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Short communication

Cycling of three solid oxide fuel cell types

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Abstract

One of the key problems of SOFCs is their slow start-up and cycling performance which is due to the thermal shock problems of zirconia electrolyte and its associated electrode and interconnect materials. Typical start-up times range from 2 to 6 h. Faster cycles can cause degradation in performance and in material integrity. The purpose of this paper is to study the transient performance of SOFCs under various (e.g. thermal and/or current load) cycling conditions, typifying start-up and shut-down as well as variable working conditions of the systems, in order to understand the degradation mechanisms. Three types of SOFC have been compared; the planar stack with metal interconnects represented by the Forschungszentrum Jülich (FZJ) configuration; the Rolls Royce Fuel Cell Systems Ltd. (RRFCS) integrated planar tube; and the Adelan pure tube. The objective was to cycle in temperature from ambient to the operating condition several times to check if degradation was occurring. To obtain thermally shock resistant systems, cell dimensions had to be reduced to the millimeter scale.

Keywords: Cycling SOFC; Thermal cycles; Planar; FZJ; Integrated planar; RRFCS; Tubular; Adelan

1. Introduction

Cycling of solid oxide fuel cells (SOFCs) is a major issue because degradation can increase rapidly with the number of temperature cycles and especially with redox cycles where the nickel anode is repeatedly oxidised and reduced. These phenomena are strongly dependent on the cell and stack architecture and so it is important to find design criteria for minimizing cycling degradation effects in different geometries. This study compares three types of SOFC design: planar, integrated planar (also sometimes referred to as plane tubular) and pure tubular in order to illustrate differences in cycling performance. The damaging effect of cycling on SOFCs has been described before to some extent but requires much further elucidation [1–7].

The main objective was to set up three SOFC geometries in thermal (and/or current load) cycling tests so that comparisons could be drawn between them. The performance of each geometry could then be measured over a number of cycles and compared to a theory based on the temperature gradients in the zirconia elements which could cause fracture or delamination according to a critical size criterion. Thus, the main factor dictating cycling failure was shown to be the dimension of the thermally stressed ceramic cell.

The work reported here was largely carried out in the real-SOFC project, a European Integrated Project aimed at solving the persisting generic problems of ageing with planar solid oxide fuel cells in a concerted action of the European fuel cell industry and research institutions. This includes gaining full understanding of degradation processes, then finding solutions to these problems to reduce ageing effects.

2. Experimental

A two-cell planar SOFC stack containing a metal interconnect plate was donated by FZJ (Fig. 1(a)) [8–11]. The two anode supported cells are placed inside metal frames. The metal frames, interconnect and end plates are sealed with a glass-ceramic. A mechanical load of 50 kg provides pressure for sealing. Hydrogen or purge gas was fed to the fuel side and air to the oxidant inlet at 2.88 L min^{-1} (3% humidity) and 6.84 L min^{-1}, respectively. The assembly was heated to 800 °C at 2 °C min^{-1} and also cooled at a similar rate as described in the test protocol below.

Single integrated planar tube arrays of cells were contributed by RRFCS Ltd. [12,13]. Each tube had 10 cells on each side and

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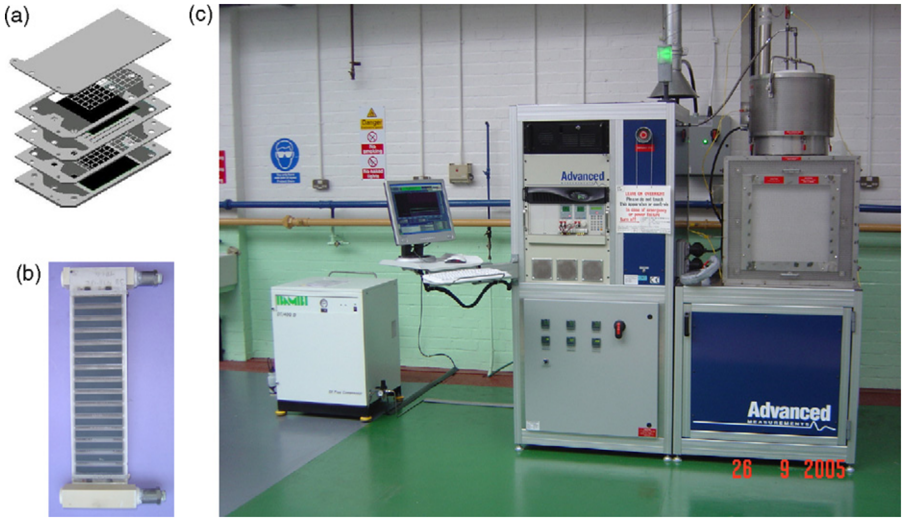

Fig. 1. (a) FZJ planar two cells stack; (b) RRFCS integrated planar tube (15 dual-cells version); (c) Advanced Measurement Inc. test station.

comprised a support structure onto which the anode, electrolyte, cathode, interconnect and sealing layers had been printed by colloidal methods (Fig. 1(b)). The tube was fed with fuel on the inside by attaching manifolds and pipes to each end. Air was flowed across the outside of the tube by feeding air into a box that surrounded the tube, to imitate the flow across a tube stack. The box was located in the furnace of an Advanced Measurement Inc. test station shown in Fig. 1(c). The temperature of the furnace was ramped up at 1 °C min^{-1} to 900 °C and preheated air and fuel were then supplied to the tube to carry out the cycling tests. Air flow was 5 L min^{-1} and fuel was 1.5 L min^{-1} (3% humidity) in a typical run.

Each test was carried out according to the specific protocol defined by the Real-SOFC project. Reduction for the RRFCS plane tube was achieved by increasing the hydrogen (containing about 3% of water vapour) flow to the anodes while gradually dropping the nitrogen flow to zero (the Jülich stack was reduced at source and provided as such for our tests). After reduction was attained, the open circuit voltage of the cells was measured. Then current was drawn from the cells to perform current loading cycle. 0.1 A was drawn for 40 s, then another 0.1 A was drawn and the process repeated until the maximum current of 2.7 A was achieved. This current was held for 5 min and then the current was lowered in 0.1 A steps until open circuit. After recording the baseline *I*–*V* curve at this temperature the tube was subjected to pre-planned thermal cycles consisting of ramping the temperature at 2 °C min^{-1} to 950 °C (the maximum value used) and then going down to the next temperature level in the same 50 °C steps till reaching the minimum of 800 °C used in the test. At each temperature the *I*–*V* curves were recorded.

A similar procedure was applied to the Jülich stack. However, due to this stack's different design, the nominal test temperature was set at 800 °C and the current steps applied were much larger comparing to the RRFCS tube case described above (i.e. 4 A per step) and because of the equipment limitations at the time, the maximum attainable value was restricted to 16 A. For both systems, after dwelling at the operating temperature for a certain time, the furnace was then cooled down to about 300 °C using controlled cooling rates of 1–2 °C min^{-1} still using hydrogen (which was than replaced with a "safe gas" i.e. mixture of nitrogen and about 5% of hydrogen for further cooling to room temperature), and another heating cycle then commenced. The change in tube/stack performance after a number of current load and/or thermal cycles was observed.

Both the above systems were susceptible to thermal shock damage and so were restricted to low heating/cooling rates of 1–2 °C min^{-1}. However, the Adelan tubular cell is known to withstand temperature ramps of 4000 °C min^{-1} (conservative estimate on the basis of the system reaching the operating temperature of about 800 °C in less than 10 s) and so this was tested in the rapid heating system of Fig. 2. Butane was fed through a valve and a venturi to draw in some air which heated a catalyst mesh before entering the tubular cell to produce heat and power. The electrical output was observed to drive a fan and could be measured by attaching a voltmeter and ammeter to the cell. The tubular cells were also tested on pure hydrogen fuel (using 20 mL min^{-1} flow rate) at up to 200 °C min^{-1} temper-

Fig. 2. Adelan tubular SOFC and hand held demonstration device that powers a fan.

Fig. 3. Temperature cycling test system for Adelan small tubular cells.

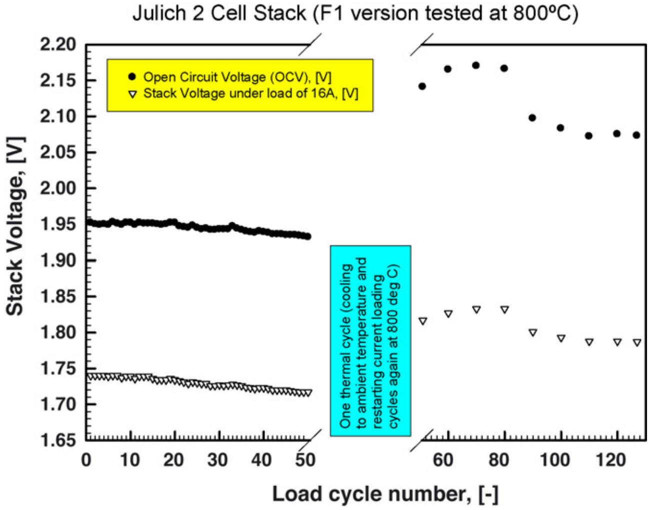

Fig. 4. Results for 1 temperature cycle and 130 load cycles of the FZJ short stack at 1 °C min^{-1}.

ature ramp rate. The rig used for these latter tests is shown in Fig. 3 and representative test results carried out at 800 °C are reported below.

3. Results

The results for electrical load and one thermal cycle of the FZJ SOFCs are shown in Fig. 4. The temperature was around 810 °C and varied with changes of the current density of the cells, rising at high and falling at low values, compared with the set point of 800 °C. For the first 20 current load cycles the voltage remained steady at both open circuit and under 16 A load, but thereafter steadily declined by 1% over 30 cycles. After the temperature cycle, it was surprising to find that the open circuit voltage then rose from 1.93 to 2.15 V and fluctuated significantly over 70 more current load cycles. The stack resistance also rose by estimated 8% after the thermal cycle (see Fig. 4). The results cannot be fully explained at present but it is possible that suspected small variations in humidity of the fuel could be held responsible for some of the unexpected changes. More thermal cycles will be carried out to check this result when new stacks become available for future work.

RRFCS 10 cells tube gave the combined thermal/current load cycling results shown in Fig. 5. Slight leaks were observed across the cells (assessed on the basis of temperature variation measured when the fuel supply system was purposefully slightly pressurised in order to check this possibility; please note that only 8 out of the total of 16 thermocouples readings available in the systems are shown in Fig. 5), indicating the presence of microcracks in the electrolyte. The intended nominal temperature for the run was set at 900 °C but the recorded temperature was around 915 °C. Up to 35 combined current/thermal cycles, the cells did not degrade substantially except for a slight increase in resistance (Fig. 5), but after that there was evidence of an interconnect delamination (from *post-mortem* analysis)

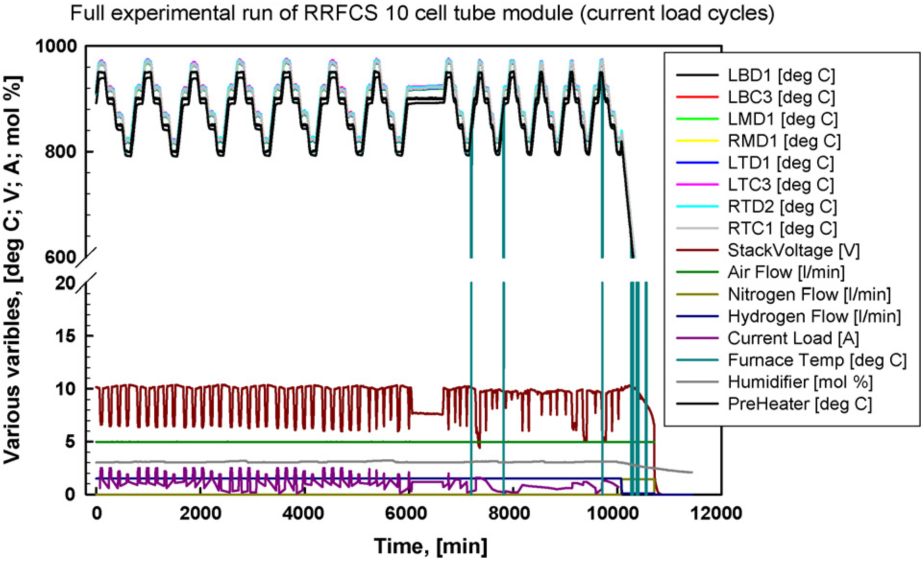

Fig. 5. Results for over 50 current load cycles of RRFCS tube performed at temperature range from 950 to 800 °C in 50 °C intervals.

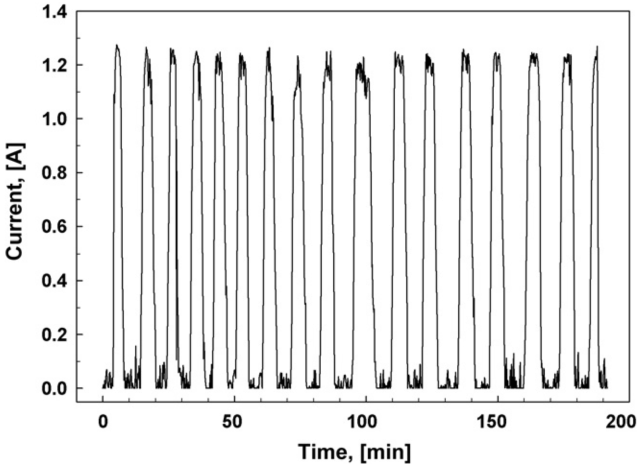

Fig. 6. Adelan cell performance tested at 800 °C for 17 thermal cycles.

which caused erratic behaviour and complete failure after 50 cycles.

The Adelan cells ramped up to operating temperature in less than 10 s and also cooled down rapidly once the butane was switched off. This meant that many hundreds of cycles could be performed in a reasonable time, in contrast to the FZJ and RRFCS short stack and tube, respectively, which required about 1 day per cycle. The other benefit of rapid cooling was the resistance to redox deterioration of the nickel cermet anodes. The anodes were falling in temperature below 300 °C in a few seconds so that oxidation of the nickel did not occur. Larger cells which take hours to cool in air become completely reoxidised after each cycle and rapidly crumble owing to the expansion of the nickel to nickel oxide. In the worst cases, only one cycle of redox is sufficient to crack the anode. Fig. 6 shows the steady performance of the tubular cells undergoing 150 °C min^{-1} temperature cycles in hydrogen to 800 °C (see Fig. 3 showing the experimental rig used).

4. Discussion

It is evident from the results above that SOFC cycling performance can be improved by several orders of magnitude through a reduction in cell dimensions from large planar SOFCs 100 mm × 100 mm to small tubular cells 2 mm in diameter. In a previous paper [4], it was argued that this is caused by a size effect stemming from fracture mechanics. Failure is stimulated by a temperature gradient which produces tensile stresses causing cracking. The temperature gradient is proportional to the ramping rate to a first approximation. Propagation of the crack depends on the strain energy stored in the stressed volume and hence depends on the size of the specimen; large plates store more energy and hence drive the crack more readily. Consequently, there is a critical size of cell above which the cells crack at a given ramping rate.

This argument needs to be tested by heating large SOFC plates under controlled conditions, then measuring failure as a function of plate size. By varying ramping rate and plate size, the critical size required for rapid start-up and cycling should be determined.

5. Conclusions

Three types of SOFC have been tested in thermal cycling experiments.

Large planar and integrated planar tube SOFCs were restricted to low ramping rates of up to 2 °C/min under controlled atmospheres and showed slight changes in cell resistance after small numbers of cycles. However, there are some reports in the open literature [11] clearly showing very little overall degradation of short Jülich stacks after at least 30 full thermal cycles. It should be pointed out that the results and the conclusions, however, would very much depend on the specific test conditions and particularly on the maximum current density applied in those test.

Small tubular SOFCs could be ramped at 4000 °C min^{-1} and showed little deterioration in performance over 50 cycles, even though the anode oxidation was not controlled.

The main conclusion is that deterioration under cycling conditions is size dependent. At a given ramping rate, there is a critical cell size below which the cells will not be damaged, depending on the temperature gradients set up during the ramping test. Therefore, small cells are recommended where cycling is an important parameter. However, it should be also noted that direct comparison of geometries used in this studies is bound to be biased towards small, tubular geometry due to the fact that the actual time of test and the associated thermally activated degradation experienced by the other two systems used was considerably longer comparing with the former. This, on the other hand, should re-emphasise the potential advantages offered by the tubular over the various planar designs that may prove beneficial or indeed essential for some applications.

Acknowledgements

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References

[1] W. Bujalski, J. Paragreen, G. Reade, S. Pyke, K. Kendall, J. Power Sources 157 (2006) 745–749.
[2] K. Kendall, M. Prica, in: U. Bossel (Ed.), 1st European SOFC Forum, Luzern, 1994, pp. 163–170.
[3] K. Kendall, W. Price, in: U. Bossel (Ed.), 1st European SOFCs Forum, Luzern, 1994, pp. 757–766.
[4] K. Kendall, G. Sales, Second International Conference on 'Ceramics in Energy Applications', Institute of Energy, London, 1994, pp. 55–63.
[5] M. Prica, T. Alston, K. Kendall, in: U. Stimming, S.C. Singhal, H. Tagawa, W. Lehnert (Eds.), Proceedings of the Fifth International Symposium on Solid Oxide Fuel Cells (Sofc-V) vol. 97(40), Pennington, NJ, 1997, pp. 619–625.
[6] K. Kendall, C.M. Finnerty, G.A. Tompsett, P. Windibank, N. Coe, Electrochemistry 68 (2000) 403–406.
[7] S.C. Singhal, K. Kendall, in: S.C. Singhal, K. Kendall (Eds.), High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications, Elsevier Ltd., Oxford, 2003, pp. 1–22 (Chapter 1).
[8] L.G.J. de Haart, I.C. Vinke, A. Janke, H. Ringel, F. Tietz, in: H. Yokokawa, S.C. Singhal (Eds.), Electrochemical Society Proceedings 2001-16, Solid Oxide Fuel Cells VII, Pennington, NJ, 2001.
[9] R. Steinberger-Wilckens, L.G.J. de Haart, I.C. Vinke, L. Blum, A. Cramer, J. Remmel, G. Blaß, F. Tietz, W.J. Quadakkers, in: S.C. Singhal, M. Dokiya

(Eds.), Proceedings of the International Symposium, Solid Oxide Fuel Cells VIII (SOFC VIII) 2003-07, The Electrochemical Society, Inc., Pennington, NJ, 2003, pp. 98–104.

[10] R. Steinberger-Wilckens, I.C. Vinke, L. Blum, J. Remmel, F. Tietz, W.J. Quadakkers, in: M. Mogensen (Ed.), 6th European Fuel Cell Forum 2004.11, Oberrohrdorf, Switzerland, 2004, pp. 11–19.

[11] L. Blum, H.-P. Buchkremer, S.M. Gross, L.G.J. de Haart, W.J. Quadakkers, R. Steinberger-Wilckens, R.W. Steinbrech, F. Tietz, in: S.C. Singhal, J. Mizusaki (Eds.), Proceedings 9th International Symposium on Solid Oxide Fuel Cells (SOFC-IX), vol. 1, The Electrochemical Society, Pennington, NJ, 2005, pp. 39–47.

[12] F.J. Gardner, M.J. Day, N.P. Brandon, M.N. Pashley, M. Cassidy, SOFC technology development at Rolls–Royce, J. Power Sources 86 (2000) 122–129.

[13] A. Spangler, G. Agnew, 9th Grove Fuel Cell Symposium, London, UK, 4–6 October, 2005.