

# The reduction of nickel–zirconia cermet anodes and the effects on supported thin electrolytes

M. Cassidy <sup>a,\*</sup>, G. Lindsay <sup>a</sup>, K. Kendall <sup>b</sup>

<sup>a</sup> Advanced Materials Centre, Napier University, 10 Colinton Road, Edinburgh EH10 5DT, UK

<sup>b</sup> Unit for Inorganic Chemistry and Materials Science, Department of Chemistry, Keele University, Staffordshire, ST5 5BG, UK

## Abstract

An important objective in the development of solid oxide fuel cells (SOFC) is to produce thin stabilized zirconia electrolytes that are supported upon the nickel–zirconia cermet anode. Although this will reduce some of the problems associated with SOFCs by permitting lower temperature operation, this design may encounter problems during the cell start-up. The first step in a start-up involves the reduction of nickel oxide in the anode to metallic nickel and the volume change associated with this may damage the supported electrolyte. In this work, the effects of this reduction both on the anode and the supported electrolyte have been investigated. The findings show that the initial reduction does not seem to damage the cell, although an increase in volume with respect to the initial volume upon reoxidation of the anode cracks the electrolyte and will fracture the cell when constrained in an operational environment. The reason for this increase appears to be linked to the sintering of the nickel while in its reduced state.

**Keywords:** Solid oxide fuel cell; Anode; Reduction; Supported electrolytes; Screen printing; Nickel; Zirconia

## 1. Introduction

It is well acknowledged that lowering operating temperatures from 1000 to 700 °C would benefit the development of solid oxide fuel cells (SOFC). Reduced temperatures would, for example, allow the use of such items as metallic interconnects which would simplify the stack and reduce the cost. One method of achieving lower temperature operation is by using thin supported zirconia films as the electrolyte. This reduces the ohmic losses across the electrolyte allowing the cell to operate efficiently at lower temperatures.

Several methods exist for depositing the electrolyte film onto the supporting structure. Some of these methods use the anode as the supporting structure, for example, calender rolling an anode/electrolyte bilayer to the correct dimensions [1], or screen printing an electrolyte onto a tape cast anode [2]. This paper concentrates on the latter approach, where an electrolyte is screen-printed onto a green anode tape and the resulting bilayer is co-sintered, although the findings may be applicable to both fabrication methodologies.

Concern has been expressed about the use of the anode as the support element in the cell. In particular, how the volume change associated with the reduction of the nickel oxide to metallic nickel would affect the integrity of the electrolyte

[3]. This paper investigates the behaviour of the anode as it is reduced, and how this behaviour affects the integrity of the supported electrolyte. Methods employed include volumetric and weight changes, microscopy and electrochemical testing.

## 2. Experimental

### 2.1. Specimen preparation

A green anode tape was first produced by tape casting, when dry 10 mm and 50 mm squares were cut. The 10 mm squares were used to determine the weight and volume changes of the anode, while the 50 mm squares had an electrolyte layer of stabilized zirconia (8 mol% yttria) applied by screen-printing. The anode squares and the bilayers were sintered in air for 2 h at 1350 °C. The thickness of the electrolyte after sintering was around 8  $\mu$ m.

The level of nickel oxide in the sintered anode was 56 wt.%, which equates to roughly 40 vol.% of metallic nickel in the cermet structure once reduced. This ensures that there is enough nickel for the electrical conduction required in the anode while retaining a coefficient of expansion that is reasonably matched to the electrolyte.

\* Corresponding author.

## 2.2. Anode reduction and reoxidation

Both unprinted anodes and bilayers were reduced in flowing gas mix consisting of 5% hydrogen and 95% argon, in a tube furnace. The heating rate of the furnace was  $5^{\circ}\text{C min}^{-1}$ , and at  $750^{\circ}\text{C}$  the tube was purged with nitrogen. At  $800^{\circ}\text{C}$  the argon/hydrogen mix was introduced and the nitrogen flow reduced. The furnace was held at  $1000^{\circ}\text{C}$  for 30 min, after which it was cooled at  $5^{\circ}\text{C min}^{-1}$ . At  $750^{\circ}\text{C}$  the reducing gas flow was stopped and the tube purged with nitrogen. A flow of nitrogen was maintained across the specimens until the furnace temperature was below  $400^{\circ}\text{C}$ , this ensured that the specimens remained in the reduced state. Specimens were reoxidized in air at  $1000^{\circ}\text{C}$  for 1 h, with heating and cooling rates of  $5^{\circ}\text{C min}^{-1}$ .

## 2.3. Measurements and observations

Anode specimens were dimensioned and weighed before and after reduction and again after reoxidation. A micrometer was used for the thickness measurements, and a computer-based image analysis package was used to determine the area, from which the specimen volume was calculated. The change in weight and volume after reduction was noted, as was the variation of the final oxidized state from the original state.

The electrolyte surfaces were observed using optical microscopy between all the stages of the experiment to look for changes or damage appearing. All specimens were observed to look for macroscopic changes such as cracking or warping.

## 2.4. Electrochemical testing

Several of the bilayers had cathodes of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  applied and were tested electrochemically. The tests assessed

Table 1  
Weight changes in the anode with reduction and oxidation

Specimen	% weight loss after reduction	% weight gain after reoxidation	% difference between final and initial weight
1	11.0	11.7	-0.51
2	11.9	10.5	-2.7*
3	11.7	12.4	-0.77
4	11.1	12.4	-0.14
5	11.4	13.2	+0.38
6	12.2	13.6	-0.33

\* Large weight loss due to material loss.

Table 2  
Volume changes in the anode with reduction and reoxidation

Specimen	% volume change on reduction	% volume change on reoxidation	% variation of the final volume from the original volume
1	-2.6	+12.1	+9.1
2	-0.36	+7.4	+7.0
3	-2.2	+5.8	+3.4
4	-4.4	+9.0	+3.8
5	-3.0	+8.4	+5.3
6	-3.2	+2.4	-0.8

the open-circuit voltage (OCV) and  $I$ - $V$  performance of the cells both on initial start-up and on restart after the anode had been allowed to reoxidize. The fuel used was 5% hydrogen in 95% argon humidified by bubbling through water at room temperature, with air as the oxidant. Tests were carried out between  $850$  and  $900^{\circ}\text{C}$ .

## 3. Results

### 3.1. Weight and volume changes

Table 1 shows the variations in anode weight after reduction and reoxidation. The percentage loss on reduction agrees well with the calculated weight loss of around 12% for an anode with a nickel oxide content of 56 wt.%. It is also evident that upon reoxidation the weight returned to within 1% of its original value, which would indicate that a complete and reversible reaction is taking place in the furnace. It is suspected that specimen No. 2 had a small amount of material loss at some point after its reoxidation.

It can be seen from Table 2 that the volume changes associated with the reduction and oxidation cycles show a greater variation than the weight changes. However, one trend does seem evident, and that is that the volume increase on reoxidation is greater than the volume decrease was during reduction. This is true in all but one case, and, in general, leads to a net gain in volume over a reduction/oxidation cycle.

### 3.2. Microscopic examination

Micrographs of the surfaces of the electrolyte film are shown in Fig. 1. From the micrographs it can be seen that there is very little difference between the surface of the as-sintered assembly (Fig. 1(a)) and the surface of an electro-

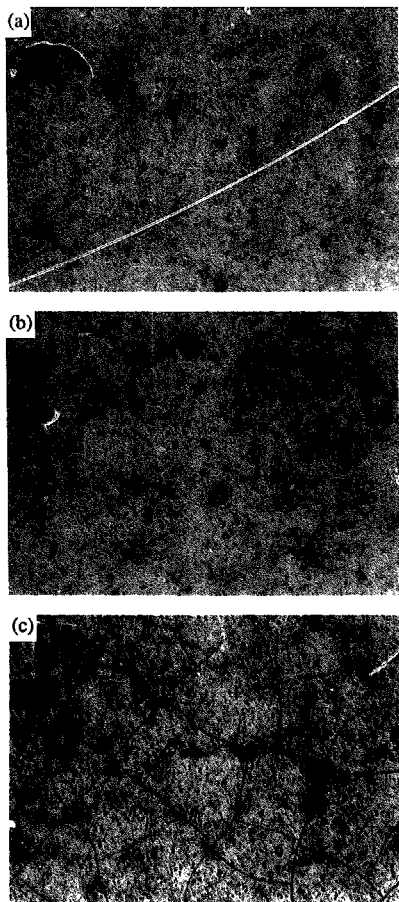


Fig. 1. Micrographs of the electrolyte surface with the supporting anode in various states of oxidation: (a) anode in the as-sintered conditions; (b) reduced anode ( $\times 200$ ), and (c) reoxidized anode ( $\times 100$ ).

lyte after anode reduction (Fig. 1(b)). This indicates that the anode has sustained no major damage during the reduction. However, after the anode has been reoxidized (Fig. 1(c)) extensive cracking is visible on the electrolyte surface, indicating that the reoxidation is the damaging step.

In other observations warping of the anodes and bilayers after reoxidation was noted, although no warping was noted after the initial reduction. This again indicates that significant changes have taken place either between reduction and reoxidation or during reoxidation itself.

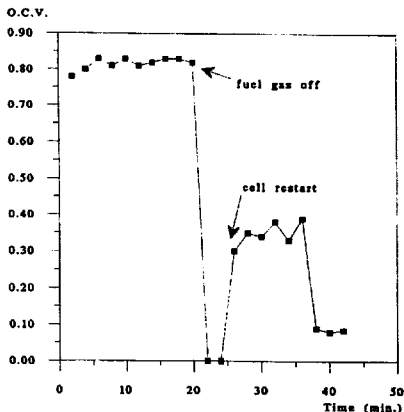


Fig. 2. Open-circuit voltage vs. time showing the effects of anode reoxidation.

### 3.3. Electrochemical testing

Cells were tested at  $850^{\circ}\text{C}$ , and they produced  $125\text{ mA cm}^{-2}$  at  $0.5\text{ V}$ ; the OCV was  $0.83\text{ V}$ . It must be recognized that the electrolyte films used in these experiments have not yet been optimized for density and so leakage is present, resulting in the low OCV. Target OCV for cells in these conditions are around  $1.0\text{ V}$ .

Fig. 2 shows the change in OCV of a cell before shut-down and restarted after the anode was allowed to reoxidize. As can be seen, after the restart the OCV is considerably lower than the initial value. This indicates that substantial leakage has been initiated during the shut-down and restart, and agrees with the cracking observed in Fig. 1(c). The lower OCV was unstable and soon collapsed. On removal from the test rig all the tested cells had fractured into many pieces, this again being in agreement with the observations of warping on reoxidation. In the test rig, the cell is held between two platens, and with its movement being restricted it will fracture instead of warping.

## 4. Discussion

From the observed results it has been shown the initial reduction of the nickel oxide on cell start-up does not seem to damage the cell. The critical step in so far as inflicting damage is concerned seems to be the reoxidation of a reduced anode, in particular the net increase in volume associated with this reoxidation. The cause of this increase may be nickel redistribution within the anode while in the metallic state. It is known that nickel will sinter readily at current fuel cell operating temperatures [4], and the evidence points to this

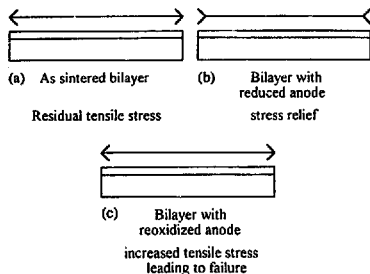


Fig. 3. Diagram of changes in the electrolyte during reduction and reoxidation.

as being the cause of the changes that lead to the damage in the cell.

During the preparation of the anode, the zirconia and the nickel oxide are milled together in a high energy planetary ball mill. This results in a very fine distribution of nickel oxide in the zirconia in the sintered anode. When the nickel oxide is reduced, the volume change that occurs is spread throughout the anode, and the zirconia can withstand the changes taking place in the small nickel oxide particles. The measured volume change is therefore quite small as it is supported by the zirconia. While in the metallic state the nickel may sinter, and coalesce into a coarser distribution of larger particles. Upon reoxidation of the nickel, the volume change occurring in the larger particles cannot be supported by the zirconia, and so the volume change is greater than when it was on reduction. This results in an increase in volume relative to the initial volume of the anode.

The scatter shown in the volume measurements indicate a non-uniform process, and this would support the argument that nickel sintering is active within the anode. The sintering would essentially be a random process controlled by many factors, such as the initial nickel oxide distribution, amount of anode porosity, and pore size distribution. The amount of net volume increase would be related to the amount of sintering that had taken place in the anode, and since the sintering

is a highly variable process, then it is reasonable to assume that the net increase in volume will also be variable. This is reflected in the wide scatter of results obtained.

There may even be a case for suggesting that the initial reduction is beneficial to the electrolyte. In the as-sintered state the electrolyte contains considerable residual tensile stresses (Fig. 3(a)). Depending on the ability of the electrolyte to creep at the reduction temperature, the volume loss may allow some stress relief. It may also close any fine cracks that are present (Fig. 3(b)). On reoxidation however, the volume increase places the electrolyte under an increased tensile stress, exceeding the elastic limit of the zirconia and causing cracking (Fig. 3(c)).

## 5. Conclusions

The findings from this study can be summarized as follows.

1. The volume change associated with the initial reduction of the nickel does not appear to damage the supported electrolyte.
2. Upon reoxidation of the cermet there is an increase in volume to a level greater than the original volume. This net increase has a catastrophic effect on the electrolyte integrity.
3. The results suggest a reason for this volume increase could be sintering of the nickel while in the reduced state into larger particles whose volume change on oxidation cannot be supported by the zirconia.
4. When an electrolyte is supported on a nickel cermet anode, reoxidation of the nickel after the initial start-up should be prevented to avoid damaging the cell.

## References

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