

ANALYSIS OF LIFE CYCLE AND DURABILITY DEGRADATION OF MICRO-TUBULAR SOLID OXIDE FUEL CELL UNDER ELECTROCHEMICAL PERFORMANCE

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Abstract: The main part of this paper is to understand the mechanisms of cyclic degradation for micro-tubular SOFC, have experimentally set up to measure the degradation process in presence of electrochemical performance and finally by confirming the theories by TGA and scanning electron microscopy (SEM). The main problem occurs in the life cycle and durability of solid oxide fuel cells (SOFCs) under cyclic operation, where cracking can occur, during start-up and shutdown. During operating, sintering occur during operation to govern degradation mechanism, causing irreversible deformation and decreasing the power output, no micro-cracking taking place Secondly redox cycling, that performed by changing the fuel flow between 20mL/min, anode of fuel to allow for oxidation of the Ni anode to occur, there is adverse effect on the electrochemical performance of micro-tubes, separate micro-cracking and de-laminations were observed. Lastly, thermal and electrical shock test were performed.

Keywords: Micro-tubular; Solid oxide fuel cells; Iso-thermal cycling; Redox cycling; Thermal and Electrical Shock; Dilatometer; Thermo-gravimetric analysis (TGA);

I. INTRODUCTION

Fuel cells are electrochemical energy conversion devices which can continuously convert the chemical energy of a fuel and an oxidant into electrical energy and heat, without involving direct combustion as an intermediate step. Since fuel cells convert chemical energy directly into electricity, they offer many advantages over traditional power sources such as improved efficiency, greater fuel diversity, high scalability, and have a lower impact on the environment. Theoretically, fuel cells can produce electricity for as long as fuel (hydrogen, ethanol, methanol, or gaseous fossil fuels like natural gas) and oxidant (oxygen or air) are fed, but its degradation on service limits the practical life of the devices. 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. The fuel cell has received a lot of attention as a promising energy converting device. A fuel cell in general is a battery-like energy generator that produces electricity through an electrochemical process without involving combustion. As fuel cells convert the

chemical energy directly into electricity, they have the potential to operate at higher efficiency than an internal combustion engine, extracting more electricity from the same amount of fuel. They are also more environmental friendly because they produce less emission than combustion system. Furthermore, fuel cells are able to continuously generate electricity as long as the fuel and the oxidant are provided to the cell. The fuel of fuel cells is stored externally and therefore, it will not become internally depleted. Fuel cells are mechanically ideal because these devices have no moving parts, making them quiet and reliable sources of power. In the UK, a climate change framework was proposed to help cut carbon emissions by 60% (based on 1990 estimates) by 2050. Short term emissions targets between 16% - 32% have been set by 2020. As part of sustainable energy development, the UK government have considered several clean energy generation technologies; Wind power [1], Tidal wave, Solar power [2], Geothermal, Biomass/Bio fuels [3]. More recently, many companies and governmental agencies have supported research of fuel cell technology for the possible uses in stationary power plants, homes, vehicles, watercraft and portable electronic devices including cell phones. A fuel cell can be defined simply as an electrochemical device that converts the chemical energy of a fuel with an oxidant into electricity by a chemical reaction. Every fuel cell has two electrodes, one positive and one negative, called, respectively, the cathode and anode. The reactions that produce electricity take place at the electrodes. Every fuel cell also has an electrolyte, which carries electrically charged particles from one electrode to the other, and a catalyst, which speeds the reactions at the electrodes. Hydrogen is the basic fuel, but fuel cells also require oxygen.

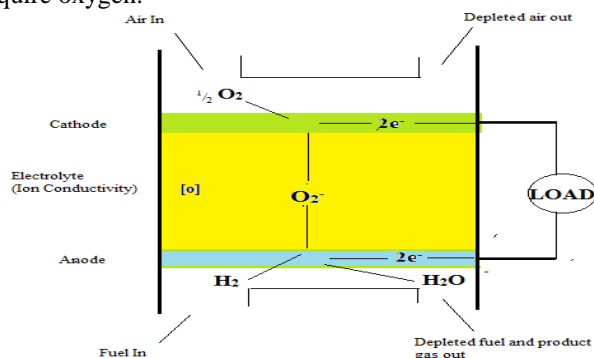


Figure 1.1 General operating principle of solid oxide fuel cell
The overall reactions in these electrodes are as follows.

Cathode half reaction: $O_2 + 4e^- \rightarrow 2O^{2-}$

Anode half reaction: $4H_2(g) + 2O^{2-}(g) \leftrightarrow 4H_2O(g) + 4e^-$

Since the fuel and oxidant combine directly to produce water and electricity, without an intermediate conversion step to mechanical energy as in heat engines, fuel cells can attain higher working efficiencies than heat engines.

Characteristics of different types of fuel cells

Fuel cells can be classified according to their operation temperatures, cell operating fuels and/or design features; nevertheless the most common classification is based on the type of electrolyte as different kinds of ions can be conducted by different types of electrolytes.

Table 1.1 summarises the characteristics of different types of fuel cells.

	PEMFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Ion-exchange Membrane	Mobilized or immobilized KOH	Immobilized liquid H ₃ PO ₄	Immobilized liquid carbonate	Ceramic
Operating temperatures (°C)	80	120-250	200	650	500-1000
Charge carrier	H ⁺	OH ⁻	H ⁺	CO ₃ ²⁻	O ²⁻
Prime cell components	Carbon-based	Carbon-based	Graphite-based	Stainless steel-based	Ceramic
Catalyst (Electrodes)	Platinum	Platinum	Platinum	Nickel	Oxide perovskite Or metal ceramic Composites
Product water management	Evaporative	Evaporative	Evaporative	Gaseous product	Gaseous product

Table 1.1 Characteristics of different types of fuel cells.

There are several designs of SOFCs and currently the micro-tubular SOFC with sub-millimeter inner diameters is being extensively investigated [21].

II. OBJECTIVE OF RESEARCH WORK

The main objective of this thesis is the degradation pathways in SOFC with a view to understanding the mechanisms, then finding methods/conditions of minimizing their effect on the electro-chemical performance of micro-tubular SOFC. The

work focuses on degradation modes i.e. micro-cracking, delamination, sintering and re-oxidation which occur in the electrode, electrolyte and interfaces.

- **Iso-Thermal Operation:** The objective is to understand SOFCs, having factors that cause degradation at steady state; high temperature causes extreme mobility in the Ni structure, leading to Ni agglomeration. Electrochemical measurements to characterize decreases in performance and dilatometry are used to confirm.
- **Redox Cycling:** The objective is to understand the redox behaviour of micro-tubular SOFCs by setting-up experiments to measure the physico-chemical changes and degradation that occur when Ni oxidizes to NiO. To investigate re-oxidation causing expansion in the anode, leading to micro-cracking, delamination and electrolyte channel cracking. will lead to increase in the resistance of the anode, thus causing performance drop. SEM is used to investigate degradation in the micro-structure while thermo-gravimetric analysis is used to measure the rate of oxidation and reduction.
- **Thermal and Electrical Shock Analysis:** The objective is to understand the thermal and electrical shock behaviours of micro-tubular SOFCs in order to understand stress accumulation, failure/micro-cracking and also to establish the critical temperature difference for failure (ΔT_c) and minimum energy required for micro-cracking to occur. A three-point-bend test to measure the decrease in fracture strength of the tubes after thermal and electrical shock testing. Shock is one of the main culprits of stress induction in the PEN of SOFC, is important to investigate its effects.

III. RELATED WORK

David Waldbillig et.al.(36); In this paper shows the redox kinetics of Ni/YSZ anodes by thermo-gravimetry (TGA) and thermo-mechanical analysis (TMA) between 450°C and 800°C. They found that there was no bulk volume change in coarse Ni/YSZ sample after re-oxidation or reduction because the expansions and contractions were accommodated in the pores of the structure. Fine samples however, did not change in volume after reduction but expanded between 0.9% -2.5% after re-oxidation, with some cracks propagating in the structure. The cracking was reduced considerably by lowering the Ni content in the anode. They also found that reduction of NiO/YSZ followed first order kinetics with activation energy of 78kJ/mol, while re-oxidation of Ni/YSZ followed parabolic kinetics at temperatures lower than 700°C; activation energy of 87kJ/mol was calculated. From this, it can be inferred that redox effects are dependent on the grain size of the anode particles. Coarse particles are less susceptible to redox deformation because they possess large pores which can accommodate such expansions. Fine particles on the other hand are more prone to redox effects because of their tiny pores which cannot accommodate expansion and thus translates to bulk volume displacement.

Bujalski et.al.(37); In this paper shows the transient behaviour of the integrated planar (IP) Rolls Royce Fuel Cells Systems (RRFCS) tube under load cycling. The project was part of the REAL-SOFC project, an EU project aimed at solving the generic problem of ageing with planar SOFC. 93 electrical load cycles were performed with marginal degradation in performance; however a slight increase in electrode resistance was observed which was attributed to electrode ageing.

Chih Kuang-Lin et.al.(38); In this paper Finite element analysis was used to characterize the thermal stresses at various stages. The parameters used to develop the model included the PEN assembly, interconnects, nickel mesh and gas tight glass-ceramic seals. The effects of temperature gradients, CTE and viscous behaviour in the glass-ceramic sealants were also characterized. It was found that the thermal expansion of the metal interconnect/frame had a greater influence on the thermal stress distribution of the cells than the glass-ceramic sealing.

Hashimoto, H. Nishino et.al.(39); This paper showing the study a new temperature monitoring method for solid oxide fuel cells (SOFCs) was proposed, and the demonstration using micro-tubular SOFCs has done. The fabricated micro-tubular SOFCs were operated under the two different conditions, and polarization during the power generation was measured. The cell resistance as a function temperature was also measured. Based on the temperature dependence of cell resistance and the measured ohmic drop during the power generation, the cell temperature was estimated. The estimated cell temperature clearly depended on operation condition and increased with increasing of the current density. The estimated cell temperature was also in nearly proportion to the temperature which was measured by a thermocouple, and it was conformed that this temperature monitoring method by electrochemical technique certainly functioned.

C.M. Dikwal, W. Bujalski et.al.(40); This paper shows during solid oxide fuel cell operation, re-oxidation of the nickel anode can occur due to a disruption in fuel supply, emergency system shutdown or leakages in the fuel delivery channel. Once oxidation occurs, the anode has to be reduced again in order to be ready for use. Cyclic reduction and oxidation (redox) is known to cause severe expansion and contraction in the anode causing significant changes to the integrity of the material interfaces leading to performance degradation and eventual failure. The redox tolerance of Ni/YSZ anode supported solid oxide fuel cell is investigated at 800 °C in partial oxidation and reduction conditions and a total of 52 redox cycles is performed. Partial oxidation is performed by shutting-off the hydrogen supply for 3 min to allow atmospheric air to oxidize the anode, while partial reduction proceeded by a flow of 20 ml min⁻¹ hydrogen for 5 min. The electrochemical performance of the cell decreased slightly after each redox cycle. An average degradation rate of 0.3% per cycle was calculated. The micro-structural changes that occurred after redox cycling is characterized by both dilatometry and scanning electron microscopy (SEM).

The theory that damage was caused by defect growth in the anode was confirmed.

Zhang et.al.(41). In this paper, developing an analytical model to predict the residual stresses in YSZ based SOFCs. They found that the major principal stresses in the anode are tensile while they are compressive in the electrolyte and cathode. It was also reported that the anode failure probability decreases with an increase in anode thickness and a decrease in electrolyte thickness. It was concluded that to keep the anode failure probability below 1×10^{-6} , the anode thickness should be greater than 700µm with an electrolyte thickness of 10µm and cathode of 20µm.

IV. MATERIAL AND METHODS

Manufacture and Preparation of Micro-Tube

The micro-tubular solid oxide fuel cells supporting anode which are 55mm long and diameter is 2.3mm which are co-extruded and supplied by Adaptive Materials Inc USA (see Figure 3). The co-sintering of sintered with YSZ at the electrolyte and NiO/YSZ at the anode.



Figure 3 Image of the NiO/YSZ tube supplied by Adaptive Materials Inc

The electrolyte measured between 15 - 20µm, where the anode was 200µm thick see in Figure 4.

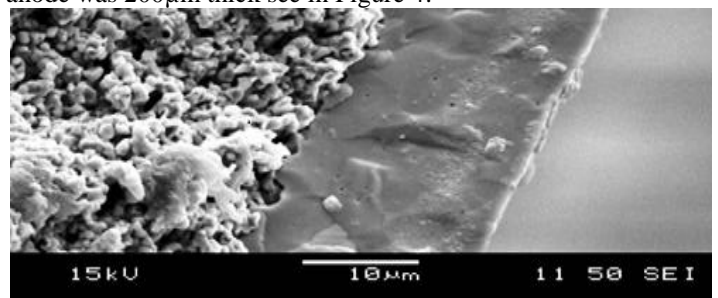


Figure 4 The micro-structure of the tube

Cathode

At cathode adequate reaction site was necessary to provided electrochemical reduction of oxygen to its ions. The optimized cathode layer was produced through, porosity, tortuosity, and pore sizes. However, two distinct cathode layers were produced as below

- (a) 50%/50% – LSM/YSZ layer
- (b) 100% – LSM layer.

According to the compositions, Weighing the powders of the two mixtures and mixed in separate bottles which are specified in table 3.1 and mixing solvent was used as acetone.

Ingredient	50%/50% – LSM/YSZ layer	100% – LSM layer
LSM (SSC 0.5/0.5)	6.5g	-
LSM (Merck 0.82/0.18)	-	20g
TOSCH (TZ8Y)	6.5g	-
Acetone	16ml	14ml
KD2	0.25g	0.4g
Terpinol (24hrs later)	-	2g
Mill beads	13 beads	16 beads
Glycerol Triolate Triolein	0.2g	-

Table2. The compositions for cathode formulation

Formulation of cathode is followed by painting of cathode ink on the raw tubes which are about 30mm of the 50%/50% – LSM/YSZ and allowed to dry under atmospheric conditions for 24 hours. The painted cathode layer was centered so as to provide the allowance of fuel injector where the fuel cells are suspended (see Figure 5).

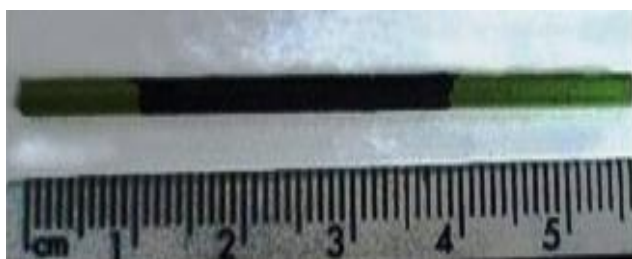


Figure 5. Showing a micro-tube with cathode applied.

In Figure 6 shows a programmed temperature profile of painted cells that were sintered in a Carbiolite™ furnace. There are four distinct stages in which the sintering process are seen by the dotted red line (temperature profile) are shown as.

- The first stage consisted of a slow ramp up at 1.5°C/min to 500°C during which the binder and solvent were burnt out.
- The second phase is the rapid ramp up at 12.5°C/min to the sintering temperature.
- The third phase was the sintering at 1150°C for 2 hours in order to adhere the two cathode layers.
- The final phase was the cooling at 20°C/min to room temperature, it should be noted that the micro-tubes are very robust which is why they can be cooled at this high rate, other fuel cell geometries are not able to withstand such rapid cooling.

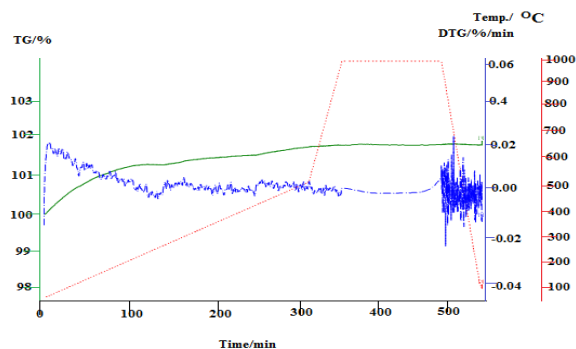


Figure 6 Sintering profile for the micro-tubes.

The characterization of SEM of sintered layer showing a cathode thickness of approximately 50µm, see under Figure 7.

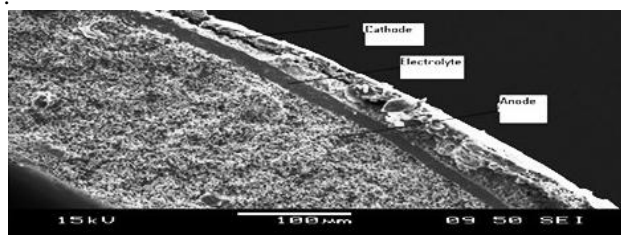


Figure 7 SEM of a micro-tube microstructure Cathode Interconnection

The electrical conductivity of the cathode was improved by using Silver ink (Alfa Aesar); Four rings were painted along with the circumference of the micro-tube with one long stripe connecting the four bands, see figure.8. The thin silver rings were made so as possible to minimize by masking the cathode area with silver paint. The cathode area was covered approximately 40% by the silver paint. Subsequently, silver wire (Good fellow 0.25mm diameter, 99.9% pure) was wound firmly around the silver bands for current collection. The length of the silver wire used was 50 cm.

Anode

Initially, Nickel mesh (Dexmet microgrid) was inserted into the micro-tube and held in place by Ni pin. This proved to be ineffective as the Ni mesh became loose at high temperature, leading to increased contact resistance. For the bulk of this study however, the anode current collection was achieved by carefully polishing off the thin electrolyte, with the aid of a fine abrasive files to expose the Ni surface. Approximately 7mm was polished off one of the ends of the micro-tube and care was taken not to exert too much force as the cells were quite brittle. Subsequently the Ni surface was wiped off with clean cloth to remove the abrasive sediments and silver ink was painted so as to enhance conductivity between the silver wire and the Ni anode, see Figure 8.

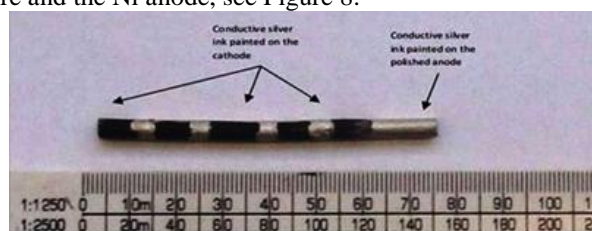


Figure 8: A micro-tube with silver ink painted on the anode and cathode for Interconnection.

Anode Reduction

Reduction of the cells proceeded after the sintering of the cathode layers. This was performed by passing 20ml of nitrogen through the cells and ramping up the furnace at 200°C/min to 750°C. Once at the reduction temperature (750°C), hydrogen was passed and the cell was held for 45 minutes until complete reduction was achieved.

Anode Current Collection Technique

Two methods of collecting current from the anode were explored; the first ('Ni mesh-and-pin' technique) was based on a Ni mesh structure which is inserted into the anode side to be in intimate contact and provide interconnection.

Internal Nickel 'Mesh-and-Pin' Interconnection Technique

A standard Ni 'mesh-and-pin' structure was used as the anode side interconnect. The Ni mesh (DexMet Micro-grid) was cut to 1.2 times the length of the micro-tube and rolled to the tube's diameter (2.3mm). The length of the Ni mesh allowed for a small percentage of the mesh to extend on the exterior of one of the tube ends for interconnection.

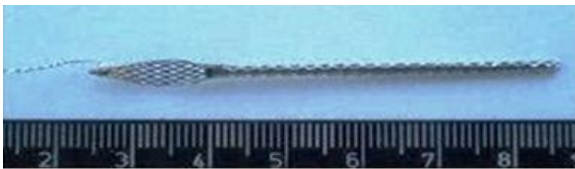


Figure 9 Showing the Ni mesh structure



Figure 10. Showing a micro-tube with the Ni mesh inserted

Figure 11. shows the electro-chemical performance of a micro-tube with this current collection technique. An initial high power density is observed at 0.65W, this high polarization curve is likely to be due to the several advantages of the Ni mesh in providing are as:

- (a) extra surface area for fuel oxidation
- (b) adequate mixing by serving as a fuel baffle
- (c) acting as a heat sink.

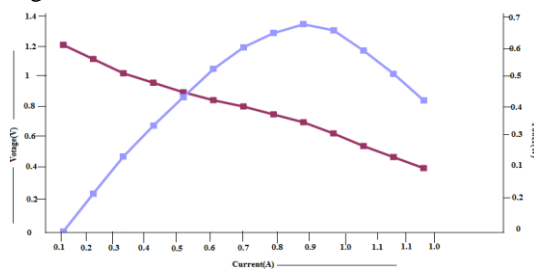


Figure 11. The power curve after 3 minutes of a micro-tube operated with mesh-and-pin interconnection.

The loose contact between the anode and the Ni mesh made it impractical for long-term operation because the cells failed constantly. The modes of failure were unpredictable and erratic; sometimes the micro-tubes failed abruptly and at other times they degraded gradually over a few hours. Repeated testing of the micro-tubes showed inconsistent behaviours as shown in Figure 12 and Figure 13 below.

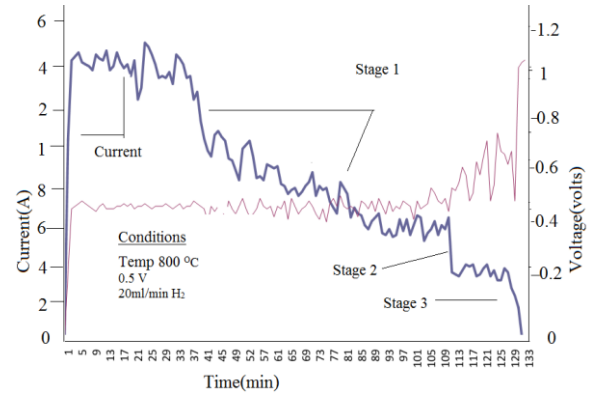


Figure 12 Showing a graduate decrease in performance when a mesh and pin Structure was used.

From Figure 12, degradation is seen to occur in three stages. In stage 1, the electrochemical performance is seen to decrease gradually from its initial peak value of 1.42A to 0.6A in 60 minutes; a degradation rate of 57.7% is calculated for this stage. In stage 2, an abrupt decrease in performance is observed from 0.6A to 0.25A; a degradation rate of 58.3% is calculated for this stage. The final stage is the cell failure point where the cell performance decreased from 0.25A to 0.

Figure 13. shows further erratic behaviour as another micro-tube is tested with the mesh-and-pin technique. The electrochemical performance degradation is seen to proceed in two stages; stage 1 sees a sharp drop in performance from a current of 1.39A to 0.34A; giving a degradation rate of 78.5%. In stage 2, the tube degrades rapidly from 0.3A to 0 after maintaining at 0.3A for 65 minutes.

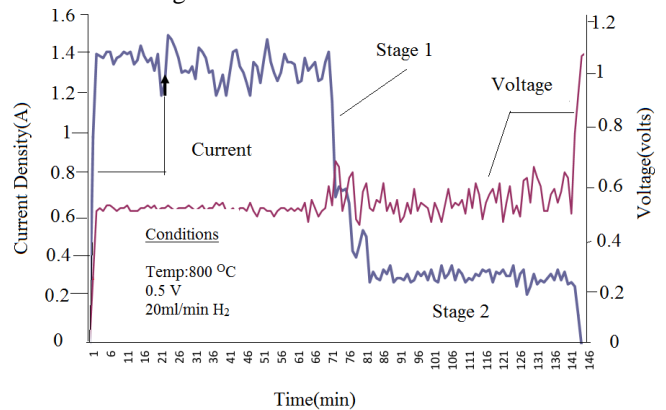


Figure 13 Showing abrupt decrease in electrochemical performance when mesh and pin structure was used.

At the commencement of the experiment a peak current of 1.39 A was observed for 70 minutes, during this period of sustained peak performance, the Ni mesh structure and the Ni anode were in intimate contact, offering low contact resistance and high electrochemical performance.

V. TYPE-STYLE AND FONTS

Discussion of Partial Redox Cycling

In all three cases above, the percentage (%) of anode oxidized is seen to increase with temperature as portrayed in Table 3..

Temperature	% Oxidation after 3 mins	% Reduction after 5 mins
600°C	4.5%	99%
700°C	6%	99%
800°C	7%	99%

Table 3 Showing the percentage of anode oxidized with temperature

Complete Redox Operation at 600°C

Figure 14, shows an initial current of 0.8A was observed as the micro-tube was held for 4 hrs at 600°C in order to achieve complete reduction. Subsequently, the hydrogen supply was shut off for 4.5 hrs in order to allow complete oxidation of the anode. With this first redox cycle, a current of 0.52 A was observed after the hydrogen supply was turned on; the degradation for this stage was 35%. The next redox cycle led to further degradation in the current from 0.52 A to 0.38 A, giving a degradation of 26.9%.

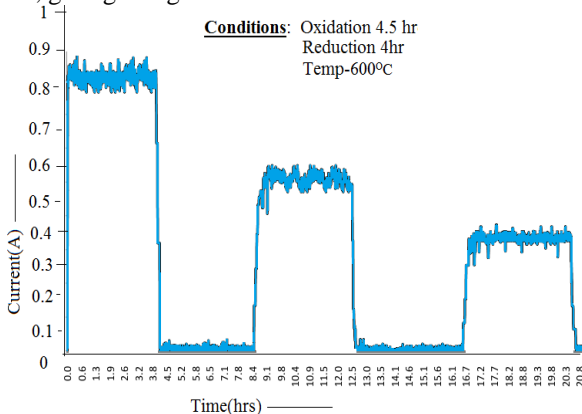


Figure 14 The redox cycling of a micro-tube at 600°C

Complete Redox Operation at 700°C

Figure 15 shows oxidation at 700°C. Initially, the atmospheric oxygen attaches to the Ni in the anode to proceed quicker than at 600°C. Because due to high temperature. The relatively lower rate of oxidation increase mass gradually. To attain completion after 3.4 hrs; significantly lower than the time for oxidation at 600°C due to increases the rate of oxidation with temperature

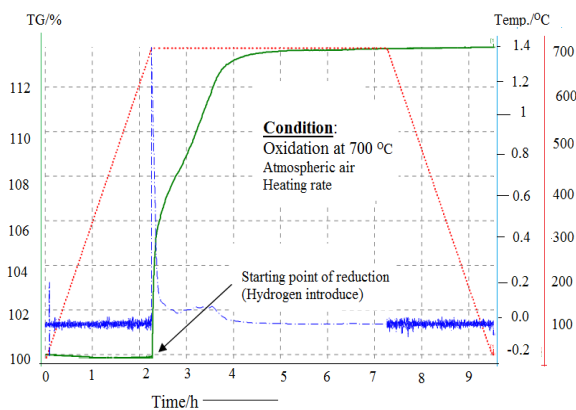


Figure 15 Showing complete oxidation of a micro-tube at 700°C

The maximum reduction rate was -0.5%/min occurred after 5 minutes. Hence 100% reduction was achieved after 3.3hrs.

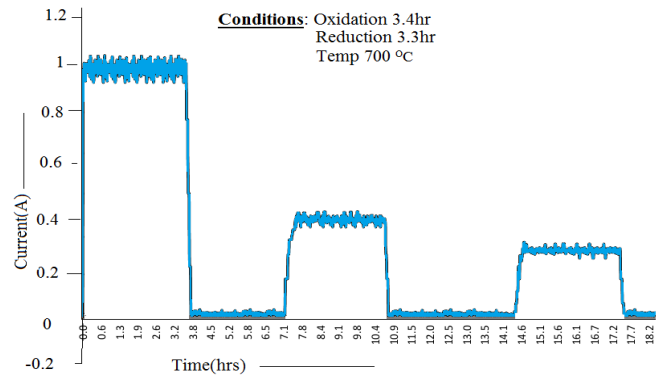


Figure 16 The complete redox cycling of a micro-tube at 700°C

Figure 16 shows at 700°C. Initially, a peak performance of 1 A is observed as hydrogen was fed, decrease up to 0.39A after the first redox cycle, 61% degradation calculate. First redox cycle has a greater deleterious effect than the second cycle.

Complete Redox Operation at 800°C

Figure 17 shows the result of the oxidation of a micro-tube at 800°C. But at 700°C Oxidation proceed rapid seen by the Δ (TG%/min) which showed a linear rate.

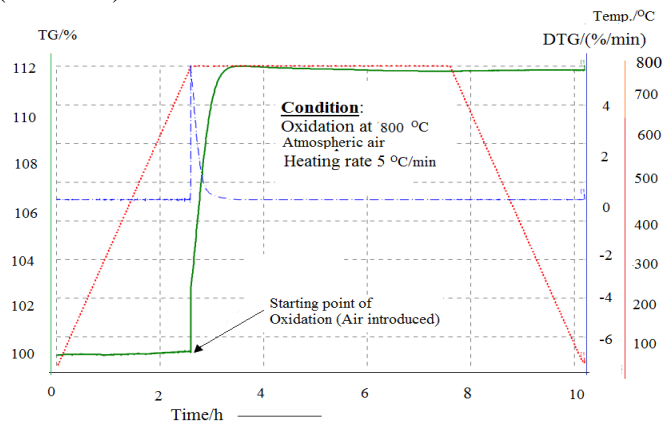


Figure 17 Showing complete oxidation of a micro-tube at 800°C

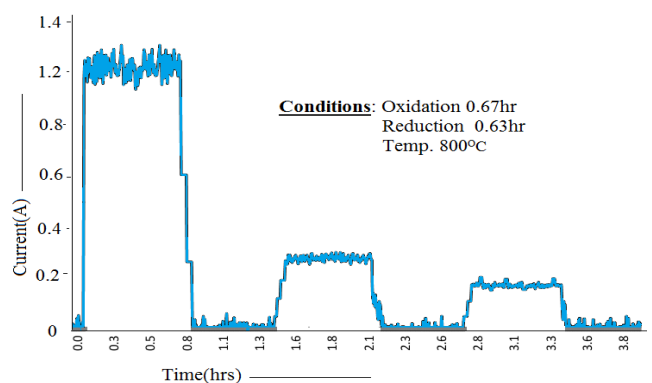


Figure 18 Showing complete redox cycling of a micro-tube at 800°C

Discussion of Complete Redox Cycling
 As shown in table 4

Temperature	Time to achieve Complete Oxidation	Time to achieve Complete Reduction	% Degradation after 1st Cycle
600°C	4.5hrs	4.0hrs	35%
700°C	3.4hrs	3.3hrs	61%
800°C	0.67hrs	0.63hrs	72%

Table 4 The redox durations and % degradation with respect to temperatures

Expansion During Redox Cycling

The oxidation of Ni to NiO is known to cause severe expansion in the bulk of SOFCs. Figure 19, Figure 20 and Figure 21 show the expansion of micro-tubular SOFC during oxidation at 600°C, 700°C and 800° respectively. In all three cases, the cells were heated in a Nitrogen atmosphere, and once at the desired temperature 20 ml/min of air was fed into the cell in order to oxidize the anode.

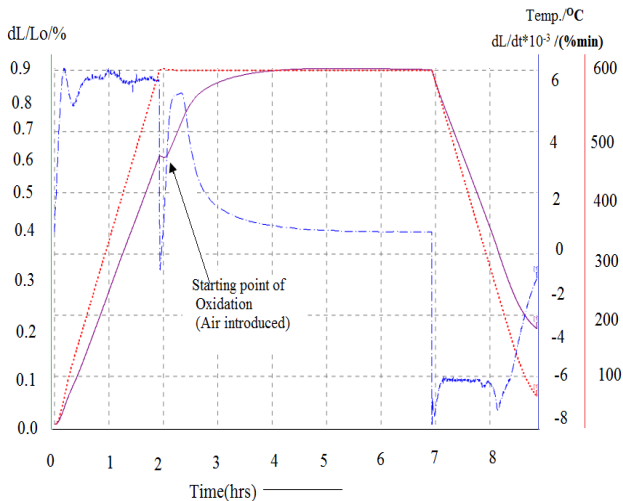


Figure 19 The expansion due to oxidation of a micro-tubular SOFC at 600°C

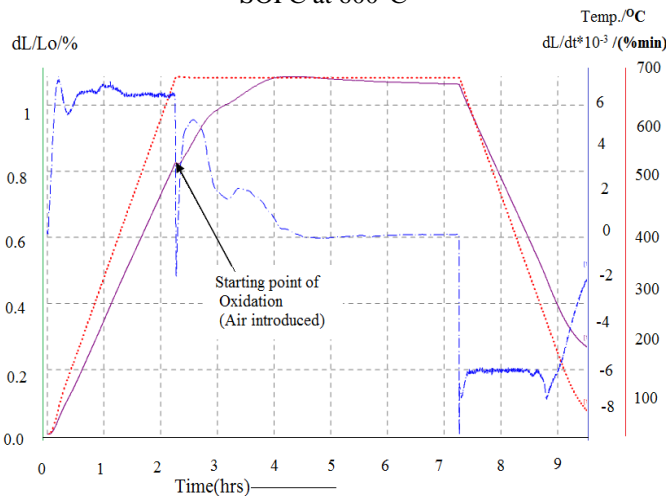


Figure 20 The expansion due to oxidation of a micro-tubular SOFC at 700°C

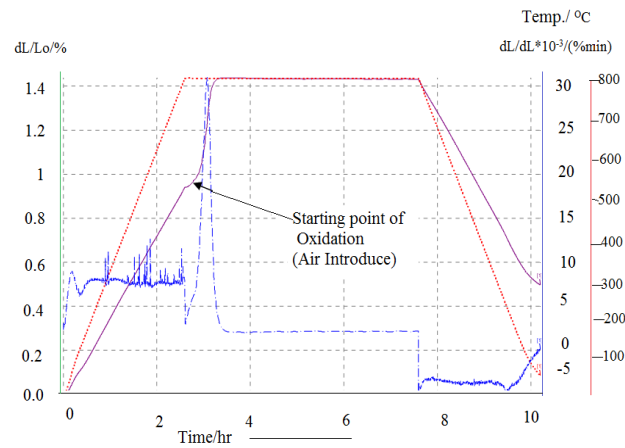


Figure 21 The expansion due to oxidation of a micro-tubular SOFC at 800°C

At 600°C, an expansion of 0.7% was observed before oxidation but with the onset of oxidation; give a final expansion of 0.9%. The effective expansion was 0.2%. At 700°C an expansion of 0.81% was observed before oxidation but with the onset of oxidation; give final expansion to 1.14%. Finally, at 800°C an expansion of 0.96% was observed before oxidation and after oxidation was 1.42%, gives a final expansion was 0.46%. However, thermal cycling experiences less degradation than redox cycling because all the cell components expand and contract relative to their CTE in thermal while redox shows expansion of the anode relative to the others.

Thermal shock of The Anode Supported Micro-Tubes

Table 5 shows the thermal shock results of the anode-supported micro-tubes. The tubes were heated to the desired shock temperature in a carbolite® furnace before being quickly removed and shocked in a bowl of water at ambient temperature.

Shock Temperature (°C)	Force (N) (After first Shock)	Force (N) (After Second shock)	Force (N) (After Third shock)
Ambient	11.4	11.5	11.3
100	10.3	7.44	7.05
150	16.13	11.62	10.59
200	15.2	11.1	9.5
250	10.51	6.45	3.22
255	10.22	8.54	Shattered
260	4.13	Shattered	Shattered
265	Shattered	Shattered	Shattered

Table 5 The minimum force of fracture of anode supported tubes after thermal shock

Electrical Shock test

Electrical shock tests were performed only on the anode-supported tubes and the results are present in tabular form in Table 6

Number of cycles	Strength after shock at 600 ^o C	Strength after shock at 700 ^o C	Strength after shock at 800 ^o C
0	202.1	204.25	202.1
2	184.9	178.45	178.45
4	172	167.7	159.1
6	159.1	152.65	139.75
8	146.2	122.55	120.4
10	129	124.7	107.5
12	118.25	94.6	88.150
13	109.65	86	0
14	90.3	0	0
15	79.55	0	0
16	0	0	0

Table 6 The change in strength of the anode supported tubes after electrical shock

At 600^oC, a voltage of 1.8V and current of 9.0A was passed through the tube and 16 electrical shock cycles were achieved before failure. For 700^oC, the voltage and current were 2.0V and 11A respectively. At 800^oC, the voltage and current were 2.0V and 12A respectively while the number of electrical shocks to failure was 13, see Figure 4.28. This decrease in strength with cycling is due to an increase in stress induced with temperature. This stress build-up will cause failure once it exceeds the critical stress value.

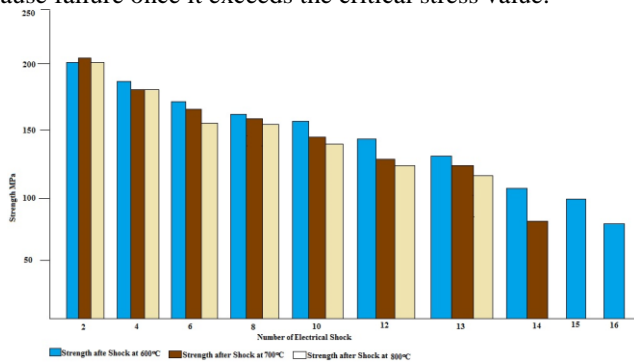


Figure 22 The change in yield strength of the anode supported micro-tubes with electrical shock

Electrical shock gives more realistic representation of temperature gradients than thermal shock because of the crude method of shocking the tubes in water. However, thermal shock was performed helps to present a case of extreme stress induction in the tubes.

VI. CONCLUSION AND FUTURE SCOPE

The degradation of micro-tubular SOFCs were studied under isothermal conditions, thermal cycling, redox cycling and electrical load cycling, in order to understand the effects of these on electro-chemical performance.. Finally, thermal and electrical shock test were preformed in order to understand micro cracking and failure. Post mortem analyses of the tubes

were performed by SEM in order to observe any changes in microstructure.

- **Isothermal Ageing :** It was found that Ni sintering was responsible for most of the initial degradation during isothermal ageing. Sintering proceeded rapidly for the first 10 hours, the Ni particles agglomerated into a dense structure leading to decreased TPB and lower electro-chemical performance however after this period the rate of sintering was found to diminish considerably because the structure assumes a more stable configuration giving steady electro-chemical performance. Irreversible deformation was also found to occur as the micro-tubes were raised to high temperature and cooled down. Dilatometry showed that the sample failed to recover back to its original length upon cooling. This irreversible deformation was the combined effect of severe stress induction at high temperature due to temperature gradients and sintering.
- Furthermore, the effect of temperature gradients on the electro-chemical performance of micro-tubes was investigated by flowing 25% excess fuel through the tubes for combustion at the cell outlet. No degradation or micro cracking was observed and their effect was adjudged to be marginal.
- **Redox Cycling:** Re-oxidation of the Ni/SZ anode was found to cause significant expansion in the anode microstructure; expansions of up to 0.2% were observed at 800^oC. This expansion caused severe stress induction or de-lamination in the tube because of the constraint imposed by the electrolyte and other cell components. Rapid oxidation also caused micro-cracking in the anode due to the rapid expansion in the anode. Partial redox cycling showed a steady decrease in performance with cycling. Each redox cycle caused micro-cracking thereby increasing the overall resistance of the anode leading to electro-chemical performance degradation. Complete redox cycling on the other hand showed severe degradation in performance, with 72% degradation observed after the first cycle at 800^oC. Gross micro-cracking and de-lamination were observed after complete oxidation due to its severe nature. Redox cycling was therefore adjudged the most deleterious form of cycling, giving the most damaging effect during SOFC operation.
- **Electrical load Cycling :** This was found to have a very marginal effect on the electro-chemical performance of the micro-tubes. Cyclic loading between OCV and 0.5V caused an increase in the temperature of the tube, especially when the cell was loaded at 0.5V. This was mainly because of the ohmic resistance of the material to the flow of electrons.
- **Thermal and Electrical Shock test :** Electrolyte supported tubes were found to be considerably stronger than anode supported tubes. They were

however found to be more prone to thermal stress induction as they failed in the 250°C - 255°C regime as against 260°C - 265°C for the anode supported micro-tubes. Electrical shock tests provided better understanding of temperature gradients and shock in SOFC. The tubes were found to be plagued mainly by the temperature gradients and hotspots which develop because of the variation in resistance along the tube. These differences in resistance led to several hotspots across the tube, causing fracture and eventual failure.

FUTURE SCOPE

- Cycling with Hydrocarbon fuels : The cycling studies reported in this project were largely performed with hydrogen as fuel. This is very idealistic because hydrogen is not yet the primary energy vector in today's society however it provided a baseline for assessing the electro-chemical performance of these tubes. Cycling with commercially available fuels like methane, propane and butane will provide valuable information about the durability and reliability of fuel cells for the present market.
- Cycling of micro-tubular SOFC Stacks : In this project, only single micro-tubes were tested. The design, fabrication and testing of SOFC stacks will provide valuable insight into other factors like interconnect degradation and failure, overall system efficiency etc. The cycling performance of each cell in a stack depends on the others; also the temperature gradients across them would vary. A few stack manufacturers have reported interconnect failure and short-circuiting during operation of stacks [207]. Thus, extensive study is required.
- Shorter Cells : During the course of this work, I have been able to show that shorter micro-tubes (25mm long) demonstrated superior cycling performance to longer (55mm long) micro-tubes. They were also found to give similar electrochemical performance to longer tubes [156]. This needs to be investigated in greater detail because of the several advantages that shorter tube present, including lower cost of fabrication, more compact designs, ease of stacking and decreased degradation. Also temperature gradients across these tubes were found to be smaller, thus giving smaller degradation indexes.
- Thermal and Electrical shock test : During the thermal shock of the micro-tubes at 150°C, a characteristic increase in strength was observed as against a decrease at other temperatures. This is not fully understood, so further investigation into the behavior of these micro-tubes and their fracture mechanics is essential.

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