible. In that context stack durability testing is clearly critical to the development of commercial systems. However, the focus of this measurement note is on assessment of *catalyst* durability using single cell testing. The use of single cell testing has a number of advantages, notably reduced complexity, tighter control of environmental variables and lower costs. While extrapolation of fuel cell behaviour from single cell data to the stack level should always be treated with caution, meaningful information about catalyst performance may be obtained in a single cell under well controlled conditions. Departures from normal operating conditions may also be simulated, e.g. cell reversal, electrode poisoning, contamination of reactant gases.

Currently there is no global consensus on standardisation of fuel cell test methods, although there are various moves afoot to remedy this. Most companies and research organisations use their own continuously evolving test methods, with relatively little knowledge transfer occurring. This means that there is no accepted basis for comparison of the performance of fuel cell stacks and components. There is a clear requirement for standardisation of such test methods. The purpose of this measurement note is to establish a preliminary framework for the evaluation of PEMFC catalyst durability using laboratory electrochemical test methods.

Test cell

For single cell testing the physical size of the MEA is important. Below around 50 cm², the active area is too small to accurately simulate the flow field patterns required in larger

stacks. Low gas flow rates at low current densities are also difficult to control. However, the use of large active areas is not straightforward on a laboratory scale due to the difficulty and cost of fabrication and the greater magnitude of the total current. Higher currents not only require larger and more expensive electronic loads to dissipate the current, but also pose problems for techniques such as impedance spectroscopy, where the bandwidth may be restricted under high load.

Some compromise is also required in the selection of membrane thickness. Relatively thick membranes should generally be used for catalyst durability tests. This results in a decrease in the level of performance but is necessary to minimise the likelihood of membrane failure during the timescale of the test. Preparation of MEAs is critical and should follow an accepted protocol that ensures reproducible performance.

Control of environmental variables

Tight control of environmental variables is essential to enable valid comparison between tests. It is important to control the following variables for both anode and cathode:

- Endplate temperature
- Humidifier temperature
- Inlet gas temperature
- Back pressure
- Gas flow rate

For single cells air cooling is generally sufficient to dissipate the heat generated at higher loads. The use of a large fan capable of generating relatively uniform air flow over the whole cell is recommended. Accurate control of heating and cooling cycles is critical to the stability of environmental conditions. In that context regular calibration of control thermocouples and accurate tuning of proportional integral derivative (PID) controllers is strongly advised.

Commercial fuel cell test stands are widely available. However these are relatively

expensive and are often over-engineered for applications such as durability testing. Hence it is sometimes more cost effective to design a bespoke testing system to meet the particular needs of a test programme. The minimum requirements for such a system are typically as follows:

- Mass flow controllers
- Gas humidifiers
- End plate heating/cooling
- Inlet gas line heaters
- Back pressure controllers
- Electronic load

These components can be controlled either manually or by software. The use of software control is usually necessary for dynamic test protocols. Commercial fuel cell test stands usually come with their own in-house software, but it is also relatively easy to control such systems using bespoke software, e.g. in Visual Basic.

Gas humidifiers are required because the proton conductivity of Nafion is dependent on water content. If dry gas is used the membrane will rapidly dehydrate, particularly at low current densities, leading to failure. Most humidifiers consist of a heated stainless steel vessel filled with deionised water, through which the inlet gas is bubbled. The temperature of the water is generally referred to as the dewpoint. Dewpoint selection is dependent on the desired relative humidity level; for a well-humidified cell the dewpoint should be within a few degrees of the cell temperature. If the dewpoint is higher than the cell temperature condensation will occur and could lead to electrode flooding. Conversely, if the dewpoint is too low dehydration of the membrane may cause the performance of the membrane to suffer. Careful heating and thermal insulation of the tubing between the humidifier and the fuel cell is required to avoid condensation. It is recommended that the dewpoint of the inlet gas is accurately calibrated using a Peltier mirror or similar probe. In-situ mapping of temperature and humidity in PEMFCs is the subject of ongoing research at NPL.

Cell conditioning

Before starting a test, the environmental conditions should be stabilised. Generally this involves allowing the cell and humidifier temperatures to reach their set values before commencing flow of fuel (hydrogen) to the anode and oxidant (air) to the cathode. Heated gas lines should be used to control the temperature of the gases at the inlets. Here the control thermocouple should be located as close as possible to the fuel cell gas inlet. Thermocouples used to measure gas temperature should be as small as possible to minimise errors due to the thermal mass of the thermocouple. If pressurisation is required, care should be taken that the differential pressure across the membrane is maintained well below the value where it will rupture (this is more critical for thinner membranes). Conditioning is then performed to hydrate the Nafion membrane and active layers of the electrodes and typically consists of operating the fuel cell at constant load for several hours (often overnight). The load should be high enough to generate adequate water at the cathode but not so high that flooding occurs. When reporting the results of fuel cell tests, details of environmental conditions and conditioning should be included.

In-situ voltammetry

A polarisation curve (a plot of potential vs current density) is the most accepted measure of performance of a fuel cell. Performance may be expressed in terms of output current density at a fixed potential (e.g. 0.6 V), maximum power output, or kinetic parameters may be calculated after correction for ohmic drops. The performance depends primarily on the activity of the cathode electrocatalyst layer, the quality of material components and the flow rate, pressure and purity of the reactant gases. The best performance is obtained when pure oxygen is fed to the cathode, but in most practical systems air is used. The nitrogen in air acts as a diluent and as a result the performance of H₂/air fuel cells suffers from both open circuit losses and mass

transport limitations relative to H₂/O₂ fuel cells. By pressurising the gas on the cathode, substantial gains in performance may be obtained. However the energy cost of compressing the gas means that there is an optimum pressure beyond which it is not economically feasible to increase the performance any further.

Measurement of polarisation curves at periodic intervals during durability testing yields information on the rate and timescale of degradation. Comparison of polarisation curves obtained with air, pure oxygen and helox (21% oxygen in helium) on the cathode may be used to shed light on degradation mechanisms. Helox gain is defined as the difference in performance between helox and air and is associated with oxygen diffusion limitations. Oxygen gain is defined as the difference in performance between oxygen and helox and reflects oxygen permeability losses. When switching between gases on the cathode, the switching valve for the gases should be located as close as possible to the test stand to minimise switching time.

When changing load during measurement of a polarisation curve, adequate time should be allowed for the system to reach steady state. For most PEMFC single cells this should be of the order of a few minutes. Ideally this involves plotting the potential in real time and establishing a criterion for attaining a steady state, e.g. < 1 mV change in potential over a defined period of time. In general, when using oxygen on the cathode the time taken to reach steady state is shorter and the noise level significantly lower than when air is used.

Unless a separate reference electrode probe is inserted into the cell, all potentials are generally measured relative to the anode. This is acceptable since pure hydrogen is typically used on the anode, but problems may arise with some gas mixtures such as reformat. It should be noted that even with pure hydrogen there will be a correction for temperature and pressure. Following sufficient purging with nitrogen, hydrogen may be supplied to the

cathode to act as a reference electrode if the anode is under investigation.

Measurement of electrochemical active surface area may be carried out by carbon monoxide (CO) stripping voltammetry. Here CO is fed to the electrode, which is held at the adsorption potential for a period of time (~ 30 min). The bulk CO is then removed by purging with nitrogen. Stripping voltammograms are then measured and correlated with the electrochemical active surface area, ensuring that complete oxidation of the adsorbed CO has occurred.

Current interrupt measurement

The ohmic losses in a fuel cell may be isolated by the current interrupt method. The principle behind this technique is that the ohmic losses vanish much faster than the Faradaic overpotentials when the current is interrupted. The fuel cell is operated at a constant current before the measurement and a voltage transient is recorded upon interruption of the current, as shown schematically in Fig. 1. The ohmic losses disappear almost immediately and the Faradaic overpotentials decay to the open circuit value over a longer timescale. It is therefore important that the data acquisition for the voltage transient is as rapid as possible in order to adequately separate the ohmic and activation losses. An oscilloscope is generally required for such measurements.

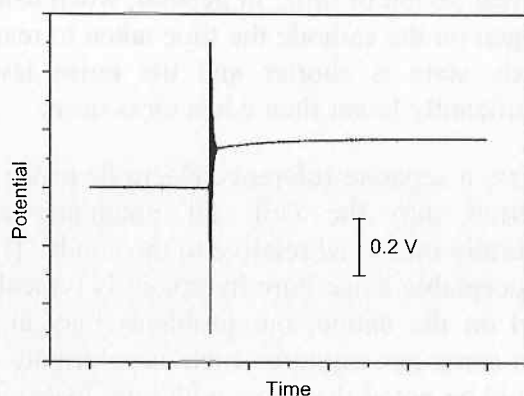


Figure 1 Typical current interrupt measurement for single cell PEMFC.

Current interrupt data are generally used to correct polarisation curves for ohmic drop, which is usually dominated by the resistance of the Nafion membrane. A Tafel plot (log of current density vs potential) may then be generated in order to determine kinetic parameters such as exchange current density and Tafel slope.

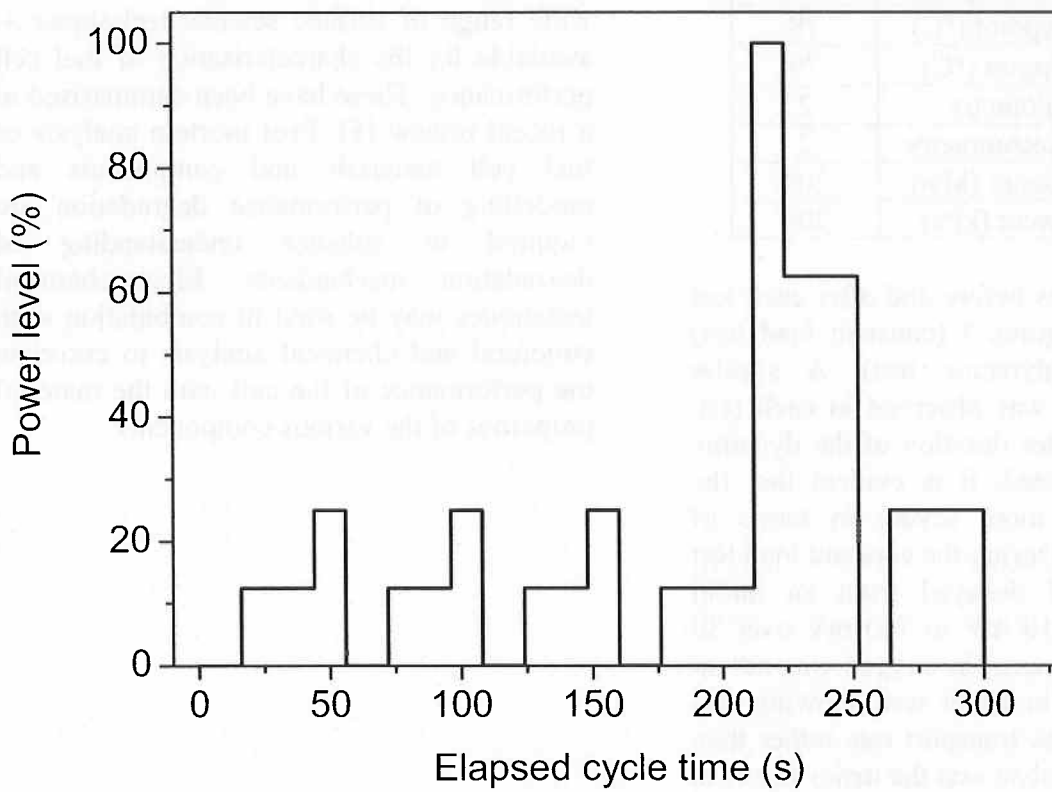
Test protocols

Much of the early work on durability testing of PEMFCs focused on long term constant load testing. It is well established that PEMFC electrodes exhibit a slow decay in performance over time (typically quoted in $\mu\text{V/h}$) due to coarsening of Pt nanoparticles, which reduces the active electrochemical area of the electrode. An important issue associated with long term testing is reliable and continuous supply of power and reactant gases. The use of Uninterruptible Power Supply (UPS) is highly recommended. Similarly, a continuous supply of gas may be achieved with the use of gas generators or manifolded gas cylinders, which avoids undesirable interruptions to tests when changing individual cylinders.

Dynamic testing is becoming increasingly common as test methods are developed which are more representative of service application. The dynamic test protocol shown in Figure 2 and detailed in Table 1 may be used to evaluate the effect of a fluctuating load on the performance of a single PEMFC. This protocol was developed by the US Fuel Cell Council to mimic the load demand in automotive applications [3]. The DTP cycle runs for 300 seconds at an average of $\sim 20\%$ power. The 100% power point is determined based on the results of an initial power calibration curve. Ideally the gas flow rates should be changed prior to each load change if the test stand is capable of this without operator intervention.

Table 1 USFCC dynamic test protocol.

Step	Duration (s)	Elapsed time (s)	Power level (%)
1	16	16	0
2	28	44	12.5
3	12	56	25
4	16	72	0
5	24	96	12.5
6	12	108	25
7	16	124	0
8	24	148	12.5
9	12	160	25
10	16	176	0
11	36	212	12.5
12	12	224	100
13	28	252	62.5
14	12	264	0
15	36	300	25
16	0	300	0

**Figure 2** USFCC dynamic test protocol.

A comparison between constant load testing and the dynamic test protocol described above was carried out at NPL. A Hydrogenics Test Systems FCATS-G50 test stand was used to control the experiments. Standard Johnson Matthey Pt/C electrodes on Nafion 115 membranes were used at both anode and cathode (catalyst loading 0.4 mg/cm^2). The test conditions are listed in Table 2. The constant load test was run for 30 days (720 hours) at a load equivalent to the average load in the dynamic test (0.135 A/cm^2). The dynamic test was run continuously for 3815 cycles (~ 13 days). Polarisation curves in both air and pure oxygen were taken periodically to monitor any changes in performance. The test conditions shown in Table 2 were maintained during measurement of the polarisation curves; where oxygen was used the stoichiometry was 10.

Table 2 Test conditions.

Cell temperature ($^{\circ}\text{C}$)	80
Cathode dewpoint ($^{\circ}\text{C}$)	79
Anode dewpoint ($^{\circ}\text{C}$)	79
Air stoichiometry	2
Hydrogen stoichiometry	2
Cathode pressure (kPa)	204
Anode pressure (kPa)	204

Polarisation curves before and after each test are plotted in Figures 3 (constant load test) and Figure 4 (dynamic test). A similar performance loss was observed in each test, although the shorter duration of the dynamic test should be noted. It is evident that the dynamic test is more severe in terms of degradation rate. During the constant load test the cell potential decayed from an initial steady value of 810 mV to 760 mV over 30 days. The performance in oxygen was not so strongly affected in either test, showing that decline in the mass transport rate rather than stability of the catalyst was the major factor in the performance loss in air.

It is generally accepted that sintering of catalyst particles is a major factor in the reduction of electrochemically active surface

area during fuel cell testing. This sintering appears to be driven by electrodisolution of platinum, the rate of which increases significantly the closer the potential at the cathode is to open circuit ($\sim 1 \text{ V}$). Potential cycling close to open circuit has been shown to have a major influence [4]. This is a factor in the more significant loss of performance in the dynamic test, where the cell is at open circuit for 25% of the time. The development of accelerated durability tests may be envisaged using potential cycling and potentiostatic tests at higher potentials.

Impedance spectroscopy is also a potentially valuable tool in the characterisation of PEMFC performance. The frequency dependence of the impedance response can be used to separate different processes within the fuel cell. These techniques are under evaluation at NPL but do not fall within the scope of this note.

In addition to electrochemical test methods, a wide range of surface science techniques is available for the characterisation of fuel cell performance. These have been summarised in a recent review [5]. Post mortem analysis of fuel cell materials and components and modelling of performance degradation are required to enhance understanding of degradation mechanisms. Electrochemical techniques may be used in combination with structural and chemical analysis to correlate the performance of the cell with the material properties of the various components.

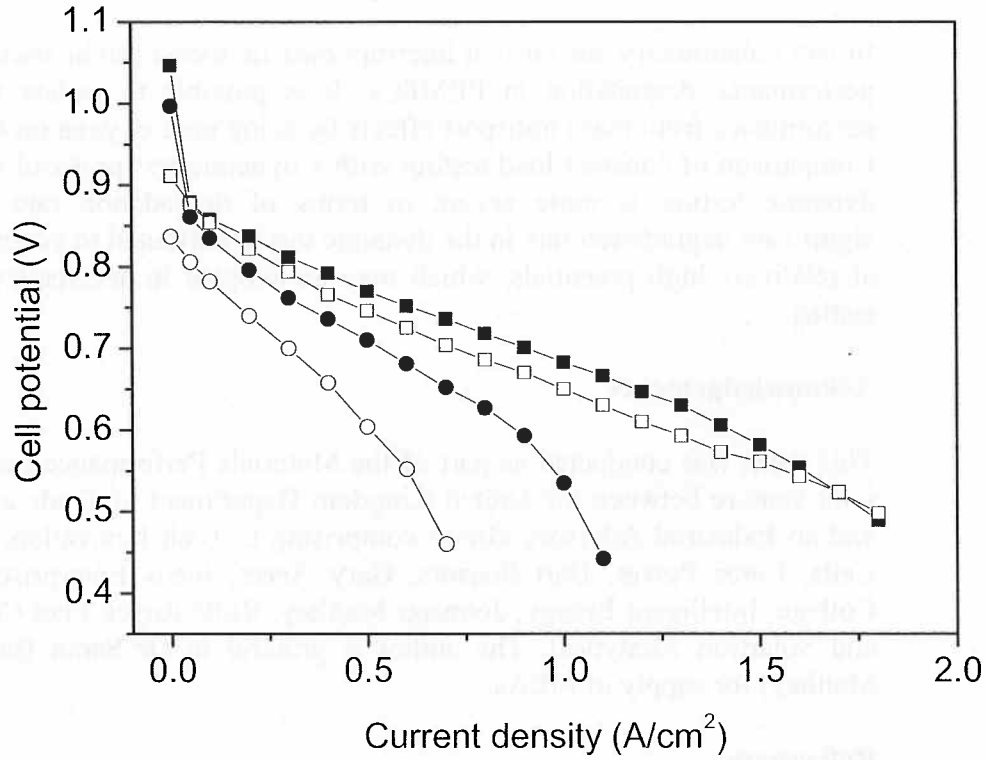


Figure 3 Polarisation curves with oxygen (squares) and air (circles) at the cathode before (full) and after (open) constant load test at 0.135 A/cm^2 for 30 days.

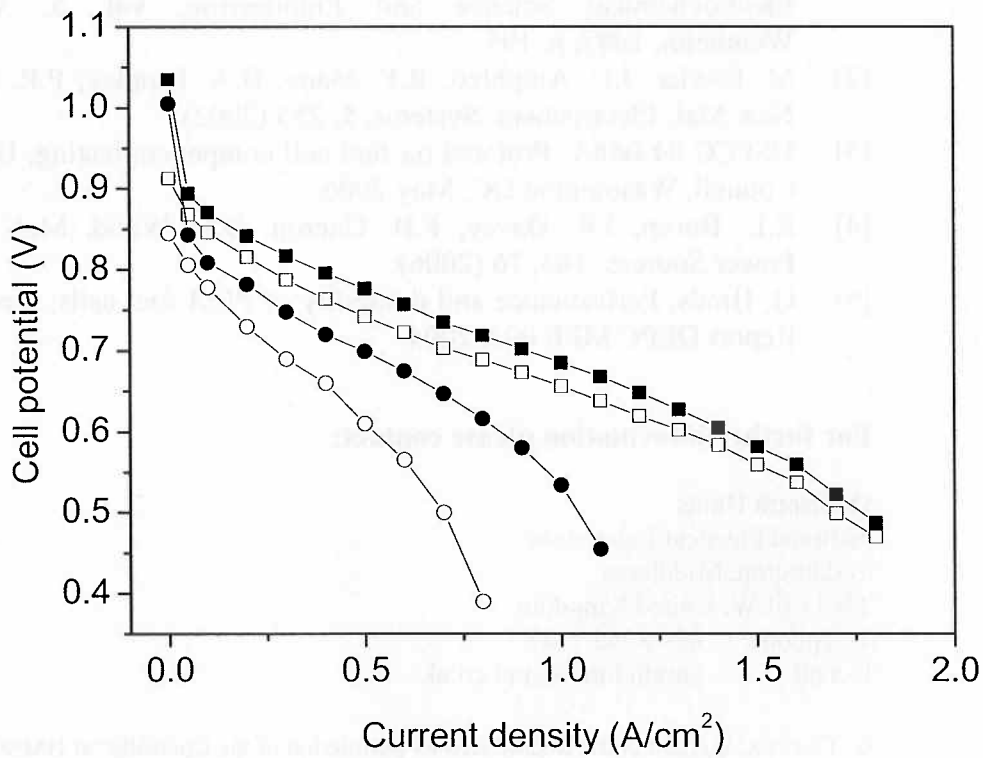


Figure 4 Polarisation curves with oxygen (squares) and air (circles) at the cathode before (full) and after (open) dynamic test (3815 cycles, 13 days).

Summary

In-situ voltammetry and current interrupt measurements can be used to monitor performance degradation in PEMFCs. It is possible to isolate the catalyst performance from mass transport effects by using pure oxygen on the cathode. Comparison of constant load testing with a dynamic test protocol showed that dynamic testing is more severe in terms of degradation rate. The more significant degradation rate in the dynamic test is attributed to potential cycling at relatively high potentials, which may be adopted in accelerated durability testing.

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