Characterization of the electrochemical performance of micro-tubular SOFC in partial reduction and oxidation conditions

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Abstract

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.

1. Introduction

The recent renaissance in fuel cell research is mainly due to the ability of fuel cells to generate clean and efficient energy by simple electrochemical reactions. Fuel cells utilize the chemical energy of fuels and convert it directly into electricity, thus bypassing the intermediate conversion step to mechanical energy, as in the case of traditional combustion engines, and therefore attaining higher theoretical efficiencies [1].

A solid oxide fuel cell is centred on a solid, impermeable ion conducting ceramic oxide electrolyte [2], usually yttria stabilised zirconia (YSZ). It is typically operated at temperatures between 650 and 950 °C where fast ionic conductivity occurs. Typical solid oxide fuel cell anodes are cermets of Ni/YSZ, the Ni-component acting as electronic conductor and fuel catalyst, while the YSZ phase serves to adhere the nickel to the electrolyte, provide a catalyst substrate and improve the stability of the anode [3]. The fabrication of anode cermets entails the mixing of coarse and fine YSZ particles with NiO nanoparticles, where coarse YSZ is used to match the thermal expansion coefficient of the anode to the electrolyte while fine particles are employed to prevent the Ni particles from agglomeration and co-sintering. This anode composition minimizes delamination of components due to thermal expansion mismatch as well as maintaining the desired porosity in the electrode [4].

Re-oxidation of the anode takes place during start-up and shutdown unless purge gas is employed to prevent re-oxidation from occurring. The use of reducing purge gas in fuel cells operation is not practical in small-scale applications [5]. Another redox prevention technique is the use of anode materials that are not susceptible to oxidation, such as ceramic oxides. However, at present no alternative anode materials have yet replaced the traditional Ni/YSZ cermet in terms of conductivity, catalytic activity and economics. Thus, the most practical option to enhance the redox tolerance of Ni/YSZ anodes is to modify their microstructure or alter their design and operating conditions.

The main problem of redox cycling is the mechanical stress caused by expansion and shrinkage, which can destroy the anode

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structure while propagating cracks or delaminations. Other factors that may contribute to failure in SOFC are increased residual stress levels, thermal shock, thermally induced stress, fatigue (as in cycling), coefficient of thermal expansion mismatch between the various membrane components and stress concentrations at defects. Solid oxide fuel cells must withstand stresses during every phase of fabrication and operation [6]. Residual stress levels during cell manufacture or at sintering temperature are known to enhance failure in SOFCs. Stress is usually locked up in the bulk of the fuel cell as strain energy, which accumulates to a certain threshold and becomes sufficient to drive cracks in the body or at the interfaces. Most materials start to build up stress even from their fabrication process. The cooling phase of the sintering process is thought to be the most stress inducing phase as it is prone to temperature gradients [7]. During the process of transformation of the powder-binder mixture to a dense ceramic there is considerable volume reduction as the slurry loses its moisture and condenses into a bulk ceramic material; there is significant increase in residual stress level during this fabrication stage. This step is quite delicate as it is prone to cracking under inappropriate manufacturing/fabrication techniques [8]. The sintering step involves particle agglomeration and volume change which can also cause damage to the microstructure.

Redox cycling acts in addition to these process stresses to cause severe physicochemical and thermo-mechanical changes in anode microstructures during the conversion from Ni to NiO. These changes could translate to electrochemical performance degradation and eventual failure by gross cracking and delamination. In this paper, micro-tubular anode supported solid oxide fuel cells of anode thickness 200 μm, electrolyte 15 μm and cathode thickness 50 μm were subjected to 52 redox cycles and the electrochemical performance was evaluated after each cycle in order to determine the degradation per cycle. Scanning electron microscopy (SEM) was used to characterize the micro-structural changes after each redox cycle while dilatometry defined the expansion and shrinkage.

2. Experimental

A number experiments have been reported on the redox cycling performance of planar SOFC [5,9–11], but little attention has been paid to the cycling behaviour of micro-tubular SOFC. Planar SOFCs are known to be plagued by certain degradation indexes, mainly high internal/residual stress levels, stress concentration i.e. edge effects and sealing/manifolding weaknesses. Micro-tubular SOFCs on the other hand are more robust and resilient to conventional degradation processes owing to their tubular geometry. Small tubes were shown to reduce temperature gradients while inhibiting cracking through the fracture mechanics size effect [17].

2.1. Cell characterization

Anode supported micro-tubular solid oxide fuel cells, 55 mm in length and 2 mm external diameter were co-extruded by Adaptive Materials Incorporated (AMI), USA [they had 15 μm thick yttria stabilised zirconia (YSZ) electrolyte and 200 μm thick

nickel oxide/YSZ anode]. The micro-tubular SOFCs were provided already sintered and unreduced. Cathode formulation and preparation was as detailed in Ref. [12], the cathode was added by hand painting followed by sintering at 1150 °C for 2 h. The cathode length which translates to the anode active area was 30 mm and three silver bands were painted across the cell to provide adequate electrical contact between the current collecting silver wire and the cathode.

2.2. Experimental rig and procedure

The test rig comprised a brick furnace containing electrical heater wires. The fuel cell was located in the furnace centre, supported by a fuel injecting manifold which carried the fuel. The hydrogen flow rate was set to 20 ml min^{-1} by the mass flow controller attached to a gas cylinder. The oxygen required by the air-electrode was obtained from the atmospheric air. Voltage and current measurements were carried-out using a potentiostat run by Labview^{TM} software on a laptop. Fig. 1 is a schematic of the cycling setup. Prior to the cycling experiment, the fuel cell was reduced in 20 ml min^{-1} of hydrogen at 750 °C for 45 min in order to achieve complete conversion of NiO/YSZ to Ni/YSZ.

The objective of the experiment was to evaluate the tolerance of the Ni/YSZ anode to partial cyclic reduction and oxidation. The open circuit voltage of the cell was measured at 1.18 V then current was drawn at 0.5 V. Cycling proceeded by running the cell in hydrogen for 5 min and subsequently shutting off the fuel supply for 3 min in order for the anode to re-oxidize. Fifty-two cycles were achieved under these conditions and the degradation was evaluated by dilatometry and SEM.

Measurements of the thermo-elastic displacement of a micro-tubular SOFC under dilatometry were carried out using a Netzsch^{TM} model TASC 414/3 pushrod dilatometer. The working temperature range of the dilatometer was between −160 and 2000 °C. Alumina crucible was used as the sample holder, and the crucible is placed inside a tube. A *proteus software* was used to control the temperature programme during which the change in length of the sample is transduced via a pushrod to a linear variable differential transducer system (LVDT). The position of the push rod and therefore the change in length of the sample is registered and converted into electronic signal.
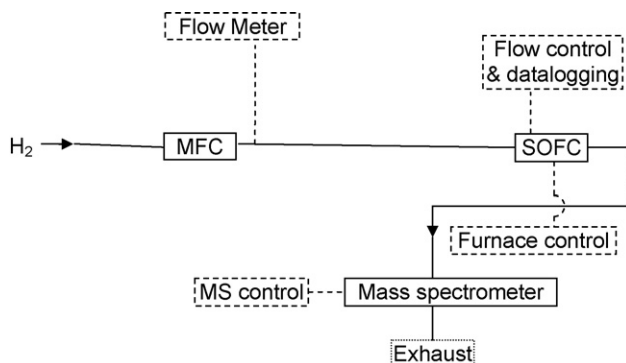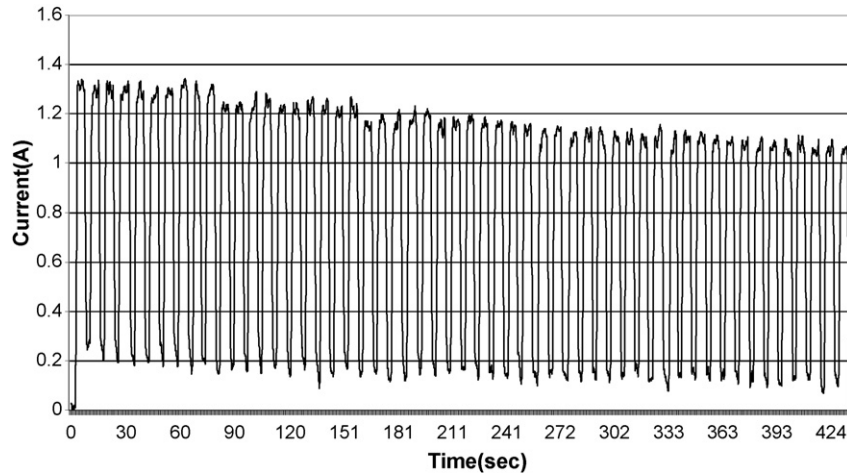

Fig. 1. A schematic diagram of the cycling rig.

Fig. 2. Results for 52 redox cycles under partial reduction and oxidation conditions.

3. Results

Results of the redox cycling of a micro-tubular SOFC in partial reduction and oxidation conditions are shown in Fig. 2. Fifty-two redox cycles were performed and the electrochemical performance was characterized. The micro-tubular SOFC was cycled between 0 and 20 ml min^{-1} in such a manner as to achieve partial reduction and oxidation. It was re-oxidized for 3 min by shutting-off the fuel supply and then subsequently reduced in 20 ml min^{-1} of hydrogen for 5 min and the electrochemical performance at 0.5 V was measured. The partial pressure of oxygen rose to 2.77×10^{-3} atm during oxidation and analysis showed that only 7% of the anode was oxidized under these conditions. A decrease in electrochemical performance after each cycle was observed. The decrease in current was linear with the number of cycles, i.e. 0.3% per cycle.

This affirms previous reports which suggest redox cycling to be a harsher test with greater deleterious effect than any other cycling test, whether temperature cycling or electrical load cycling [13]. Usually with electrical load cycling or thermal cycling, minimal degradation is observed after each cycle. Hundred of thermal and electrical load cycles have been performed by Bujalski et al., with minimal degradation. The mechanism of redox cycling is very different from that of temperature cycling, in the sense that the former involves the expansion and contraction of the anode microstructure only, whereas temperature cycling involves the bulk volume displacement of the whole cell components due to a change in thermal energy supplied by the heating furnace. Thermal cycling generally tests the thermal shock resilience of the membrane components, by subjecting them to huge temperature gradient whereas redox cycling test the physicochemical characteristics of the anode by assessing the expansion characteristics of the anode relative to the other components. Zirconia is known to posses average thermal shock resilience/redox tolerance properties and its abundance and low cost makes it suitable as fuel cell component [14].
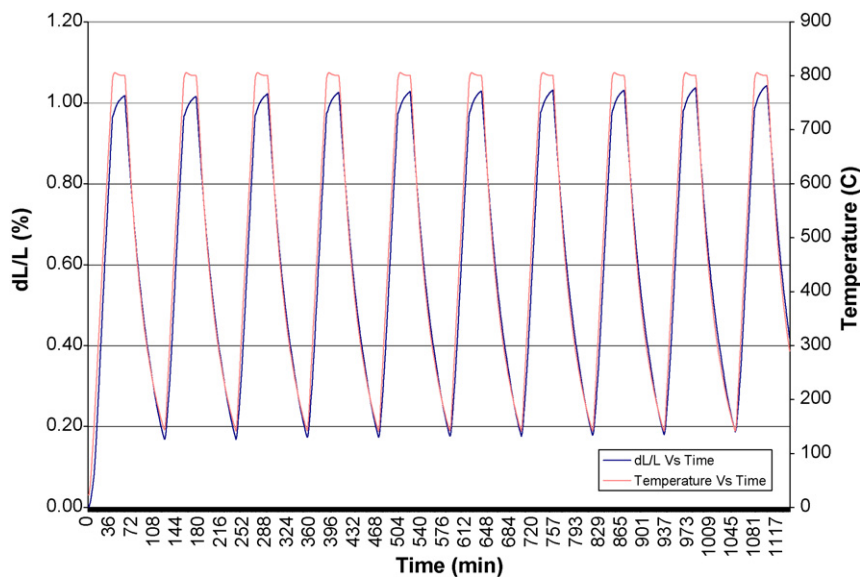

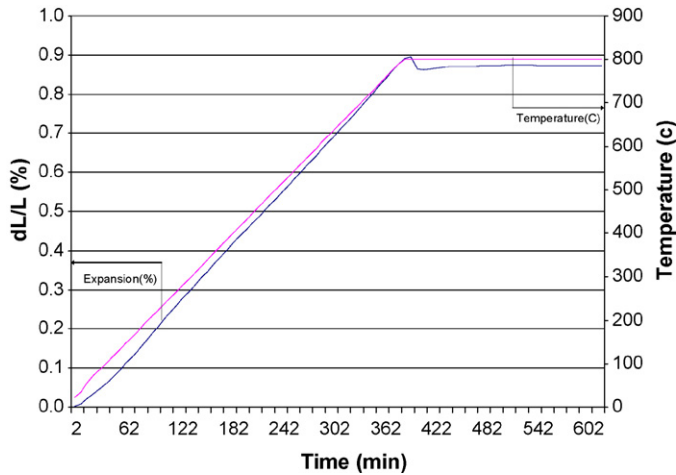Fig. 3. Showing the thermo-elastic displacement of an unreduced micro-tubular SOFC under dilatometry.

Fig. 4. Showing the contraction of the anode upon reduction.

Fig. 6. SEM micrograph of an unreduced micro-tubular SOFC micro-structure.

Fig. 3 is a graphical representation of the thermo-elastic displacement between 150 and 800 °C of an unreduced micro-tubular SOFC under dilatometry, a total of nine thermal cycles were achieved. The micro-tubular SOFC sample was inserted in an alumina crucible and mounted on the dilatometer, 100 ml min^{-1} of argon gas was used to maintain inertness during the experiment. A ramp rate of 20 K min^{-1} was used from ambient temperature to 800 °C and the thermo-elastic expansion of the sample was measured by the pushrod of the dilatometer.

The response of a micro-tubular SOFC under reduction conditions is represented in Fig. 4. An unreduced micro-tubular SOFC is raised to 800 °C at 2 K min^{-1} in nitrogen gas. Subsequently, the nitrogen supply is shut-off and hydrogen is allowed to reduce the cell. The thermo-elastic displacement of the sample is measured by the pushrod of a dilatometer.

Also the oxidation behaviour of a micro-tubular SOFC was investigated under dilatometry (Fig. 5) by raising the sample from ambient temperature to 800 °C at 2 K min^{-1} in argon gas. At the end of the ramping sequence, air at 20 ml min^{-1} was allowed to oxidize the anode and the corresponding thermo-elastic displacement was measured.
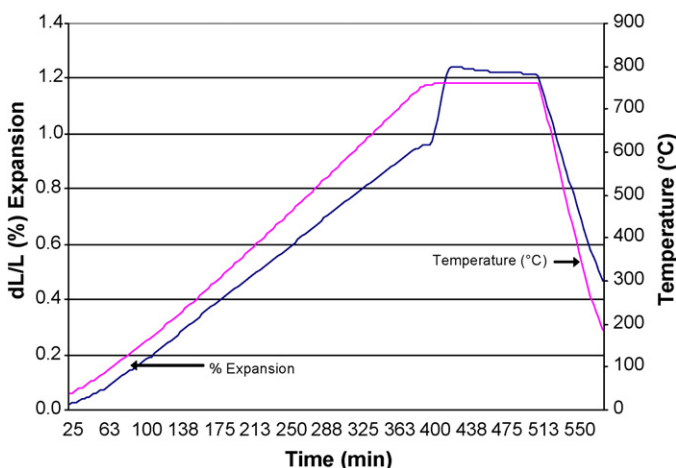
Figs. 6 and 7 show SEM micrographs of typically unreduced and reduced anode supported SOFC. The unreduced micro-tubular SOFC anode presented a semi-dense and slightly porous microstructure, mainly due to the NiO/YSZ particles that make-up the anode. The anode microstructure is represented by the large grey Ni portions while the outer-white layer is the thin YSZ electrolyte. The anode microstructure was somewhat non-uniform and showed a highly interconnected structure, while the electrolyte is seen to be dense and impermeable. The reduced anode showed a highly porous and interconnected structure. A layer of fine anode particles which are somewhat dark-grey is observed below the electrolyte, which is somewhat dense and non-porous. This is are essentially the finer Ni/YSZ phases used to prevent rupture and delamination at the electrolyte–anode interface by providing a similar thermal expansion coefficient to the YSZ electrolyte at high temperature.

The pore distribution of the reduced anode is observed to be more even than in the case of the unreduced microstructure. This is mainly due to the oxygen-molecule-voids that develop when the oxygen atom is stripped-off the Ni atom by hydrogen during reduction. The electrolyte is seen to be dense, bulk and impermeable, preventing seepage of fuel from the anode side to the cathode.

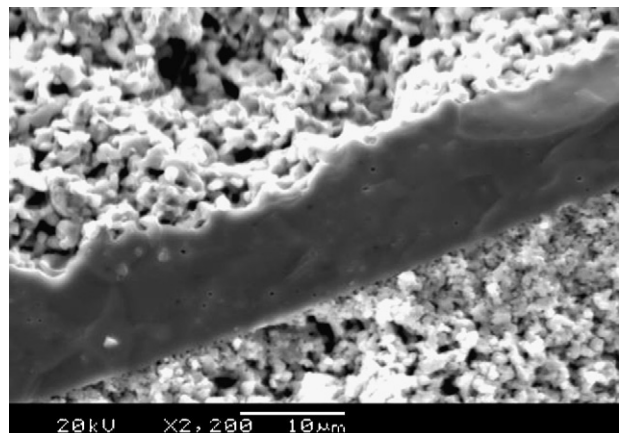Fig. 5. Showing the expansion of the anode upon oxidation.

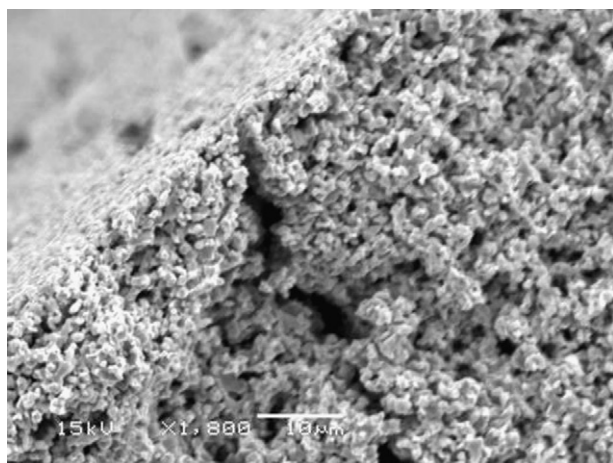Fig. 7. An SEM micrograph of a reduced micro-tubular SOFC microstructure.

Fig. 8. Showing a crack in the micro-structure after final reduction of a micro-tubular SOFC cycled 52 times.

Also shown in Fig. 8 are SEM micrographs after final reduction of an anode supported micro-tubular SOFC cycled 52 times under redox conditions. The individual Ni and YSZ phases can be seen quite clearly; the Ni-phase is represented by the grey portions while the YSZ-phase are the large white connecting portions. A large crack is seen propagating from the interior of the anode and projecting outwards towards the electrolyte. Anode re-oxidation accounts for a huge expansion in the microstructure, whereas reduction causes shrinkage, thus cyclic oxidation and reduction will enhance stress accumulation in the bulk of the material causing it to crack at the weakest points.

Figs. 9 and 10 are SEM micrographs showing delamination after final reduction at the anode–electrolyte interface of a micro-tubular SOFC cycled 52 times under redox conditions. Two delamination zones are visible below the electrolyte. These delamination cracks are suspected to be mainly due to stress build up at this interface because of the expansion and contraction of the anode during redox cycling. Delamination cracks give rise to increase in internal ohmic losses, owing to the fact that they impair oxide-ion flux at the electrolyte–electrode interface. The losses caused by delaminations at the electrode–electrolyte
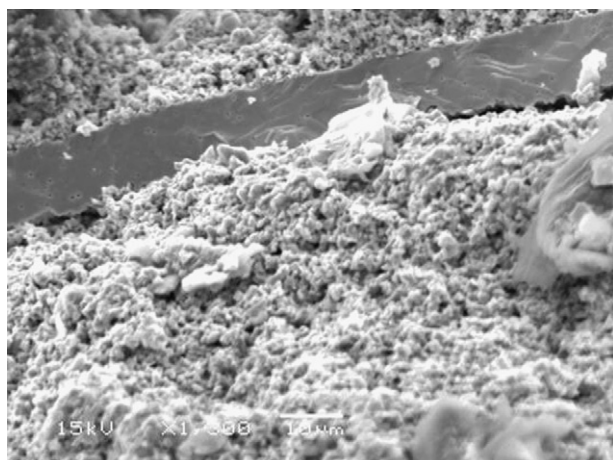

Fig. 9. A micrograph showing two delamination cracks at the electrolyte–anode interface after final reduction.
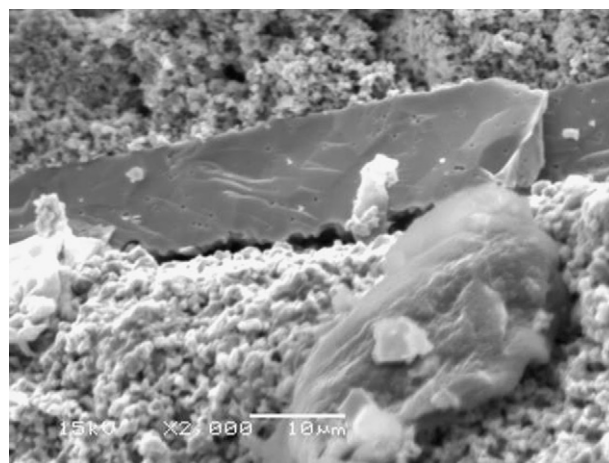

Fig. 10. A micrograph showing a delamination crack below the electrolyte–anode interface after final reduction.

interfaces are largely responsible for the degradation in electrochemical performance in SOFCs. These losses can be investigated via micro-structural characterization and modelling techniques can be applied to crack-affected regions to gain an understanding into the mechanism of electrochemical degradation of micro-tubular SOFCs.

4. Discussion

SEM micrographs have been used to show the changes in microstructure of the SOFC components under different test conditions.

Fig. 6 shows the micrograph of an unreduced micro-tubular cell, the particles are seen to be very dense and well interconnected with smaller and few pores. This is very typical because the microtubes are co-extruded as NiO/YSZ—YSZ cermets. The structure is a semi-conducting ceramic in this phase, owing to the fact that the Ni present is in oxide state. The oxide ions tend to clog-up the pores available thus portraying a dense and slightly porous structure. On the other hand Fig. 7 is a micrograph of a cell reduced for 45 min in hydrogen. The pores sizes/pore density is higher than the previous case owing to the reduction of nickel from its oxide state. The structure is seen to be well interconnected and highly porous. The porosity of the anode is an important metric in analyzing the functionality of the anode because porous anodes give greater contact area for catalytic oxidation thereby enhancing performance. The porosity of anodes should range between 30 and 50%.

4.1. Micro-crack formation in the anode

In Fig. 8 a microcrack is propagated through the anode; it is seen to project from the hollow interior towards the electrolyte. This crack is the result of stress build up and fatigue due to continuous cycling. Redox cycling induces severe stresses in the body of fuel cells owing to cyclic expansion and contraction when the anode re-oxidizes and reduces in cycles. The reduction and oxidation of nickel will result in large bulk volume changes. In theory, the bulk volume of a fully dense NiO sample should

contract by 40.9% upon reduction and should expand by 69.2% upon oxidation [11].

These cyclic expansions and contractions are sufficient to drive cracks at the weakest joints of the structure. Usually a small micro-crack would develop, but as cycling continues and more stress energy is accumulated in the crack, it begins to propagate and expand until a huge crack is visible, giving rise to an increase in electrode resistance. The overall resistance of the anode increases when there is an obstruction in the path of electron flow such that the electrons would have to take longer paths. Micro-cracks enhance this phenomenon because they act as barriers against electron flow. Generation and propagation of cracks is better explained via fracture mechanics, which is beyond the scope of this study.

In the event of re-oxidation, there is expansion in the anode which causes breakage due to stress induction in the Ni microstructure. A breakage results to an increase in overall anode resistance due to longer electron paths. Increase in resistance will result to a decrease in the power density and thus a decrease in the electrochemical performance.

Re-oxidation → Expansion → Breakage

→ Increasedresistance → Degradation

4.2. Delamination at the electrolyte–electrode interface

Delamination in solid oxide fuel cells is not uncommon when solid oxide fuel cells are subjected to redox cycling. It is the result of an expansion mismatch between the components; during thermal cycling the individual cell components expand by the index of their respective thermal expansion coefficients, giving rise to a bulk displacement. Whereas redox cycling occurs at the anode only, and as such any expansion or contraction takes place in the anode alone. This causes tension and stress accumulation at the anode–electrolyte interface. The accumulated stress has the capacity to develop and propagate delamination cracks at the interface. Delamination cracks form insulative barriers that prevent ion exchange between electrolyte and electrodes.

In this study delamination cracks are treated as ion-conduction obstructions that lead to the distortion of ions at the electrolyte–electrode interface. This distortion serves to lengthen transport paths and therefore lead to an increase in the overall ohmic losses. For increasingly thin electrolytes, this ion-conduction distortions may lead to the effective loss of electroactive area at both the electrode and electrolyte interfaces [15].

For interfaces with no delamination and low electrolyte resistance, there is uniform flux density at both the cathode–electrolyte and anode–electrolyte interfaces. With the commencement of delamination, the effective electro-active area of the interface becomes significantly reduced and an insulative void is created. These voids serve to prevent ions from contacting the electroactive surfaces, thus leading to loss of electrons. The mode of transfer of ions in the electrolyte is however not been fully understood, and in this study an assumption has been made that the flow of ions is radial (i.e. across the width of the electrolyte) and not axial. The implication of this assumption is that the ions flow in straight paths, thus any ions that are in the path of the delamination crack will be masked and lost in the void. A modelling study is required to fully understand the mode of transport of ions in the electrolyte and to provide insight into the effect of delamination cracks on the electrochemical performance of micro-tubular SOFC.

4.3. Oxygen partial pressure gradient

An oxygen partial pressure gradient is bound to develop in the anode when the oxidation process commences because the oxygen enters at the open end of the tube and commences reaction with Ni there and gradually advances up the tube. Such conversion along the tube's length would give rise to a state of tension between the converted and unconverted areas. Stresses are likely to develop under this condition thereby enhancing degradation.

4.4. Electrochemical degradation

The degradation in electrochemical performance during redox cycling is a combine effect of the two phenomena explained above. After each redox cycle the electrochemical performance is seen to decrease by a factor of 0.3%. The main culprit of electrochemical degradation in SOFC performance is stress accumulation, which raise the residual stress level of the fuel cell to a threshold sufficient to cause degradation.

4.5. Thermo-mechanical analysis (dilatometry)

The thermo-elastic expansions after each cycle were perfectly reversible for the unreduced micro-tubular SOFC (Fig. 3). At 150 and 800 °C, expansions of 0.2 and 1% respectively were observed. A coefficient of thermal expansion of $1.25 \times 10^{-5} \, °C^{-1}$ was calculated. The complete reversibility of the sample is an indication that its laminate design is satisfactory and has the capacity to withstand considerable thermal gradients. Zirconia is known to posses average thermal shock characteristics and has gained wide applications in high temperature applications. However, longer cycles may give rise to significant degradations as the residual stress levels may increase causing performance degradation or failure.

The thermo-mechanical results for the reduction of a micro-tubular SOFC is portrayed in Fig. 4. It is observed that the anode shrinked by 0.02% upon reduction. This shrinkage has the capacity to pull the anode from the electrolyte thereby creating tensile stresses at the anode–electrolyte interface. If these tensile stresses become severe, delamination may occur at the interface.

The behaviour of a micro-tubular SOFC under oxidation is shown in Fig. 5. The sample expanded by 0.14% upon oxidation. Similar to reduction, the movement primarily occurs at the anode but as the anode expands, it is constrained by the electrolyte. Such a constraint causes stress build up at the anode–electrolyte

interface which results to cracking or fracture in the dense electrolyte. A fracture crack in the electrolyte is likely to cause a decrease in the open circuit voltage of the fuel cell.

5. Conclusion

The effect of redox cycling on Ni–YSZ anode has been investigated in partial reduction and oxidation conditions. Redox cycling has been found to cause significant degradation in the microstructure of SOFC.

Two modes of degradation in micro-tubular SOFC have been identified: (a) anode degradation due to micro-crack formation; and (b) degradation due to delamination at the electrode–electrolyte interfaces. The former degrades the anode by enhancing internal ohmic losses in the microstructure; this happens by an increase in the resistance of the anode due to the formation of micro-crack which creates longer paths for electrons to travel. Micro-cracks also create instability in the electrode microstructure and they are known to decrease the integrity and durability of fuel cells.

Delaminations are also identified as principal causes of degradation in micro-tubular SOFC. They are very common during redox cycling mainly because redox cycling causes severe expansions in the anode microstructure inducing stresses and tension at interfaces. Delaminations can be minimized by closely matching the expansion coefficients of the composite materials.

Also, 52 redox cycles were performed on micro-tubular SOFC at 800 °C and the micro-structural changes and electrochemical performance were characterized.

There was degradation in the electrochemical performance after each redox cycle, the degradation being 0.3% per cycle. Previously reported results on thermal cycling test, performed on planar SOFC have shown that redox cycling has greater deleterious effect than thermal cycling [16].

Also dilatometry has been used to characterize the expansions and contractions that occur upon oxidation and reduction.

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