Cycling durability studies of IP-SOFC

Ghzzai Almutairi*, Kevin Kendall and Waldemar Bujalski
Centre for Hydrogen and Fuel Cell Research, School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Abstract
The function of a cycling test is the investigation of fuel cell stability and degradation behaviour under non-steady operating conditions. Cell quality becomes increasingly likely to degenerate at greater numbers of cycles. This work seeks to comprehensively test the durability of three tubes (tubes 1–3) of the integrated-planar solid oxide fuel cell (IP-SOFC) (Rolls Royce Fuel Cell Systems Ltd). The three IP-SOFC tubes were tested at a constant current of 1 A at 900°C for more than 1200 h for tubes 1 and 3, and more than 4940 h for tube 2. The fuel utilization was 13.94%, and the average voltage degradation rate measured was 1.3 and 1.5% per 1000 h for tubes 2 and 3, respectively. After 1200 h work, tube 1 failed because the air supply was cut off from the test station due to compressor overheating. Subsequently, the station closed all gas supply for safety, but the furnace continued to work at a temperature of 900°C for 16 h. The tube showed clear signs of damage leading to complete failure.

Keywords: IP-SOFC; degradation; cycling tests

Received 31 May 2011; accepted 14 July 2011

1 INTRODUCTION
The recent renaissance in solid oxide fuel cell (SOFC) research largely derives from growing interest in the design and implementation of effective, low carbon energy converting devices to replace conventional combustion technology and its reliance on fossil fuels. SOFC is currently the most promising of these new technologies, displaying lower pollution emissions, high electrical efficiency and a potential for low operating costs in the future. Increasing concern about the environment and global warming has given greater impetus to research into the use of fuel cells, where the possibility exists of achieving greater efficiency through the use of hydrogen, methanol, natural gas or higher hydrocarbons [1, 2].

A major obstacle to the implementation and widespread use of SOFC exists in the form of cycling operation which can damage the cells irreversibly. This paper will study the impact that current load cycling and thermal cycling have on the integrated-planar SOFC (IP-SOFC) made by Rolls Royce Fuel Cell Systems Ltd (RRFCS). Current load cycling consists of raising the current to maximum current density and then decreasing the current to zero, a process that is repeated several times. Cycling current accelerates the degradation of the overall cell voltage, principally through cathode deterioration [3]. Thermal cycling consists of raising and lowering the temperature through the use of elevated temperature ramps at heating and cooling stages (i.e. initiating and terminating fuel cell operation) resulting in mechanical damage to the fuel cell materials [4]. Thermal shock and stresses arise when there is a change in temperature in the constituent materials of SOFC, potentially leading to non-uniform distributions of temperature as a result of the electrochemical reaction. These can propagate defects and cracks in the material, especially if there is expansion and shrinkage which arises from the redox reaction [5–8]. Due to the number of separate components involved in the manufacture of SOFC, thermal cycling will create thermal stress from a mismatch in the coefficients of thermal expansion between different materials [9].

Commercial application of SOFC technology depends on a number of crucial design parameters, such as reliability, durability [10] and long-term stability. A lifetime of more than 40 000 h is a standard requirement for stationary applications, while auxiliary power units in transportation applications require ~20 000 h, with more frequent thermal cycling [11]. Long-term use will tend to result in degradation in the performance of a cell, primarily through chemical instability at the interface in stationary applications; and with thermomechanical instability being the main cause in the case of transportation applications [12].

This paper tests the durability of the IP-SOFC, through the use of accelerated ageing techniques including load and thermal cycles aiming to simulate weeks and years of damage over much shorter periods of testing durations. Our group has also investigated the effect of two differing reduction techniques on the long-term performance of IP-SOFC tubes.
2 EXPERIMENTAL STUDY

The IP-SOFC (tubes 1–3) utilized in this project operate in the same way as the standard SOFC, which employ natural gas or hydrogen as fuel. The design of the IP-SOFC is based on a rectangular flat porous ceramic tube, enabling a fuel supply to the anode. The tube is screen printed with the anode (Ni/YSZ-based), cathode (not specified), electrolyte (YSZ) and interconnected layers. Each tube comprises 30 cell pairs connected in series, each with a cell area of 6 cm² [13, 14], shown in Figure 1.

IP-SOFC tubes were tested inside a specially designed box located within the furnace of an Advanced Measurements Inc. (Canada) testing station (as shown in Figure 2). This testing procedure was designed to test the performance of SOFCs over a temperature range up to 1000°C. In order to do this, the device measures up to 30 voltage inputs, 32 temperatures and has an electronic load capable of 100 W of power. The test station is equipped with Integrity software, which allows the precise control of gas flows, operating temperature and humidity, in order to provide a versatile, fully automated test system.

The cell tube was fed with hydrogen via manifolds and pipes forming a closed-loop system for the fuel. Air was evenly distributed from the bottom of the cell house surrounding the cell tube, itself inside the furnace of an Advanced Measurements test station. Air passed across both outside surfaces of the cells on the cathode side. The initial stage in this experiment was to clear dust from the path of gases, which was achieved using the nitrogen flow for 300 s. The temperature of the cells was increased to 900°C at 1°C/min without fuel, air or safe gas, until the temperature of the furnace reached its set point (900°C), then the system was kept running to stabilize thermally for ~1 h. The cell tube subsequently was fed with hydrogen, preheated to 120°C, at a flow rate of 1.5 l/min and by preheated air through the cathode side at a flow rate of 5 l/min. The anode reduction step involved a decrease in nitrogen and an increase in hydrogen by 5%, keeping the total flow at 1.5 l/min. These parameters were in accordance with operating conditions stipulated by the manufacturers, reduction taking place via gradual introduction of hydrogen across a reduction profile. Tubes 1 and 3 were reduced over 30 min, while tube 2 was reduced over 60 min, as seen in Figure 3.

After reduction, the cells operated under electronic load at zero for 1 day until the open-circuit voltage (OCV) stabilized. The OCV was then measured and the first $I-V$ curve was drawn for the entire current range used, i.e. from 0 to 1.8 A. The cells were subsequently cooled to 400°C at a rate of 1°C/min, then the pure hydrogen was changed to safe gas (mixture of N₂ at 1.425 with H₂ at 0.075 l/min) to enable further cooling to 60°C. The furnace was reheated to 400°C, at which point the fuel was changed to pure hydrogen, after which the furnace temperature was increased to 900°C for conducting further tests.

Once reduced, the tubes were stabilized at OCV for 24 h. An $I-V$ curve was derived by cycling from OCV to a current of 1.8 A, then back to OCV. The tubes were then restarted and steady operation at 1.0 A was commenced. In order to clearly track the performance of the tubes, $I-V$ curves were drawn every 48 h. The process was stopped after 20 days and the performance was assessed. The IP-SOFC test was then restarted and run for 18 days, after which it was re-assessed and run for a further 18 days. This resulted in a total testing time of over 1200 h for tubes 1 and 2.

The thermal cycling test was then applied to tube 1, which was heated to 900°C at 1°C/min and allowed to cool naturally to room temperature. The temperature of tube 1 was then increased to 900°C, in increments of 5°C/min and re-cooled. This process was repeated seven times, with $I-V$ curves taken at every cycling step. This stage was followed by the application
of current load cycling on tube 3, following the same conditions and tests as used on tube 1.

3 RESULTS AND DISCUSSION

Figure 4 presents the results from the durability test, with current and thermal cycles for IP-SOFC. The top curves show the temperature $\sim$900°C, with a slight increase ($+5^\circ$C) as a result of heat generated due to the current load of the cells. The four temperature cycles from room temperature to 900°C can clearly be seen, at 50, 360, 660 and 950 h. The two curves showing smaller oscillations were the voltage and current, which were varied to measure $I$–$V$ curves every 40 h.

3.1 Effect of reduction method on tube performance

In order to ascertain the effect of reduction method on tube performance, tubes 1 and 3 were reduced over 30 min, while tube 2 was reduced over 60 min, as shown in Figure 3. Tube 2 was reduced slowly, resulting in improvement in the performance of the tube by 1.5% over 200 h. Tubes 1 and 3 were reduced more quickly, showing a steady reduction in the performance over the test duration.

3.2 Long-term durability test

The durability test was applied to three tubes of IP-SOFC with the constant current of 1 A at 900°C. This took place over a duration of more than 1200 h for tubes 1 and 3, and more than 4940 h for tube 2, with fuel utilization of 13.94%. The results are shown in Figure 5.

3.2.1 Long-term durability of tube 1

As can be seen in Figure 5, the OCV of tube 1 remained stable at 31.8 V throughout the testing phase, equivalent to 1.06 V for each single cell. This phase amounted to 1200 h, containing seven current load cycles and three thermal cycles. The voltage dropped to around 23.6 V under the applied maximum current, which was 1.8 A. A very slight decrease was recorded in the value of the voltage, which likely occurred as a result of
the impact of current load cycles on the performance of the cell during the first 500 h. After this point, the air supply was cut off from the station due to compressor overheating, resulting in the station closing gas supplies for safety, after which the furnace continued to work at a temperature of 900°C for 16 h. Tube 1 did not appear to have been adversely affected by this situation, showing no obvious cracking or damage of the cell through visual inspection. However, the working and cooling of the cell without gas for long periods of time may have resulted in the expansion of the nickel to nickel oxide, in which case restarting the tube in a gas-rich environment may have caused accelerated reduction due to a defect in the composition of the tube material [15].

A clear deterioration in the performance of the tube began to emerge; the total decline was of \(~2\) V after 1200 h of work at maximum. In general, an 8.4% degradation in the performance of tube 1 could be seen. The I–V curve and power curve for all current load cycles are shown in Figure 6, demonstrating that there was a gradual decline in the performance of the cell over time and a growth in the number of current load cycles due to increased ohmic resistance during operating. The maximum power of tube 1 was 42 W, which was reached at a current density of \(~0.3\) A/cm\(^2\) then started to decline as a result of the reasons mentioned earlier.

### 3.2.2 The thermal cycling test

The thermal cycling test was applied in order to clarify the effects of thermal fluctuations on tube performance. Tube 1 was ramped to its operating temperature of 900°C in increments of 5°C per minute, then allowed to cool to room temperature.

![OCV and voltage at 1.8 A versus time.](image)

![I–V and power curves for tube 1.](image)
temperature through a process of natural cooling. This process was repeated five times, as can be seen in Figure 7. It is also clear that OCV was steady at 32 V, whereas the voltage dropped at the maximum current. This caused the experiment to fail as a result of the voltage limit of the test station, which was 18 V. The thermal cycling test was sufficient to damage tube 1, however, because the cell was operated under harsh conditions, specifically a 16 h run without gas.

Figure 8 shows the large cracking in the surface of tube 1. This damage was observed through visual inspection after tube 1 was removed from the furnace and checked.

3.2.3 Long-term durability test of tubes 2 and 3
The durability test of tubes 2 and 3 was conducted under a constant current (0.17 A/cm²) at 900°C for more than 1200 and 4940 h, respectively, during which time the OCV remained steady (Figure 5). There was a slight decline in the voltage under design point load defined as 1.8 A for tubes 2 and 3. This degradation was due to many reasons, for example, the temperature gradient has resulted in degradation during a run, with varying expansion coefficients between components, especially in anode materials [16]. Second, it was due to increasing ohmic resistance, which is likely to occur because of the operation of the cell over a long period can be seen to affect the stability of materials, especially interconnected material, which led to the degradation of cell performance. A comparison between the two pictures, with particular attention to the red circle area of special interconnect materials, shows clear damage to the interconnect material where some interconnected components were destroyed as shown in Figure 9. The average voltage degradation rate was calculated as 1.5% per 1000 h for both tubes 2 and 3.

4 CONCLUSIONS AND FURTHER WORK
Durability testing of the RRFCS IP-SOFC tubes has shown that degradation of the performance occurs under steady operation and as a result of cycling temperature.
This degradation was affected by the reduction protocol; tube 2 was reduced over a long time and slower reduction steps. This led to an altered performance of tube 2.

Tubes 2 and 3 ran steadily and gave a voltage degradation (1.5% per 1000 h of operation), which was the same for both when operated at constant current for a long period (more than 1200 and 4940 h, respectively). Durability test of the tubes has shown to accelerate the deterioration of tube performance due to increasing ohmic resistance and damage to the interconnected materials which must also be taken into account.

The effect of temperature cycling was found to cause particularly high levels of mechanical damage to tube materials when restarting or cooling.

For this to be conclusively proven, significant further work must be undertaken in order to ascertain detailed explanations of the mechanisms involved. This work would require large number, carefully planned and executed experimental runs followed by detailed, in-depth analysis on changes in microstructure of the various layers and components of the IP-SOFC systems. This work is ongoing at present.

REFERENCES


