EVALUATION OF PEN STRUCTURES INCORPORATING SUPPORTED THICK FILM Ce₀.₉Gd₀.₁O₁.₉₅ ELECTROLYTES

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ABSTRACT

Thick film (~10μm) CGO electrolytes have been deposited on porous anode substrates, and the PEN assembly completed by the addition of duplex LSCF cathodes. Incremental improvements to the processing procedures have produced PEN structures with improved performances but the area specific resistivity (ASR) values (~1.5 Ωcm² at 600°C) were higher than expected. Accordingly the associated power densities, using air and H₂/H₂O (97/3) supplies, were around 0.1 Wcm⁻² at 600°C. Analysis of the I-V data suggests that the principal problem is associated with high ASR values for the thick film electrolytes which is attributed to the dissolution of water produced at the anode and a consequent reduction in the oxygen vacancy concentration.

INTRODUCTION AND EXPERIMENTAL

Excellent results (1,2) were reported for PEN structures incorporating self-supported Ce₀.₉Gd₀.₁O₁.₉₅ electrolytes (115μm thick), Ni-ZrO₂ (CeO₂ wash-coat) anodes, and La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋ₓ (LSCF) cathodes, at the 4th Intl. SOFC Symposium at Yokohama (June,1995) by a collaborative programme involving ECN and Imperial College. With air as the oxidant and H₂/H₂O (97/3) fuel, power densities as high as 0.45 Wcm⁻² at 700°C and 0.21 Wcm⁻² at 600°C were recorded.

In principle, therefore, even greater power densities should be possible at 600°C if the electrolyte resistance could be reduced by using electrode supported thick film (~10μm) CGO structures. This was the approach adopted by Imperial College, and preliminary results (0.07 Wcm⁻²) at 600°C have already been reported (3). Details of the experimental procedures were described in this reference and can be summarised as follows. Thick film CGO electrolyte powder (Rhone-Poulenc) was deposited from tape-cast slurries onto NiO-ZrO₂ anode substrates supplied by ECN, and the bi-layer sintered at 1300°C. This procedure yielded dense impermeable 10μm thick CGO electrolyte layers which adhered well to the anode substrate. A duplex cathode layer was fabricated...
by initially depositing a thin layer (<1μm) of almost dense LSCF onto the electrolyte using electrostatic spray pyrolysis (ESP), followed by a heat treatment for 2 hours at 650°C. A thicker (~30μm) porous layer of A-site deficient LSCF powder (SSC) was next deposited from a tape-cast slurry and the whole assembly sintered at 900°C. The rationale, and evidence, for the improved performance of this duplex cathode structure has already been reported (4,5,6,7,8). For evaluation of the I-V characteristics the PEN assembly was sealed to the end of an AISI 446 ferritic stainless steel tube using a glass seal (Corning glass 8190).

Incremental improvements to the experimental procedure have to date (Dec. 1996) resulted in a structure capable of producing 0.17Wcm⁻² at 650°C and 0.1W at 600°C as shown in Fig.1. The present contribution is principally concerned with an analysis and interpretation of these performance data.

**INTERPRETATION OF I-V DATA**

The development of electronic conductivity in CeO₂ based electrolytes exposed to the low oxygen partial pressures prevailing at the anode is well documented (9,10), and can be attributed to the following reaction:

\[ O_2^- + O_2 \rightarrow 2O^- + 2e^- \]

Initial attempts (9,10,11,12) to model the I-V characteristics of mixed conducting electrolytes assumed completely reversible electrode behaviour. However, the original expressions of Riess (9) have been modified by Godickemeier, Sasaki, Gauckler, and Riess (13,14,15) to take electrode polarisation into account. It should be noted that even under OCV conditions electrode polarisation can occur as the electronic leakage current will allow a flux of oxygen through the PEN structure which will produce polarisation losses in the cathode and anode, thus further reducing the OCV value.

In order to take electrode polarisation into account GSGR introduced empirical electrode resistivity parameters which were derived from current interruption techniques assuming relevant rate-determining electrochemical behaviour (e.g. Tafel or adsorption kinetics). By adopting appropriate values for the electrode parameters it was possible using this approach to reproduce the general features of the I-V characteristics of PEN structures incorporating CeO₂ based electrolytes.

However it is still possible to model the I-V behaviour in the absence of experimental electrode polarisation data by assuming, for example, that the electrode resistivities are essentially ohmic (i.e. constant) at least for small overpotentials (<100mV). This assumption can also be justified using the approach of Steele (4) which
uses oxygen exchange data to model electrode kinetics. More complicated expressions (e.g. Tafel law behaviour) can also be introduced, if required, to interpret the experimental data.

The symbols used in the present paper can be identified in Fig.2 which represents the cross-section of a PEN structure.

The Nernst voltage, $V_n$, will be determined by the oxygen partial pressures, $P(l)$, $P(h)$, imposed at the external surfaces of the anode and cathode, respectively, by the fuel and oxidant supplies. The observed cell voltage, $V_{mc}$, generated by the mixed conducting electrolyte will be determined by the magnitude of the electronic leakage current, $j_e$, and the actual oxygen partial pressures established at the anode/electrolyte interface $P(a)$, and cathode/interface $P(c)$, after allowing for the electrode polarisation losses arising from the electrode ASR values, $R_a$, $R_c$. The quantity, $j_o$, is the oxygen ion current passing through the electrolyte exhibiting an ion ASR value of $R_j$, which is essentially constant at a fixed temperature, and independent of the voltage generated across the electrolyte. The value of $R_j$, which represents the total ionic resistivity (i.e. includes the grain boundary contribution) can be calculated from the following expression derived from measurements on dense pellets of CGO fabricated from powders supplied by Rhone-Poulenc:

$$\sigma_j T = 4.27 \times 10^5 \exp(-0.74/kT) \text{ S cm}^{-1} \text{ K} \quad [1]$$

The magnitude of the electronic conductivity is a function of both temperature and oxygen partial pressure. The following expression (16) was obtained by evaluating relevant data in the literature:

$$\sigma_e T = 3.55 \times 10^8 \exp(-2.25/kT) P_{O_2}^{-1/4} \text{ S cm}^{-1} \text{ K} \quad [2]$$

By combining equations [1] and [2], the following equation for $P(-)$, which is the oxygen partial pressure at which $\sigma_i = \sigma_e$, can be obtained:

$$\ln P(-) = 4 \ln \left( \frac{\sigma_e}{\sigma_i} \right) - 4(E_e - E_j)/kT$$

i.e. $\ln P(-) = 4 \ln (8.31 \times 10^2) - 4(1.51)/kT$

Following Riess (9),

$$V_{mc} = V_n - j_e R_i$$, where $V_n =$ Nernst voltage, and $R_i =$ ionic resistivity

$$j_e = \frac{(\sigma_e \text{ at } P_o/L)(V_n - V_{mc})}{(\text{Exp}(F/RT*V_{mc}) - 1)(1 - \text{Exp}(-F/RT*(V_n - V_{mc})))},$$
The above equations were derived assuming reversible electrodes (i.e. $R_a = R_e = 0$). In reality the electrode resistances will be finite, and the presence of ionic and electronic currents even under OCV conditions will produce overpotentials so that the oxygen partial pressures $[P(a), P(c)]$ imposed at the electrolyte/electrode interfaces will not be the same as the external oxygen partial pressures $[P(l), P(h)]$. As the electrodes are good electronic conductors then overpotentials due to the electronic current under OCV conditions can usually be neglected. It is necessary, however, to take into account overpotentials due to oxygen fluxes (ionic currents) through the electrodes. Using this approach,

\[
\sigma_e \text{ at } P_e = \sigma_{ij}(P_e/P_c)^{1/4}
\]

\[
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\[
V_{mc} = V_{th} - j_f R_i \text{ where } V_{th} = V_n - j_f (R_a + R_c)
\]

i.e. \[
V_{mc} = V_n - j_f (R_i + R_a + R_c)
\]

\[
 j_e = \frac{(\sigma_e \text{ at } P_e)/L \cdot (V_{th} - V_{mc}) \cdot (\text{Exp}(F/RT \cdot V_{mc}) - 1)/\text{Exp}(F/RT \cdot (V_{th} - V_{mc}))}{1 - \text{Exp}(-F/RT \cdot j_f R_i)}
\]

\[
j_e = \frac{\sigma_{ij} \cdot (P_e - \text{Exp}(-4RT/F(V_{th} + j_f R_c)))^{1/4}}{1 - \text{Exp}(-F/RT \cdot j_f R_i)} \cdot \text{Exp}(F/RT \cdot (V_{th} - V_{mc}) - 1)
\]  \[3\]

Note: under OCV conditions $j_e = j_f$, and so the above equation can be solved.

**ANALYSIS OF I-V CHARACTERISTICS AT 600°C**

Self-supported CGO Electrolyte

Data (1,2) obtained with the following 5x5cm PEN structure,

\[
\text{LSCF/Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95(115\mu m)}/\text{Ni-ZrO}_2 \text{ (CeO}_2\text{)},
\]

supplied with air and $H_2/H_2O(97/3)$ were initially analysed. The flow rates of these gases were very high ($375\text{ml.min}^{-1}$) resulting in low conversion rates, and thus the assumption of constant values for the imposed oxygen partial pressures at the external surfaces of the electrodes is a reasonable approximation. The only unknown values in expression [3] are ASR data ($R_a, R_c$) for the two electrodes. However to reproduce the main features of the data it was necessary to assume that $R_a = R_c = 0.3\Omega\text{cm}^2$, and a modified value (1.0\$\Omega\text{cm}^2$) for the electrolyte resistivity. This value is approximately double the value (0.438\$\Omega\text{cm}^2$) calculated from expression [1].

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The calculated I-V curve is shown in Fig.3, which also incorporates the value (130mAcm\(^{-2}\)) for the electronic leakage current under OCV conditions.

**Electrode-supported Thick Film (10\(\mu\)m) CGO Electrolyte PEN Structure**

Assuming total electrode resistivity values of 0.5\(\Omega\)cm\(^2\) (i.e. \(R_a = R_c = 0.25\Omega\)cm\(^2\)) and the modified ionic conductivity value (\(\sigma_i = 0.0115\text{Scm}^{-1}\)) used in Fig 3, the calculated I-V characteristics at 600°C for an electrode supported thick film (10\(\mu\)m) CGO electrolyte PEN structure are depicted in Fig. 4. Attention is drawn to the relatively low OCV (0.77V), and large electronic leakage current (610mAcm\(^{-2}\)) at zero total current (i.e. OCV). However in principle it is still possible to generate power densities greater than 0.5Wcm\(^{-2}\), assuming of course that the electrode structures can sustain the high current densities generated by the very large leakage currents.

Our own experiments with anode supported thick film (10\(\mu\)m) CGO PEN structures indicate lower power densities (around 0.1 Wcm\(^{-2}\) at 600°C), but with higher OCV voltages (typically 0.82V), and typical I-V results are incorporated in Fig 4 for comparison. The shape of the experimental curve is different (see Fig.4), and the cell ASR values (eg 1.5\(\Omega\)cm\(^2\) at 600°C) are much higher than predicted (0.587\(\Omega\)cm\(^2\)). The only way to model these results was to assign a relatively high value (~1\(\Omega\)cm\(^2\) instead of 0.087\(\Omega\)cm\(^2\), that is approx. 10x higher) to the electrolyte resistivity. Assigning higher values to the electrode resistivities depressed the OCV voltages much below those recorded, and was rejected as the likely explanation as the characteristic horizontal portion of the curve, which is diagnostic for electronic leakage, was also suppressed, suggesting a much reduced electronic leakage current due to a higher electrolyte resistivity.

Initially it was considered that the high resistivities were due to contamination of the grain boundaries by compounds such as Gd\(_2\)NiO\(_4\), Gd\(_2\)Zr\(_2\)O\(_7\), produced during the high temperature sintering operation when the CGO electrolyte was in contact with the NiO-ZrO\(_2\) anode. Elemental mapping in the SEM provided some support for this interpretation as these elements were indeed located within the CGO electrolyte but their distribution indicated a general low level contamination rather than a specific concentration at the grain boundaries. Investigations into anode kinetics by Kiratzis et al (18) however lead to an alternative explanation. During AC impedance measurements at 475°C it was observed that the increase in total conductivity at low oxygen partial pressures which is associated with the formation of electronic charge carriers due to the reduction of Ce\(^{4+}\) did not follow the expected \(P_{O_2}^{-1/4}\) dependence which is well documented in the literature. Instead the variation in conductivity exhibited a \(P_{O_2}\) relationship around -0.15 (i.e. -1/6 or -1/7). This and other observations that the conductivity appeared to be a function of the \(P_{H_2O}\) imposed at the anode led to the
realisation that probably protons were being inserted into the CGO at low temperatures according to the reaction,

\[ V_o^- + H_2O \Rightarrow O_o^2 + 2H \]  \[4\]

Such reactions were known to occur in acceptor- doped perovskites, such as SrCe\(_{0.95}\)Gd\(_{0.05}\)O\(_{3-x}\), but the influence of dissolved water in acceptor-doped fluorite structures was generally considered to be insignificant.

The following defect reaction was considered to represent the situation at low Po\(_2\) partial pressures established by H\(_2\)O/H\(_2\) equilibria (i.e. anodic conditions):

\[ Gd_2O_3 + 2H_i \Rightarrow 2Gd^{3+} + O_o^{2-} + 3V_o^- + 2e^- + H_2O + \frac{1}{2}O_2 \]  \[5\]

Using this expression it can be shown that \( \sigma_n \propto (Po_2)^{-1/7} \), in accordance with the experimental observations.

Further work is in progress to quantify the concentration of water dissolved in CGO at low temperatures, and our results do demonstrate that dissolution of water and filling of the oxygen ion vacancies can account for the high electrolyte resistivities required by the modelling calculations to interpret the I-V behaviour of the thick film PEN structures.

Although the results are not given here, a cathode supported CGO film cell was also prepared for comparison with the anode supported cell. The performance at 600°C using the same moist H\(_2\)/CO\(_2\) fuel was almost equivalent, with an OCV of approximately 0.75 V and a cell resistance of 1.6 \( \Omega \) cm\(^2\). The investigations on the cathode supported cell allowed the Ni-ZrO\(_2\) cermet anodes to be replaced by Pt anodes. This ensured that the high cell resistances recorded in the I-V experiments could not be assigned to the formation of an interfacial layer of NiO arising from the large leakage flux of oxygen ions.

It may be concluded therefore that the combination of water dissolution in the thick films, and electrode polarisation due to electronic leakage currents combine to make the technological application of thick film IT-SOFC improbable, as it appears impossible to exploit the wider ionic domain predicted at 500°C. It appears that the electronic/ionic leakage currents associated with thick film electrolytes will always allow relatively high water vapour partial pressures to be generated at the electrolyte/anode interface thus ensuring that the concentration of anion vacancies will be significantly reduced.
CONTROL OF ELECTRONIC LEAKAGE CURRENTS

To avoid the large electronic leakage currents associated with thick film CGO assemblies (see Fig 4) the CGO can be replaced by anode supported thick film La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$ (LSGM) electrolyte PEN structures, or a thin layer of LSGM can be deposited on the anode side of the CGO PEN structure to block the electronic current (19). However dissolution of water is also likely to occur in LSGM at low temperatures (~600°C) resulting in increased electrolyte resistivities, although the water vapour partial pressures may be reduced at the anode/electrolyte interface. Indeed it appears that the use of acceptor doped electrolytes for fuel cell applications below about 600°C is unlikely to be successful.

Thick film GCO electrolyte PEN structures deposited on ferritic stainless steel are mechanically tough and likely to be satisfy the thermal shock requirements required for small scale CHP and electric vehicle applications (cf. zirconia thermal barriers on turbine blades), and so it would still be advantageous to reduce the electronic leakage characteristics of these structures. The effect of reducing the P(-) value is modelled in Fig. 5, and some success in this direction will be reported (18). Thick film PEN structures incorporating modified CGO now require to be scaled-up to determine whether SOFC units incorporating ceria based electrolytes have a viable commercial future.

CONCLUSIONS

Power densities of around 0.2Wcm$^{-2}$ have been obtained at 600°C using self-supported CGO electrolytes but so far it has not been possible to demonstrate the higher power densities anticipated for thick film PEN structures at these temperatures. Interpretation of the thick film I-V results suggests that the resistivities of the thick film CGO electrolytes are very high probably due to the dissolution of water arising from the high water vapour partial pressures generated at the anode/electrolyte interface due to the large electronic/ionic leakage currents. Future technological applications of thick film CGO PEN structures will require development strategies that minimise the electronic leakage current, either by depositing electronic blocking layers (e.g. LSGM), or using additives to control the level of the electronic current.

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Figure 1. Current-voltage performance of the anode-supported cell with Pd-promoted cathode at 550°C-650°C under moist H₂/CO₂ fuel

Figure 2. Schematic diagram of mixed conducting PEN structure
Figure 3. Modelling of current-voltage performance (L = 115 μm)

Figure 4. Modelling of current-voltage performance (L = 10 μm)

Figure 5. Modelling of current-voltage performance (L = 10 μm, low P(-))

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