

SOFC system with integrated catalytic fuel processing

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Abstract

In recent years, there has been much interest in the development of solid oxide fuel cell technology operating directly on hydrocarbon fuels. The development of a catalytic fuel processing system, which is integrated with the solid oxide fuel cell (SOFC) power source is outlined here. The catalytic device utilises a novel three-way catalytic system consisting of an in situ pre-reformer catalyst, the fuel cell anode catalyst and a platinum-based combustion catalyst. The three individual catalytic stages have been tested in a model catalytic microreactor. Both temperature-programmed and isothermal reaction techniques have been applied. Results from these experiments were used to design the demonstration SOFC unit. The apparatus used for catalytic characterisation can also perform in situ electrochemical measurements as described in previous papers [C.M. Finnerty, R.H. Cunningham, K. Kendall, R.M. Ormerod, *Chem. Commun.* (1998) 915–916; C.M. Finnerty, N.J. Coe, R.H. Cunningham, R.M. Ormerod, *Catal. Today* 46 (1998) 137–145]. This enabled the performance of the SOFC to be determined at a range of temperatures and reaction conditions, with current output of 290 mA cm⁻² at 0.5 V, being recorded. Methane and butane have been evaluated as fuels. Thus, optimisation of the in situ partial oxidation pre-reforming catalyst was essential, with catalysts producing high H₂/CO ratios at reaction temperatures between 873 K and 1173 K being chosen. These included Ru and Ni/Mo-based catalysts. Hydrocarbon fuels were directly injected into the catalytic SOFC system. Microreactor measurements revealed the reaction mechanisms as the fuel was transported through the three-catalyst device. The demonstration system showed that the fuel processing could be successfully integrated with the SOFC stack. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

A key problem in solid oxide fuel cell (SOFC) development is the integration of the fuel oxidation reactions into the total system. Part of this problem area has already been addressed in catalytic clean-up devices on automobiles [3,4]. Difficulties of warm-up, thermal shock, temperature differentials and life-time had been studied in that application.

Here, the insertion of zirconia tubular cells into a ceramic catalytic reactor is discussed. Hydrocarbon fuels, such as methane and butane, were used. Air was introduced to prevent coking and to enhance fuel reforming. The catalytic supports were commercial cordierite foams and extrusions. The objective was to define catalyst compositions, which would allow integration of the pre-refor-

ming, fuel cell operation and total oxidation at the exhaust, while generating power from the SOFCs.

The catalytic system, outlined effectively, divides total oxidation into three separate stages within an integrated system. The first stage is a partial combustion step or partial oxidation of reactant fuel, for example, methane (Eq. 1):



This exothermic reaction was performed over a Ru catalyst supported on a ceramic substrate. Other workers have shown this to be an active partial oxidation catalyst for methane and other hydrocarbons [5–7]. Carbon deposition, which can deactivate the catalyst over time, can easily occur at this stage. This can be limited by altering the fuel-to-oxidant ratio. When higher hydrocarbons are reacted, such as butane, chain splitting can also occur, producing a mixture of hydrogen, CO, CO₂ and other shorter-chain hydrocarbons.

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The second catalytic reaction took place over the nickel-based SOFC anode electrode, where the high operating temperature of the SOFC enabled a certain amount of in situ fuel reforming when either oxygen or steam was added to the hydrocarbon fuel. This in situ reforming mechanism was also influenced by the load applied to the operating fuel cell. Under electrical load conditions, fuel conversion was increased and carbon deposition could be reduced [1,8]. Both the catalytic and electrochemical reforming mechanisms produced hydrogen and CO for electrochemical oxidation and, thus, power production.

As with many nickel-based catalysts in a carbon-rich reaction environment, carbon deposition can be a problem. Carbon formation on nickel-based electrodes can either encapsulate active surfaces, reducing fuel conversion and hydrogen production to give inferior performance, or form filaments, which force the nickel away from the YSZ support, destroying current pathways, again limiting performance. The addition of molybdenum and cerium metal oxides to nickel-based catalysts has been observed to reduce carbon deposition, and in some cases, increases fuel conversion. CeO_2 and MoO_3 have been observed to promote the catalytic and electrochemical reforming of hydrocarbons [9–12]. These improvements, under load conditions and a variety of reforming conditions, have also been accompanied by a further reduction in carbon deposition, and, thus, CeO_2 and MoO_3 have been added to the nickel-based anodes used in this SOFC system. The ability of both the ceria and molybdenum oxides to exist in a variety of oxidation states promotes oxygen ion exchange through the anode enhancing electrochemical performance and the removal of deposited carbon [10,11].

The third stage of the catalytic process was the total combustion of the remaining hydrocarbon fuel and reaction products to produce the reaction heat for the device, that is, to obtain the correct operating temperature for the SOFCs within the unit. Platinum has been widely used and studied as combustion catalyst for hydrocarbon fuels [13–15]. Platinum is commonly supported on alumina when used as a combustion catalyst and is found to be highly active for alkane combustion, especially when the reaction environment favours reduction. However, platinum has been found to be active on a variety of supports and, due to the thermal expansion limitations of alumina foams, the platinum was supported on a low thermal expansion cordierite foam to prevent cracking and degradation of the burner head. Previous studies have shown that preparation and pre-treatment of platinum combustion catalyst can dramatically influence the observed activity and durability of the catalyst [14].

Other small-scale SOFC systems devised in these laboratories have produced their required reaction heat from catalytic combustion of a hydrocarbon fuel. The relatively fast warm-up times achieved take maximum advantage of the thermal shock properties of the thin-walled zirconia tube design used in this system [16]. However, these

designs only incorporate three to five active cells and, thus, power outputs are low. The aim of this work was to produce a low NO_x catalytic reactor operating in the range of 800–900°C, which could run on a variety of hydrocarbon fuels, in this case methane and butane incorporating an integrated pre-reforming and viable SOFC system in the 7–10 W range. Possible applications of this technology indicate combined heat and power (CHP), remote power production and battery replacement [17].

2. Experimental

2.1. Development and evaluation of an integrated SOFC–catalytic burner device

2.1.1. Catalyst and SOFC preparation

The pre-reforming catalyst was prepared via wet impregnation of the cordierite support foam (Morgan materials, UK). The foam was first washed with acetone and then dried overnight at 90°C. The Ru solution was prepared by dissolving the appropriate mass of RuCl_3 in ethanol, such that the resulting solution would provide a 5 wt.% Ru-supported catalyst. The foam was removed from the oven and dipped in the Ru solution. The foam was removed after 5 min, allowed to air dry and then calcined at 600°C for 2 h. The Pt combustion catalyst was prepared in the same manner with the masses of the soluble Pt salt resulting in a 2.5 wt.% doping.

The SOFCs used in this device were prepared via methods described in previous papers [1,2,18]. Two types of SOFCs were used in this device (Fig. 1). The secondary cells were the same as those previously described, whereas the primary SOFCs were not. The primary SOFCs were prepared from the same anode and cathode inks, as previously done. The 8 mol% YSZ (Tosoh) electrolyte tubes were cut to suitable lengths and then cleaned in acetone

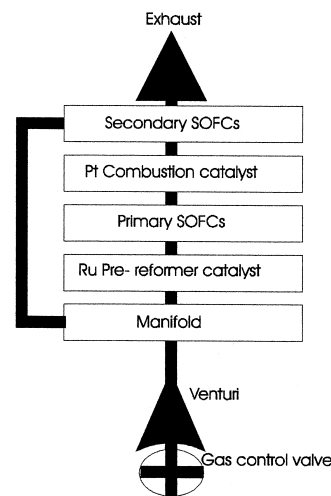


Fig. 1. Schematic of the integrated SOFC–catalytic burner system.

and dried. The tubes were coated in an 8 mol% YSZ (Tosoh) slurry, consisting of calcined 8 mol% YSZ, passed through a 100- μm sieve, methanol and polyvinyl butyrol (PVB). These tubes were then dried and calcined at 1500°C for 1 h. The anode slurries were painted on the outside of the YSZ tube, and the cathodes coated on the inside, then co-fired at 1300°C for 1 h. A thin layer of silver paste with a silver wire connector was used as current collection for the cathode, and the anode was wound with Ni wire.

2.2. The integrated SOFC–catalytic burner system

The integrated SOFC–catalyst system consists of three catalytic stages and a hydrocarbon gas supply. The hydrocarbon gas, methane or butane, was supplied to the integrated burner via an adjustable air pre-mix inlet to the unit manifold. At this point, the gas was manifolded to the catalytic combustion zone containing the pre-reformer. The pre-mix was also fed to the secondary SOFCs. A diagram of the burner system is shown in Fig. 1.

The butane/air mixture entering the combustion zone was ignited via an electric spark generator. Once the combustion foam was heated to 350°C, the gas supply was interrupted, extinguishing the flame front. The gas was then switched back on and catalytic combustion was initiated. Some of the oxygen for the combustion reaction was supplied directly in the fuel air pre-mix, and the remaining air required was drawn in from the atmosphere. As the combustion reaction proceeded, the internal temperature of the device increased. The reaction heat required to initiate the catalytic pre-reforming reaction was supplied via heat conduction from the combustion foam. Once the pre-reformer was active, hydrogen was produced and the environment between the two foams became suitable for the primary SOFCs. The oxygen supply to the cathodes of the primary SOFC was supplied by a fan. Power could then be drawn from these cells as the operating temperature was reached, and the reformat and unreacted hydrocarbon fuel passed over the YSZ/Ceria/Nickel (YCN) anodes.

Reaction products and unreacted fuel were then passed through to the combustion foam. The combustion foam also supplied the required reaction heat to the secondary SOFC rack. The hydrocarbon fuel was manifolded directly to the secondary SOFCs, as shown in Fig. 1. The cells used in this reaction environment were doped with 5 wt.% molybdenum. The cells were contained within a quartz tube, which protruded outside the burner system to ensure that the oxygen concentration at the cathode remained sufficiently high to produce power.

The original fuel air mixture, which was slightly fuel-rich, favouring the partial oxidation reaction was manifolded directly to the secondary SOFCs where it was reformed in situ over the fuel electrodes; the remaining unreacted fuel entered the combustion zone.

Once the desired reaction temperature was reached, the secondary SOFC produced power, which in turn powered

the fan unit enabling the primary SOFCs to produce electrical power.

2.3. Characterisation of the three-stage catalytic system

Both the catalytic and electrochemical performance of the integrated SOFC–catalytic burner system were studied on a custom-built gas testing system, consisting of a gas-tight manifold, a Eurotherm-controlled furnace, an on-line quadrupole mass spectrometer, and, when testing SOFCs, a potentiostat. The manifold was able to supply hydrogen, oxygen, and hydrocarbon fuels in an inert helium flow. The system also allowed a complete range of different fuel-to-oxygen ratios in the reactant feed, enabling the study of the partial oxidation reforming reactions. Further details of this apparatus are given in previous works [2,8].

As with previous studies, steady-state isothermal techniques were used to study partial oxidation reactions over the anode materials and to obtain electrochemical performance data for the individual cells. Temperature-programmed techniques were used to evaluate catalytic activity and product gas distribution amongst the three catalytic stages of the system. These experiments were also used to obtain information on the relative initiation temperatures for each of the three catalytic stages. Post-reaction temperature-programmed oxidation was used to determine the amount and nature of carbon deposited during reaction.

Electrochemical measurements were made using hydrogen at applied potentials between 0.5 V and open circuit voltage (OCV) at a variety of reaction temperatures. These measurements were used as a form of quality control to determine which cells were to be included in the system. The best cells were then tested using hydrocarbon fuels to determine the overall electrical performance of the unit.

3. Results and discussion

3.1. Thermal and electrical performance

A major issue with the widespread application of SOFC devices has been that of slow warm-up time required to prevent thermal shock damage. The tubular system developed in these laboratories has high thermal shock resistance, enabling rapid start times. In Fig. 2, the temperature profile for the integrated SOFC–catalytic burner (ISCB) system is compared to the previously developed Adelan[®] unit.

The ISCB had a rapid warm-up time and reached an operational temperature of 750°C within 5 min of start-up; this is over 200°C higher than that of the Adelan[®] unit after the same time. The increased operating temperature enables higher performance to be achieved. The labels T1 and T2 apply to the internal temperature of the primary and secondary SOFC stacks, respectively. T1 is around

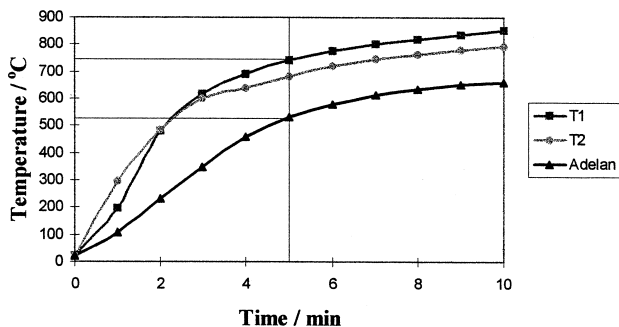


Fig. 2. Temperature warm-up profile for small-scale SOFC devices.

50°C higher than T2, as the primary cells are located between a partial oxidation catalyst and a combustion catalyst both providing two heat sources; whereas, the secondary cells rely on heat transmitted through the combustion catalyst foam. After 10 min of operation, a stable reaction temperature of 850°C was reached at T1 and 800°C at T2.

The performances of both the primary and secondary SOFCs have been recorded using butane as the fuel at these temperatures. The primary cells, with the fuel electrode on the outside of the YSZ electrolyte tube, gave an average of 250 mA per cell at 0.5 V from a 2-cm active cell length. This accounted to an overall power output of 4.5 W for the primary stack of 36 cells. The performance of the secondary stack was better, even at the lower operating temperature. The average performance per cell was 350 mA at 0.5 V, giving a power output of 4.03 W for the 22-cell stack. When the outputs from the two racks were combined, the ISCB provided 8.53 W of electrical power. However, some of this power was used to drive the electric fan, which consumed 0.45 W; therefore, only around 8 W of useful electrical power was produced.

3.2. Catalytic performance

The catalytic performance of the system was also studied using methane as a model hydrocarbon fuel, individually examining the different catalytic regions, that is, pre-reformer, SOFC and combustion catalyst. Fig. 3 shows the temperature-programmed partial oxidation of methane over the 5 wt.% Ru cordierite-supported pre-reformer catalyst.

The results in Fig. 3 show that the reaction initiated at 400°C; however, hydrogen concentrations sufficient for reduction of fuel cell anodes, and the enhancement of electrochemical operation, were not produced until the reaction temperature exceeded 670°C. This figure also displays the importance of temperature control within the catalytic device. As the reaction temperature approached 800°C, the methane conversion increases towards 100%. This may be beneficial for fuel cell operation, but the system relies on unreacted fuel reaching the Pt combustion catalyst to provide reaction heat; therefore, 100% fuel

conversion at this point would imply a reduction in the overall operating temperature.

The second stage of the catalytic modeling using methane entailed inserting an SOFC after the pre-reforming catalyst, and comparing the product composition after reaction over both components. The reaction was again found to commence above 400°C, with hydrogen being produced in similar concentrations at a lower temperature of 620°C. The most noticeable difference was the increased methane conversion at lower temperatures, with 100% conversion being reached at 750°C. As noted above, this may not be considered an ideal situation for the system; this problem was overcome only by coating those strips of the pre-reforming catalyst directly under the SOFC. This provided a route for unreacted hydrocarbon fuel to pass directly to the combustion catalyst whilst still providing partially reformed fuel to the SOFCs. The carbon deposition on the standard nickel anode SOFCs during operation under these conditions, was reduced, probably due to the reduced requirement for the electrode to act both as a reforming catalyst and an electrode. No carbon deposition was observed over the molybdenum- and ceria-doped electrodes; this was attributed to their previously observed enhanced electrochemical activity.

The third stage was to include the combustion catalyst, which produced CO₂ and H₂O at the exhaust.

Once the device had been validated using methane, in order to test the individual components, the hydrocarbon fuel was changed to butane and catalytic experiments were undertaken on the whole operating system, probing through each catalyst element in turn. Fig. 4 shows the actual gas phase composition through the working device after 15 min of operation, thus allowing steady state conditions to be reached.

The oxygen-to-butane ratio after the air pre-mix valve was found to be 4.5. This would favour some form of partial oxidation reaction, as full combustion would require a ratio of 6.5, as shown in Eq. 2.



As the reactant gas passed over the Ru catalyst, a partial oxidation reaction was observed; some of the butane re-

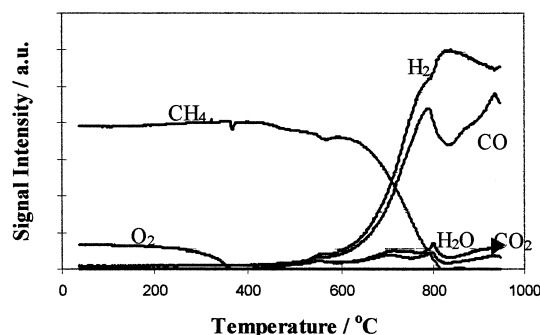


Fig. 3. Temperature-programmed partial oxidation reaction over 5 wt.% Ru-doped catalyst.

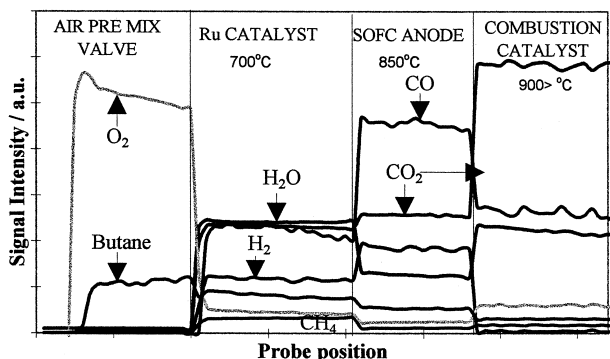


Fig. 4. Gas phase composition through the integrated SOFC-catalytic burner.

acted to produce hydrogen, CO and CO₂, and some H₂O, perhaps via the reaction shown below:



Methane evolution was also observed and, although not shown in Fig. 4, other hydrocarbons such as propane were also observed. The production of water and CO₂ suggested that the air-to-fuel ratio may slightly favour combustion; this, however, would be beneficial when the reaction of the SOFC anode is considered.

As the gas stream entered the SOFC region, the product gas composition again changed as in situ reforming occurred over the nickel-based electrodes. Water and methane were consumed, suggesting steam reforming, and partial oxidation reactions were responsible for the observed increase in fuel conversion and hydrogen production (see reactions 1, 4 and 5).



The high-temperature environment in this region of the burner would promote these reactions and encourage reforming of higher hydrocarbons via a similar route. The reforming of higher hydrocarbons could proceed via an initial cracking reaction, and then further reforming or by direct reforming over the nickel surface of the anode. Previous studies by this group [2,8] have shown that this in situ reforming reaction can be influenced by load; therefore, under heavy load conditions, product gas composition could again change, favouring water and CO₂ evolution, which, in turn, could increase fuel conversion as the reforming reactions are accelerated.

The final stage of the catalytic system was then reached at the combustion zone. As expected, there was a shift in composition towards CO₂ and water evolution as the hydrocarbon and gas products were combusted. This shift towards combustion products, even though the primary air-feed ratio inhibits it, showed that the catalytic combus-

tion reaction was fed by secondary air, and the observed CO concentration may be reduced by increasing this flow of oxygen.

4. Conclusions

(1) SOFCs have been inserted in an integrated catalytic fuel processing system, comprising of a Ru-based pre-reformer, a fuel cell reaction zone, followed by a Pt total oxidation catalyst, all combined within a unique manifolded system, as shown in Fig. 1.

(2) Catalytic testing and optimisation of the individual elements have shown that the system can give good thermal and electrical performance with relatively uniform temperature distribution. Measured chemical gradients through the ISCB have shown that the reaction environment evolves as it passes through each of the individual stage. However, the reaction environment within each individual element is uniform.

(3) The total system warmed up in 5 min and provided a lightweight and portable power supply around 8 W_e, which could be useful in small-scale hybrid systems.

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