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Journal of Power Sources 157 (2006) 745–749

JOURNAL OF POWER SOURCES
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Short communication

Cycling studies of solid oxide fuel cells

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Received 14 October 2005; received in revised form 16 January 2006; accepted 23 January 2006
Available online 13 March 2006

Abstract

The purpose of this work was to study the transient performance of solid oxide fuel cells (SOFCs) under several cycling conditions, in order to understand the degradation mechanisms. Initially, the Rolls Royce Fuel Cell IP-SOFC (Integrated Planar SOFC) single tube was investigated. The objective was to cycle up to 100 times to check if degradation was occurring and to assess its extent. In this paper the results of loading cycles at nominally constant operating temperature are reported. Work on two other kinds of cycles, i.e. thermal and redox, for this type of tube has commenced and the results will be reported in the follow-up paper.

Keywords: Cycling; SOFC; Electrical load cycles

1. Introduction

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 [1–3]. Typical start-up times range from 2 to 15 h. Faster cycles can cause degradation in performance and in material integrity. The SOFC advantages over the other fuel cell technologies (such as those based on alkaline, polymer and molten-carbonate chemistries) and further developments in its components and design in order to make it successful in the near future, have been clearly outlined in Stevenson et al. [4]. The work reported here was carried out in the Real-SOFC Project, a European Integrated Project aimed at solving the persisting generic problems of ageing with Planar SOFC in a concerted action of the European fuel cell industry and research institutions. This includes gaining better understanding of degradation processes, finding solutions to reduce ageing and producing improved materials that then will be tested in stacks. In this process further consideration will be given to the design of cost effective materials, low cost components and optimised manufacturing process. The objectives of this study were to carry out between 50 and 100 cycles of operation in order to detect degradation pathways that could be explained and then subsequently used, in the future, for verification of existing simulation models for such systems [5,6] or new ones that are also to be developed as a part of this work programme. Material behaviour and fluid flow characteristics of the system are inherently coupled with the unit specific geometry which, in turn, defines heat and mass transfer properties, i.e. temperature and concentration gradients in the tube or bundle/stack. The damaging effects of cycling on SOFCs has been described before to some extent but requires much further elucidation [7–11]. However, one should not underestimate the practical difficulties in collecting reliable and reproducible data sets from test rigs as well as potential pitfalls in attempts to achieve proper evaluation of the experimental results. This task is even more difficult for comparison of data collected from different sources or in attempts of translating data from a single cell into stack geometries. These issues have been outlined for SOFC technology by Primdahl et al. [12] and the ways of minimising the undesirable effects of possible misinterpretation of the experimental results have been proposed.

2. Experimental

Single tube arrays of cells were contributed by Rolls Royce Fuel Cell [13,14]. A tube had 15 cells on each side and comprised a support structure onto which the anode, electrolyte, cathode, interconnect and sealing layers had been printed by colloidal

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doi:10.1016/j.jpowsour.2006.01.060

Fig. 1. Rolls Royce Fuels Cell tube.

Fig. 2. Advanced Measurements Inc. test station.

methods (Fig. 1). 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 which surrounded the tube, to imitate the flow across a tube stack. The box was located in the furnace of an Advanced Measurements (AMI Inc., Calgary, Canada) test station shown in Fig. 2. Operation of the station was fully automated and controlled using National Instrument Based Integrity (v. 3.5) software developed by the unit provider and assured high degree of reproducibility of the attempted experimental runs. The temperatures of the preheater and furnace were ramped up at 1 °C min^{-1} to 900 °C, with no fuel, air or safe gas flowing through the system till the set temperatures were reached and the whole system stabilised for about 4 h. Preheated air (close to the operating temperature) and fuel (supplied at about 120 °C in order to avoid possible water condensation in fuel supply line) were then supplied to the test unit to carry out the cycling tests. Air flow was 5 l min^{-1} and fuel was 1.5 l min^{-1} in a typical run thus adhering to the manufacturer's prescribed operating conditions for this type of tube.

Each test was carried out according to the specific protocol defined by Rolls Royce and the Real-SOFC Project. Reduction was achieved by increasing the hydrogen flow to the anodes while gradually dropping the nitrogen flow allowing 2 min for each step and controlling all the time (as closely as possible) the fuel humidity level at 3%. After reduction was attained, the open circuit voltage of the cells was maintained and monitored allowing 10 min stabilisation period for the system. Then current of 0.1 A was drawn for 40 s from the cells followed by another 0.1 A current increase in the same manner and the process was repeated until the maximum current of 2.7 A was achieved. This loading cycle constituted the first *I*–*V* curve for the system. The final current load was held for 1 h and then it was lowered in 0.1 A steps until open circuit which was then maintained for 30 min, i.e. before another load cycle would commence. Fifty cycles of current loading were performed under steady furnace

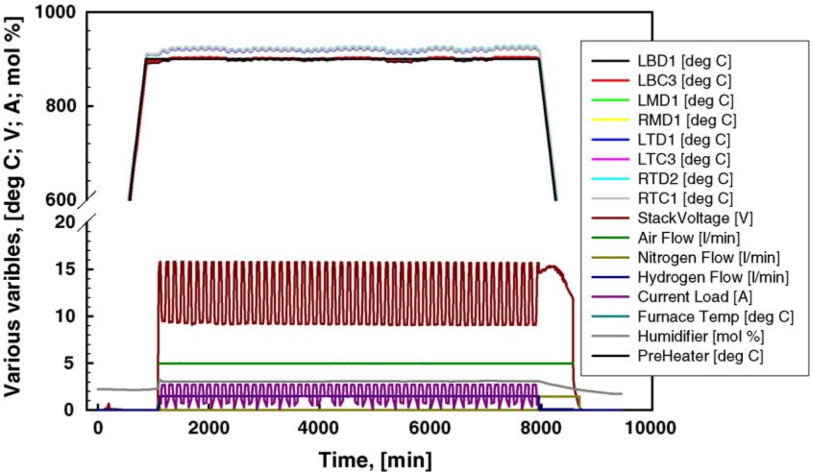

Fig. 3. Result for 50 current load cycles.

conditions and the rig was then cooled at 1 °C min^{-1} down to 300 °C. In order to avoid possibility of oxidizing the anode, this stage was carefully managed by using "safe gas", i.e. mixture of 5% hydrogen with 95% nitrogen and 0% humidity at flow rate of 1.5 l min^{-1} on the fuel side and maintaining air flow at 5 l min^{-1} throughout the cooling period. From then on, the flows were shut down to zero and the system was allowed to cool naturally to ambient temperature.

Similar experimental procedures were adopted in follow-up experiment aiming at achieving 100 load cycles using the same tube. No fuel or air flows were used at the stage of raising the system temperature to the nominal operating value of 900 °C and no anode reduction stage was required either.

3. Results

The results of the first run of 50 cycles are shown in Fig. 3.

The upper curve showing large oscillations was the voltage output from the 15 cells. At open circuit this was almost 16 V, dropping to just above 9 V at full current. It was evident that the voltage curve remained fairly steady over the 50 cycles. The lower oscillating curve was the current output which also remained steady through the cycling run for both OCV and full current load conditions.

The top curves show the readings from the thermocouples spaced around the cell tube in the box and furnace. The temperature ramp and stabilisation at 900 °C are shown. It was noticed that during the stabilisation period of 4 h the temperatures of air preheater and in the furnace remained virtually constant and fully controlled at 900 °C. However, the line above this level is the temperature of the cells themselves which were monitored by eight thermocouples positioned around the fuel cell tube in the box all gave very similar readings of being slightly hotter than the furnace at about 910 °C. In additional experiments designed to identify the cause for the observed temperature differences it was discovered that the original positioning of the thermocouple used for controlling the furnace temperature gave this degree of offset comparing with the real temperature measured around the tube of the fuel cell in the box (data not shown). This temperature tended to increase further by 3–5 °C when hydrogen was introduced in a form of fuel (or "safe" gas) and this can be attributed to possible pinholes and hydrogen seepage through the fuel cell tube wall structure, burning in the surrounding air, thus increasing the temperature around the tube via convection of the heat in remarkably uniform manner judging by similar temperature response by all the mentioned above eight thermocouples. Another possible explanation for this effect is increased radiation from the "glowing" cells due to hydrogen flow and leading to temperature increase in the confined box space which is then picked up by the thermocouples placed there. These effects need to be investigated further.

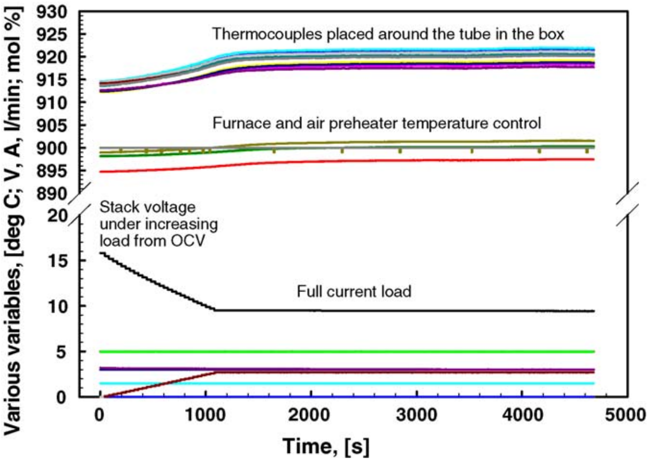

Fig. 4. Typical temperatures and stack voltage profiles under increasing load.

Further temperature increase of 2–4 °C was always noted as a result of ohmic losses occurring under current load conditions. Thus the real operating temperature of the tube was around 920 °C and varied with the current flowing through the cells, i.e. rising at high current and falling at low current (see Figs. 4 and 5, respectively, for representative examples of the behaviour).

When the furnace was cooled and the tube inspected, it was evident that there were slight discolorations in some regions of the cells. No sources of major leaks were detected but slight changes in structure and performance of the cells was found, as illustrated in Fig. 6 which demonstrates a slight increase in overall resistance after 50 cycles.

The tube proved to be very robust and has shown very small overall depreciation in performance after full 50 load cycles. Therefore, further cycling was attempted in order to test the limits of resilience of the cell design. It was initially planned to carry out up to 50 more load cycles on this tube (see description in Section 2) but due to intermittent software problem during the run "only" 43 were executed and 31 of those were fully successful ones, i.e. the increase to the total load of 2.7 A could be applied without exceeding the imposed safety limit of 9 V for the tube voltage (equivalent of 0.6 V for a single cell). This limit was reached at the 32nd load cycle in the repeated run. The last successful run is also shown in Fig. 6. In this figure

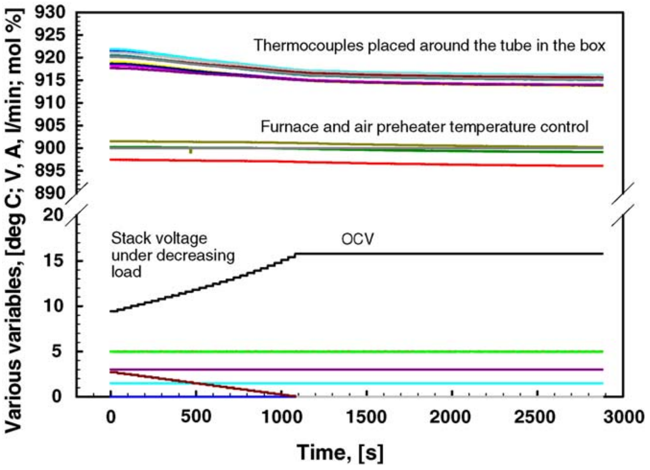

Fig. 5. Typical temperatures and stack voltage profiles under decreasing load.

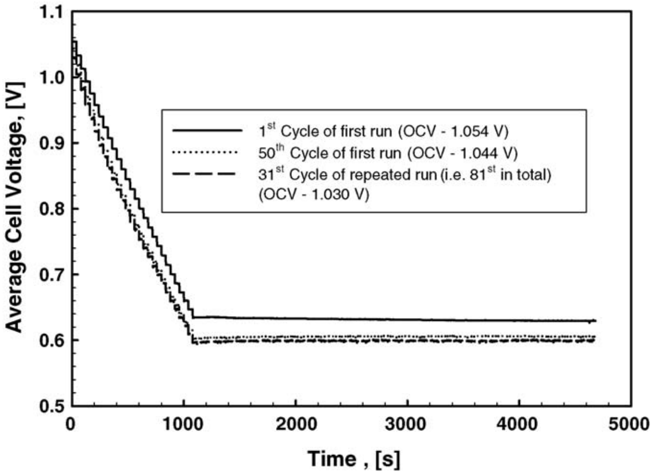

Fig. 6. Change in average cell voltage after 50 and 81 current load cycles.

it can be clearly seen that there was only small decrease in the tube performance between the 50th and the 81st load cycle at full load applied. Also the OCV's shown in the figure for those runs reveal relatively small depreciation of the tube performance in that respect. This value for the very last, 93rd cycle, was measured as 1.022 V again showing very little decrease in the system performance.

4. Conclusions and further work

The experimental rig enabled fully programmable/automated operation of the test thus providing a regime for reproducible testing conditions in cycling tests. The conditions for the test itself were in accordance with the stack providers requirements/limits and were specified for the programme of "standardisation" agreed by the Real-SOFC participants. Temperature (16 thermocouples monitoring within the test box as well as air preheater and furnace temperature) and electronic load control allowed detailed monitoring of cyclic behaviour. First run consisted of 50 full cycles (up and down, i.e. from open circuit to design value of electronic load of 2.7 A). The nominal temperature for the cycling work was set at 900 °C but the actual one experienced by the tube in the box was about 920 °C for reasons already explained in Section 3.

The module has shown some increase in resistance at the end of the cycling process. Initial visual inspection of the module in the test box identified a possible defect in one of the cells, however, when the module was removed from the box after completion of additional cycling tests leading to 93 cycles in total no physical damage to its structure was identified.

Overall, the tube performed very well. Even after reaching the limit for the allowed minimum tube voltage of 9 V under full load (i.e. 2.7 A) the cut-off point was reached at the next load level of 2.6 A for all the remaining test cycles.

It is also worth noting that, in additional complementary work (data not shown) with this generation of tube, we have tried much faster starting times for the unit by ramping up the temperature at up to 10 °C min^{-1} (i.e. 10 times faster compared with heating rates used in the present work) and no mechanical damage (due to generated thermal stresses) occurred. This offers some possibility of significantly decreasing the start-up times for these systems.

The next tests will include temperature cycling of varying severity. Further tests will involve redox cycling which is known to cause damage to the nickel cermet anode integrity relatively easily.

It is also planned to test the next generation of the Rolls Royce tubes and stacks as well as next generation F type stacks from Forschungszentrum Jülich GmbH (Germany) [15].

Acknowledgements

This work was supported by the European Commission. Cooperation great help from Advanced Measurements (AMI Inc., Calgary, Canada) in designing our test facilities and manufacturing the test rig as well as guiding expertise in deployment of the test software (National Instruments Based Integrity v. 3.5) is also acknowledged.

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