

Fuel reforming and electrical performance studies in intermediate temperature ceria–gadolinia-based SOFCs

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Accepted 24 November 1999

Abstract

The methane reforming and carbon deposition characteristics of two nickel/ceria–gadolinia cermet anodes have been studied over the temperature range 550–700°C, for use in intermediate temperature ceria–gadolinia (CGO)-based solid oxide fuel cells (SOFCs), using conventional catalytic methods and temperature-programmed spectroscopy. The electrical performance and durability of planar CGO-based SOFCs with a 280- μ m-thick CGO electrolyte, screen printed cathode and different screen printed nickel/CGO cermet anodes have been studied over the temperature range 500–650°C. Temperature-programmed reduction has been used to study the reduction characteristics of the anodes, and indicates the presence of “bulk” NiO particles and smaller NiO particles in intimate contact with the ceria. Both anodes show good activity towards methane steam reforming with methane activation occurring at temperatures as low as 210°C; steady-state steam reforming of methane was observed using a methane-rich mixture at 650°C, with 20% methane conversion. Post-reaction temperature-programmed oxidation has been used to determine the amount of carbon deposited during reforming and the strength of its interaction with the anode. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: SOFCs; Reforming; Ceria; Anode; Fuel; Methane

1. Introduction

Solid oxide fuel cells (SOFCs) offer possible advantages over other fuel cell systems because the high operating temperature gives flexibility in the choice of fuel. In particular, it allows an option for operating the cell directly on natural gas or other hydrocarbon fuels, internally reforming the fuel within the fuel cell [1]. There are several major operational problems associated with routinely operating SOFCs on hydrocarbons. Carbon deposition on the anode at the high operating temperatures can be problematic and can lead to deactivation, loss of cell performance and poor durability. There are still relatively few catalytic and spectroscopic studies of SOFCs which have used hydrocarbons directly; the majority of studies still use hydrogen as the fuel. Many have focused on the electrical performance of the fuel cell, determining the influence of electrode composition, structure and other process parameters in terms of current densities [2–4], or have concentrated on important aspects of materials development.

The vast majority of SOFC studies use yttria-stabilised zirconia as the solid electrolyte [1,5,6], which necessitates an operating temperature of 700–1000°C in order for acceptable power densities to be achieved. Ceria–gadolinia (CGO) is an alternative electrolyte material which offers the possibility of lower temperature SOFC operation, in the range 500–650°C [7–10]. It could reduce demands on other components within the SOFC, particularly the interconnect, and hence reduce costs [9,10]. As noted above, there are relatively few studies of the catalysis and surface chemistry associated with internal reforming in SOFCs [11–14]. This is particularly true of CGO-based SOFCs, where there is almost a total absence of studies using fuels directly.

Internal reforming of methane over nickel/zirconia cermet anodes in zirconia-based SOFCs has been reported previously. The electrochemical performance and durability of tubular zirconia SOFCs have been described over the temperature range 750–900°C [13–16]. That work reported the test system developed to study the fuel reforming catalysis and surface reaction pathways in SOFCs operating on methane [17–19]; it investigated the anode reduction characteristics, methane activation, methane steam

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reforming and the nature and extent of carbon deposition on the anode [12–16].

A study of intermediate temperature CGO-based SOFCs is now described. The electrical performance and durability of planar ceria-based SOFCs with different nickel/ceria cermet anodes have been studied over the temperature range 500–650°C using a test system purposely-built for carrying out electrochemical measurements on planar SOFC test samples. Methane reforming has been studied using nickel/ceria anodes over the relevant SOFC operating temperature range of 550–700°C. The influence of operating temperature and anode formulation on the fuel utilisation, reforming activity and carbon deposition have been studied using steady-state catalytic measurements and by temperature-programmed spectroscopy. Temperature-programmed reduction (TPR) has been used to study the reduction characteristics of the nickel/ceria anodes; temperature-programmed reaction spectroscopy (TPRS) has been used to investigate methane activation and the surface reaction pathways occurring as a function of steam reforming temperature. Temperature-programmed oxidation (TPO) has been used to determine the amount of carbon deposition on the anode during reforming and the strength of the interaction of the carbon with the anode.

2. Experimental

2.1. Preparation of SOFC test samples and anode powders

CGO-based SOFC test samples were prepared by viscous plastic processing of the ceria–10% gadolinia (Rhodia) solid electrolyte to form small circular discs 45 mm in diameter and 280 μm thick. These were subjected to a two-stage firing process, firstly to 1400°C using a specific firing procedure, before cooling to room temperature and subsequent firing to 1500°C. The electrodes were applied by screen printing. A single anode layer 35 μm thick and 2.7 cm^2 was printed and dried in air at room temperature before being fired to 1200°C using a specific firing procedure. A two-layer cathode was used, the first layer being 70 mol% lanthanum strontium ferric cobaltite (LSCF), $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (Rhodia) and 30 mol% CGO (Rhodia), with a pure LSCF second layer, each layer being 35 μm thick. The test sample was fired to 1150°C following application of the first cathode layer, and again to 1150°C following application of the second layer, using the same specific firing procedure in each case.

Two nickel oxide–CGO cermet anodes have been used in this work. One anode was a commercial anode obtained from Praxair, and had a composition of 85 mol% NiO/15 mol% CGO. The second anode was prepared by physically mixing nickel oxide (Novamet) with coarse and fine CGO powder (Rhodia). The anode had a composition of 75 mol% NiO/25 mol% CGO. The two anodes were then slurried in a screen medium (Cookson Matthey) and either

screen printed onto the CGO electrolyte to produce the SOFC test samples, or dried in air at 50°C before being fired to 1200°C. An identical firing procedure was employed to the one used for the anodes screen printed onto the CGO electrolyte, to form the powders used in the catalytic experiments.

2.2. Fuel reforming experiments and SOFC catalysis test system

The catalytic experiments were carried out using the SOFC test system developed in this laboratory [17–19]. The apparatus consisted of a furnace operated by a temperature controller which allowed linear temperature control. The reactor inlet was linked to a stainless-steel gas manifold which allowed complete flexibility in gas handling, gas composition, the choice of fuel and fuel/steam ratio, enabling study of a wide range of operating conditions and fuel compositions. The reactor outlet was linked via a heated gas sampling system to an on-line mass spectrometer (Leda-Mass Satellite) which permitted the internal reforming catalysis to be continuously monitored, and the surface chemistry occurring at the anode to be investigated using temperature-programmed spectroscopy.

After firing, the powdered anode samples were loaded into the catalytic reactor and reduced in flowing hydrogen for 1 h at 923 K. Steady-state methane steam reforming was carried out by passing a methane/steam mixture over the reduced anode at reaction temperature. TPO was used to characterise the nature and quantity of deposited carbon following each reforming experiment. Temperature-programmed methane steam reforming experiments were carried out by subjecting the pre-reduced sample to a temperature ramp of 10 K min^{-1} up to 1173 K under a flow of the reforming mixture. TPR and TPO measurements were carried out using a heating rate of 10 K min^{-1} , in 10% H_2/He and 10% O_2/He mixtures, respectively.

2.3. Cell performance studies and SOFC electrochemical test system

The electrochemical performance and durability of the SOFC samples were studied in a specially designed test system developed in this laboratory. The system will be described in detail elsewhere [20]. The system consisted of a high temperature stainless-steel housing which accommodated the 50-mm diameter planar test samples. The anode and cathode compartments of the cell housing were fed by stainless-steel manifolding, which allowed a controlled flow of fuel to the anode compartment and air to the cathode compartment. 10% H_2/N_2 , which passed through a water saturator, was used as the fuel and bottled air was used as the source of oxygen for the cathode. Flow rates of 150 ml min^{-1} of H_2/N_2 and 100 ml min^{-1} of air were used. The stainless steel housing was enclosed in a custom-built furnace (Lenton), which allowed precision

linear temperature control up to 1000°C. Current collection was achieved by platinum meshes pushed into contact with the two electrodes. The Pt meshes were then connected via Pt leads to an electrochemical interface (Solartron 1286 EIS), which allowed electrochemical impedance spectroscopy measurements to be carried out, in addition to current/potential measurements.

3. Results

3.1. Temperature-programmed reduction

TPR was used to study the anode reduction characteristics. The Praxair 85 mol% NiO/ceria anode showed a sharp reduction maximum at 610 K and a broader reduction peak at 813 K, whilst the 75 mol% NiO/ceria anode showed very similar reduction characteristics, with reduction maxima at 606 and 818 K. Reduction of a 10% NiO/ceria sample, prepared by wet impregnation of an aqueous solution of nickel (II) nitrate, also showed two reduction maxima, at 688 and 765 K [21].

3.2. Temperature-programmed methane steam reforming

Temperature-programmed methane steam reforming measurements were carried out on the pre-reduced anode samples using a 5:1 methane/steam gas mixture. Over the Praxair Ni/ceria anode, product formation, indicating methane activation and the onset of methane reforming, was observed at 482 K. The rate of methane steam reforming increased with temperature, with a sharp increase in syn gas production occurring above 900 K. Over the in-house 75 mol% Ni/ceria anode, the onset of methane reforming occurred at 548 K. Again, methane conversion increased with temperature, with a sharp increase occurring above ~ 910 K.

Following each temperature-programmed methane steam reforming experiment, a TPO measurement was carried out to determine the amount of carbon deposition through

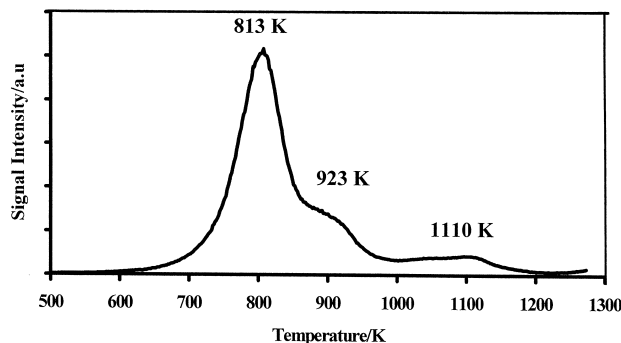


Fig. 1. Temperature-programmed oxidation of a Praxair 85 mol% Ni/CGO anode following temperature-programmed methane reforming in a 5:1 methane/steam mixture to 1173 K.

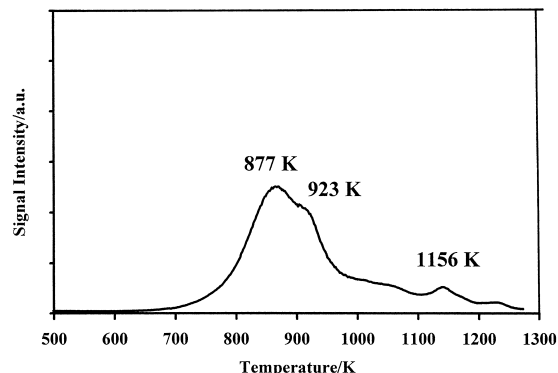


Fig. 2. Temperature-programmed oxidation of a 75 mol% Ni/CGO anode following temperature-programmed methane reforming in a 5:1 methane/steam mixture to 1173 K.

methane decomposition and CO disproportionation (Boudouard reaction), as well as its strength of interaction with the anode. Figs. 1 and 2 show the TPO spectra following temperature-programmed methane steam reforming in a 5:1 methane/steam mixture over the Praxair Ni/CGO anode and the in-house 75 mol% Ni/CGO anode, up to 1173 K. Both spectra show three distinct CO₂ desorption maxima, corresponding to carbon removal, at 813, 923 and 1110 K on the Praxair anode, and at 877, 923 and 1156 K on the other anode. The principal difference between the two anodes is the temperature and relative intensity of the first CO₂ desorption peak.

3.3. Steady-state methane reforming

5:1 methane/steam mixtures were passed over the pre-reduced Ni/ceria anodes at different reaction temperatures, within the temperature range 550–700°C, to study the reforming characteristics of the two different anodes. The influence of reaction temperature on the methane reforming activity and syn gas selectivity, and the amount of carbon deposition and its strength of interaction with the anode were investigated. Fig. 3 shows the exit gas compo-

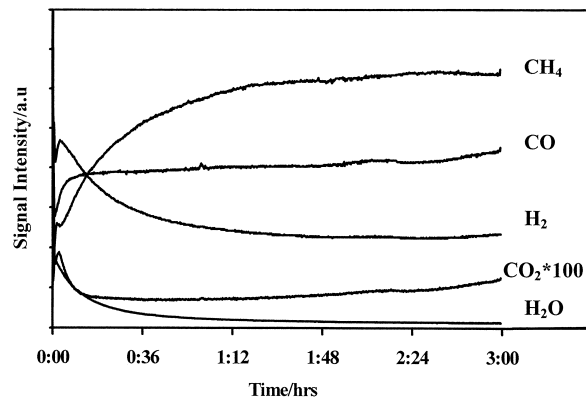


Fig. 3. Exit gas compositions following exposure of a pre-reduced Praxair 85 mol% Ni/CGO anode to a 5:1 methane/steam mixture at 923 K.

sition when the Praxair Ni/CGO anode was exposed to a 5:1 methane/steam mixture at 650°C. Upon introduction of the methane/steam mixture, rapid uptake of methane was observed together with H₂ production and also CO formation. The methane conversion slowly decreased to a steady-state conversion of around 20% after about 90 min. Initially, some CO₂ was also produced, though this rapidly fell to a very low level with high CO selectivity observed.

Fig. 4 shows the corresponding exit gas composition following steam reforming over the 75 mol% Ni/CGO anode under the same experimental conditions. Again, rapid uptake of methane, together with H₂, CO, H₂O and CO₂ formation, is initially observed. However, steady-state methane conversion, of 17%, is reached after only 8 min. Selectivity to CO, although still high, is lower than on the Praxair anode, whilst the H₂/CO ratio is also appreciably higher over this anode. Following each reforming experiment, a post-reaction TPO measurement was carried out to evaluate the nature and level of carbon deposition during reforming at different reaction temperatures. These results will be reported in detail elsewhere [22].

3.4. Cell performance and durability studies

The electrochemical performance of planar CGO-based SOFCs incorporating each anode was studied over the temperature range 500–650°C. Fig. 5 shows the current density/cell potential/power density characteristics for a planar CGO SOFC with a two-layer LSCF/CGO and LSCF cathode and a Praxair Ni/CGO anode, at 600°C using 10% H₂/N₂ as the fuel. The maximum power output observed was 90 mW cm⁻². The same cell was tested for its long term durability and stability to thermal cycling. The cell was tested at 650°C for 100 h, during which time it was cooled down to room temperature and heated back up to 650°C four times. Excellent stability and reproducibility following thermal cycling was observed, with only a 2% decrease in power density observed over 100 h. A test sample with the 75 mol% Ni/ceria, anode performed much less well, showing a much lower power

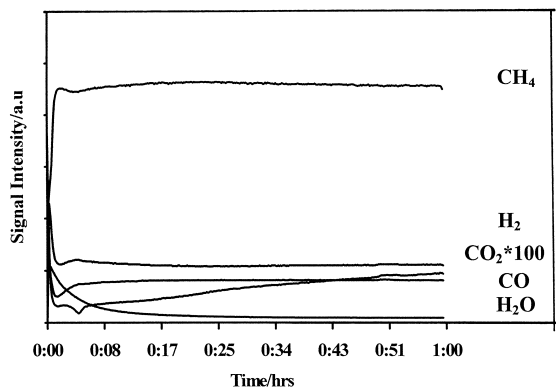


Fig. 4. Exit gas compositions following exposure of a pre-reduced 75 mol% Ni/CGO anode to a 5:1 methane/steam mixture at 923 K.

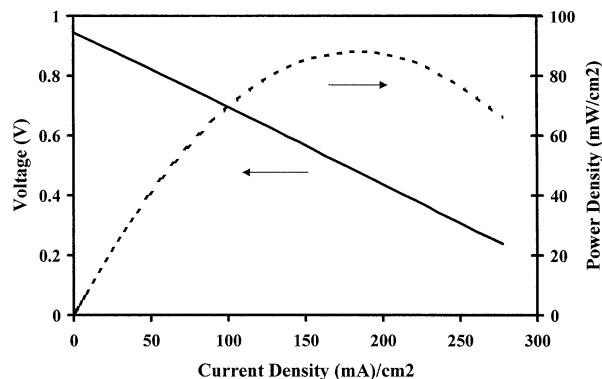


Fig. 5. Current density/potential/power density plot for a planar 280 μm CGO SOFC test sample with LSCF cathode and a Praxair 85 mol% Ni/CGO anode, at 873 K in wet 10% H₂/N₂.

output and poor durability, with a rapid decrease in power output observed over time at 600°C using 10% H₂/N₂ as the fuel.

4. Discussion

4.1. Temperature-programmed reduction

The reduction characteristics of the NiO/CGO anodes are markedly different from those observed for NiO/zirconia cermets, where a single reduction maximum is observed, at 758 K for a 50 vol.% NiO/zirconia cermet and at 707 K for a 90 vol.% NiO/zirconia cermet [17]. The sharp low temperature reduction maximum for the NiO/ceria anodes occurs at appreciably lower temperatures than these (610 and 606 K), whilst the broader higher temperature reduction maximum occurs at significantly higher temperatures (813 and 818 K). Similar reduction profiles have been observed for the reduction of nickel oxide dispersed on high area oxide supports [21,23,24]. The low temperature peak is generally attributed to the reduction of larger NiO particles which are similar in nature to pure bulk nickel oxide, whilst the high temperature reduction peak is attributed to smaller NiO particles in intimate contact with the oxide support. A 10% NiO/CeO₂ catalyst, prepared by wet impregnation of an aqueous solution of nickel (II) nitrate, gave rise to two reduction maxima at 688 and 765 K [21]. Thus, the TPR data can be interpreted in terms of larger “bulk-like” NiO particles and smaller ones which are strongly interacting with the CGO as in a conventional dispersed supported catalyst. This contrasts with the NiO/zirconia cermets studied previously.

4.2. Temperature-programmed methane steam reforming

TPRS measurements show that methane conversion occurs on these anodes at temperatures as low as 482 K in

the case of the Praxair 85 mol% Ni/ceria anode, and at 548 K on our 75 mol% Ni/ceria anode. These temperatures compare very favourably with dispersed nickel catalysts, prepared by wet impregnation, where methane activation through partial oxidation occurs in the temperature range 589–645 K, depending on the support [21]; the onset temperature for reaction on a 10% Ni/CeO₂ catalyst prepared by wet impregnation, is 645 K [21]. The onset of product formation through methane steam reforming over a 20% Ni/Al₂O₃ catalyst, prepared by wet impregnation, is 615 K [25]. On both anodes, CO₂ is the first carbon oxide formed and is the predominant oxide at low temperatures, reflecting the low surface coverage of methane relative to water. Rapid conversion of methane occurs above 900 K and above ~920 K over the Praxair and the in-house Ni/ceria anodes, respectively. Non steady-state conversions were ~40% and ~20% on the Praxair and in-house Ni/CGO anodes, respectively, at 923 K, which corresponds to a realistic operating temperature for CGO-based SOFCs. Almost complete methane conversion was observed above ~1050 K. Over the entire temperature range, the Praxair 85 mol% Ni/CGO anode shows higher activity than our own 75 mol% Ni/CGO anode, but both exhibit excellent activity compared to conventional supported nickel catalysts [21,25] and Ni/zirconia cermet anodes [13,14,16].

4.3. Steady state methane steam reforming

The two anodes show similar steady-state activity in terms of methane conversion, with the Praxair Ni/ceria anodes showing slightly higher activity at 650°C; ~20% conversion compared to ~17% over in-house Ni/ceria anodes. A significant difference between the two anodes under steady-state reforming conditions is the much higher level of CO₂ formed over in-house Ni/ceria anodes. Together with the significantly higher H₂/CO ratio observed, this suggests that the Water Gas Shift Reaction is occurring to a much greater extent on this anode, in addition to slightly increased methane decomposition. Interestingly, steady-state activity was reached within 8 min over in-house anodes compared to ~90 min over the Praxair Ni/ceria anodes. There is a much higher initial H₂, but not CO, production in the latter case, suggesting that methane decomposition occurs readily on this anode upon initial exposure to the steam reforming mixture.

4.4. Carbon deposition

Post-reaction TPO was used to study the carbon deposited on the two anodes during reforming. Following temperature-programmed steam reforming in a 5:1 methane/steam mixture, carbon was removed from in-house Ni/ceria anodes in two principal processes, at 877 and 923 K, as well as a small amount at much higher temperature, 1156 K. These temperatures are very similar

to the carbon removal temperatures observed following methane steam reforming on Ni/zirconia cermet anodes [13,14,16]. However, reforming over the commercial Praxair Ni/CGO anodes under the same conditions results in the majority of the deposited carbon interacting more weakly with the anode, being removed as CO₂ at the significantly lower temperature of 813 K.

4.5. SOFC performance and durability studies

The current density/cell potential measurements obtained for the planar CGO-based SOFC with the Praxair 85 mol% Ni/CGO anode gave a maximum power density of 90 mW cm⁻² at a cell operating temperature of 600°C. The SOFC shows excellent durability and resistance to thermal cycling, with less than a 2% loss of power over 100 h of operation and four cycles of cooling to room temperature and heating to 600°C. The power output was very encouraging considering that the thickness of the electrolyte was 280 μm, comparing favourably with other studies; a power density of 200 mW cm⁻² has been reported for a CGO-based SOFC with an electrolyte thickness of 115 μm, operating at 600°C [10].

The performance of the SOFC sample with the physically mixed 75 mol% Ni/CGO anode was much less favourable, both in terms of power output and durability. The poor performance is attributed to sintering of the Ni particles in the anode on exposure to hydrogen at 600°C, leading to a loss of surface area and deactivation. The factors affecting the poor performance and durability of this anode and the much better performance and durability of the Praxair anode are the subject of a continuing detailed study.

5. Summary

Two Ni/CGO cermet anodes have been characterised and studied for their methane reforming activity. The reduction characteristics indicate the presence of “bulk” NiO particles and smaller NiO particles in intimate contact with the ceria. Both anodes show high activity towards methane steam reforming, with methane activation occurring at temperatures as low as 482 K on a Praxair 85 mol% Ni/CGO anode and 548 K on a prepared 75 mol% Ni/CGO anode; this is lower than the activation temperatures observed on supported nickel catalysts prepared by wet impregnation.

At 650°C, a realistic operating temperature for CGO-based SOFCs, steady-state steam reforming of methane was observed over both anodes using a methane-rich feed, with 20% and 17% methane conversion over the Praxair and in-house anodes, respectively. TPO indicates that, following reforming over the Praxair anode, a majority of the carbon deposited forms a weakly interacting carbon

species. This is removed by oxygen at a significantly lower temperature than from in-house 75 mol% Ni/ceria anode: 813 K compared to 877 and 923 K; this was compared with Ni/zirconia cermet anodes studied previously.

Planar CGO-based SOFCs with a 280 μm thick CGO electrolyte, prepared by viscous plastic processing, a screen printed two-layer LSCF/CGO and LSCF cathode and a screen printed Praxair 85 mol% Ni/CGO anode, gave a maximum power density of 90 mW cm^{-2} at a cell temperature of 600°C. They gave excellent durability over 100 h operation and temperature cycling, with less than 2% loss of power. The same SOFC, but with a prepared 75 mol% Ni/CGO anode, gave poor power output and durability, probably due to the sintering of nickel particles in the anode microstructure.

Acknowledgements

The financial support of the UK Department of Trade and Industry and the Engineering and Physical Sciences Research Council through the Postgraduate Training Partnership Scheme is gratefully acknowledged, as is the Refractories and Industrial Ceramics Committee of CERAM Research.

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