

Propane conversion over a Ru/CGO catalyst and its application in intermediate temperature solid oxide fuel cells

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Abstract

A Ru/CGO catalyst was investigated in combination with a Cu current collector for the direct electro-oxidation and internal reforming of propane in a solid oxide fuel cell. The electrochemical power densities for the direct oxidation were larger than in the internal reforming process at 750 °C. The electrochemical performance in the presence of propane was significantly affected by the polarization resistance which was about three times larger than that obtained for the SOFC fed with hydrogen at 750 °C. However, out-of-cell steam reforming tests showed a C₃H₈ conversion to syngas approaching 90% at 800 °C. Thus, significant enhancements may be achieved by properly optimizing the anode structure. No formation of carbon deposits was observed both upon operation of the anode in the direct oxidation and internal reforming processes at 750 °C.

1. Introduction

The direct oxidation of hydrocarbons in intermediate temperature solid oxide fuel cells (IT-SOFCs) has been intensively investigated in the last years due to the high intrinsic efficiency of the direct electrochemical oxidation process. Significant attention has been focused on methane electro-oxidation by using electrocatalysts such as Cu/CeO₂, Ni–Cu and various perovskites [1–3]. Encouraging results have been achieved at temperatures below 800 °C especially in the presence of ceria as electrolyte. IT-SOFCs typically operate at temperatures ≤ 800 °C allowing the use of cheap ferritic stainless steel interconnectors. Doped ceria electrolytes are characterised by suitable ionic conductivity at these temperatures.

Some attempts have been addressed to the direct oxidation of larger molecular weight hydrocarbons [1]. It has been observed that the reaction rates for the direct electrochemical oxidation of propane are lower than for methane; moreover, propane oxidation is more affected by the cracking process producing carbon fibres poisoning of the anode surface especially in the case of Ni-based catalysts. The formation of carbon deposits also occurs under steam reforming conditions at intermediate temperatures if inappropriate steam/carbon ratios (S/C) are used. Accordingly, it appears necessary to investigate alternative catalysts for both direct electro-oxidation and steam reforming of propane in IT-SOFCs.

Recently, several investigations have addressed the use of Ru as a promoter of anodic processes in SOFCs [4–6]. We have focused our efforts on the investigation of the effect of Ru in combination with ceria as oxidation catalyst for propane in intermediate temperature SOFCs, i.e. Ru/Ce_{0.8}Gd_{0.2}O_{1.9} (CGO). In order to evaluate the characteristics of this catalytic system, out-of-cell experiments have been carried out for the propane steam reforming and both direct electro-oxidation and internal reforming have been evaluated in a ceria-electrolyte supported single cell. In this latter case, a suitable current collector, i.e. Cu, was added to the composite anodic layer to achieve proper electronic percolation within the layer.

2. Experimental details

2.1. Ru/CGO catalyst

The Ru/CGO catalyst was prepared by the incipient wetness method [6]. The CGO powder (Praxair) was impregnated with a solution of RuCl₃ in ethanol at 50 °C. The powder was first dried at room temperature and then calcined in an oven at 500 °C for 5 h (heating rate, 1 °C min⁻¹; cooling rate, 2 °C min⁻¹). Reduction was carried out in 5:95 H₂/Ar flow at 400 °C. The resulting Ru content was about 18% (wt/wt), as

resulting by X-ray fluorescence analysis (XRF Explorer, Bruker).

XRD analysis was carried out with a X'PERT Philips diffractometer equipped with CuK α source. Both Bragg-Brentano and thin film (grazing angle) modes were used. The morphology of fresh and used catalysts was investigated by transmission electron microscopy (TEM) using a Philips CM12 instrument. Specimens were prepared by ultrasonic dispersion of the catalysts in isopropyl alcohol. A drop of suspension was deposited on a carbon-coated grid. A Carlo Erba CHNS-O elemental analyzer was used to determine the amount of deposited carbon on the catalysts after steam reforming catalytic experiments and electrochemical operation.

2.2. Catalytic activity

Catalytic activity measurements for propane steam reforming were carried out at atmospheric pressure in a quartz microreactor (internal diameter = 4 mm) placed in a ceramic tube furnace, at a space velocity of 60,000 h⁻¹, in the temperature range 600–800 °C. The catalyst, placed between quartz wool in the middle of the reactor, was diluted with SiC (SiC/catalyst = 2). The temperature of the catalyst bed was monitored with a thermocouple sheathed in a quartz thermowell inserted into the reactor bed. An isocratic pump was used to feed water in the stream to an evaporator heated at 200 °C and to control the steam to carbon ratio (S/C) in the reaction gas mixture entering the microreactor. The gas lines were maintained at approximately 70 °C to prevent condensation. Before passing into the gas-chromatograph, water was eliminated from the reactor outlet gases by a condenser kept at 25 °C. Gases were fed with calibrated mass flow controllers (Brooks 5850S) after purification by Deoxo Gas Clean Filters (Chrom-pack) and a molecular sieve trap. The steam to carbon (S/C) inlet flow ratio was adjusted to 2.5. The total inlet flow was fixed at 150 cm³ min⁻¹, using nitrogen as balance. Reaction product gases were analyzed using a Varian micro GC. The catalytic activity results were generally taken 90 min after the setting of the reaction conditions, when reproducible data were obtained for 60 min at least. Propane steam reforming (S/C = 2.5) was investigated between 600 and 800 °C at 1 atm, and at a GHSV of 60,000 h⁻¹

2.3. SOFC characterization

In order to evaluate the behaviour of the Ru/CGO catalyst in a SOFC fed with propane, it was necessary to combine this catalyst with a suitable current collector such as Copper. This does not interfere with the catalytic activity and also avoids promoting the cracking process. It is known that no carbon formation occurs on Cu upon exposure to dry hydrocarbons but there is also no catalytic effect by copper on the electrochemical oxidation [2]. To facilitate the electronic conduction

through the catalytic layer, the ratio between the CuO precursor (current collector) and catalyst (Ru–CGO) was maintained as 70:30 wt%. Thus the total Ru content in the anode layer was about 6% wt.

The SOFC device used in this study consisted of a button cell (1 cm² active area) containing three layers:

- anode: composite of Ru–CGO catalyst (30% wt) and CuO (70% wt) (thickness: 15 μ m)
- electrolyte membrane: CGO (CeGd_{0.2}O_{1.9} thickness: 250 μ m)
- cathode: Composite of LSFCE (La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃) and CGO (thickness: 15 μ m)

The synthesis of the CGO powder was made by a co-precipitation method described elsewhere [7]. The CGO powder was compacted by uniaxial pressing (300 MPa). The green pellet was treated at 1450 °C for 6 h in air to obtain a supporting electrolyte membrane ($\rho_{\text{rel}} > 95\%$).

The LSFCE cathode was deposited by spray painting using isopropanol as dispersant. The raw powder was purchased from Praxair. The cathode layer deposit was fired at 1100 °C for 2 h in air to ensure good adhesion to the membrane. The anode containing a mixture of reduced Ru/CGO 30% wt. and 70% wt. Cu (as CuO) was also deposited by spraying using the same organic vehicle as for the cathode and thermal treated at 1100 °C for 2 h in inert (Ar) environment. For the anode, a raw powder containing Ru in the metallic form was used since significantly lower losses of Ru from the layer were observed after firing than in the case of a RuO₂-containing powder. In a previous paper [4], it was reported that some loss of RuO₂ occurs upon firing a thick supporting anode at 1450 °C in air. In the present work, we observed a complete loss of RuO₂ from a thin anode layer in several experiments carried out under the same conditions. Thus, the use of metallic Ru (Ru sublimation temperature is about 2300 °C) and an inert environment were necessary during the firing process. Finally, the cell was mounted on an alumina tube and sealed with quartz adhesive (AREMCO) and heated between 500 and 750 °C in the presence of H₂ diluted in a He stream. At 750 °C the gas was switched to dry propane or a propane–water mixture to investigate the direct oxidation or reforming process. During internal reforming, an HPLC pump was used to feed precise amounts of liquid water that was vaporized in the propane stream. Electrochemical polarization and ac-impedance measurements were performed on electrolyte supported single cells at 750 °C using an AUTOLAB PGSTAT30 Metrohm potentiostat/galvanostat and frequency-response analyzer (FRA) equipped with 20A booster. Electric gold wires were connected to the cell. A thermocouple was positioned close to the cell. Impedance spectra were obtained in the frequency range from 10 to 1 MHz with applied ac-voltage amplitude of 10 mV rms. All impedance measurements were taken under open-circuit conditions.

3. Results and discussion

3.1. Physico-chemical analysis of the Ru/CGO catalyst

TEM observation of the Ru/CGO catalyst (Figure 1) shows a distribution of fine spherical Ru particles of about 20 nm on large irregular shape CGO particle support. The lattice spacing observed at high magnification for the Ru particles corresponds to the characteristic reflection of hexagonal close-packed Ru structure. The XRD patterns of the fresh catalyst and after the steam reforming operation at 800 °C are shown in Figure 2. The main reflections in all patterns are due to the cubic crystallographic structure of gadolinia doped ceria. The reflections due to RuO₂ are clearly visible in the diffraction pattern of the calcined sample (a). After reduction, Ru peaks become evident (b). The mean particle size for metallic Ru in the X-ray patterns determined from the Sherrer equation, corresponds to about 20 nm confirming the result obtained from TEM analysis. No significant change in the Ru particle size is observed after 120 h of operation. The pattern of the catalyst after the steam reforming process (out-of-cell

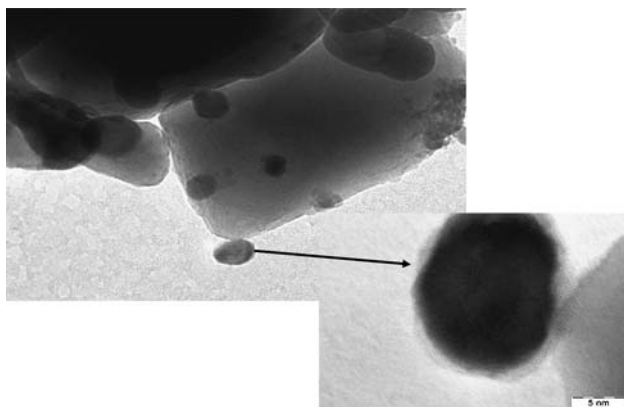


Fig. 1. TEM images of 20% Ru/CGO catalyst. The small particles are composed of metallic Ru.

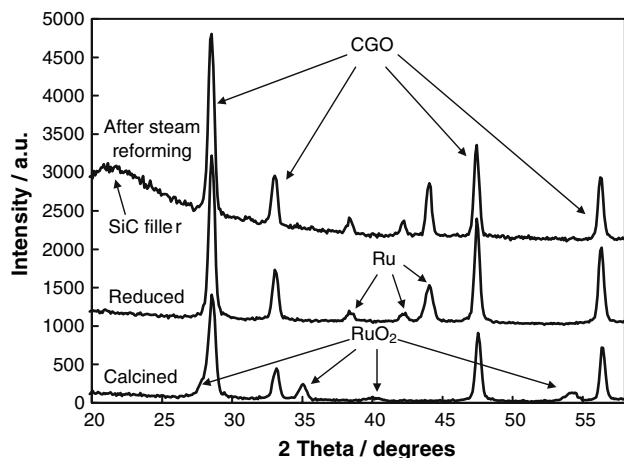


Fig. 2. XRD patterns of the Ru/CGO catalyst calcined, reduced, and after the steam-reforming test.

test) does not show any significant formation of graphitic carbon deposits. The X-ray scattering at about 22° is due to the catalyst dilution with SiC used for the out-of-cell steam reforming experiment. No evidence of carbon deposits was observed from TEM and CHNS-O analyses after the steam reforming test.

3.2. Steam reforming process

The effect of temperature on the steam reforming catalytic activity of 20 wt% Ru/CGO catalyst was investigated. Conversions and products distribution are presented in Table 1. Almost complete propane conversion was observed in the temperature range investigated. The syngas concentration in the reactor outlet increases with temperature, passing from 75% at 600 °C to 88% at 800 °C. In contrast, both CO₂ and CH₄ in the outlet stream decreased with temperature. A life-time catalytic test (steam reforming process) was carried out at 800 °C. Table 2 and Figure 3 show the distribution of reaction products as a function of time. Conversion and selectivity remained almost constant during the life-time. No decay of catalytic activity was observed with time and the concentration of syngas in the outlet stream was about 90% during the experiment. As observed above, no carbon deposits were detected after catalyst operation in propane during the steam reforming experiments. This indicates that the catalyst does not promote cracking under such conditions.

3.3. Electrochemical investigation

Figure 4 shows the XRD pattern of the anode layer obtained in the grazing angle mode (1° incidence angle). It reveals the presence of the typical reflections of Ru, Cu and CGO. A slight enrichment in Ru is observed in the outer layer (grazing angle mode). However, no

Table 1. Distribution of products in the out-of-cell steam reforming tests

% products					
T (°C)	H ₂	CO	CO ₂	CH ₄	C
600	64.96	7.59	13.68	13.56	0.21
700	68.80	14.10	9.20	7.48	0.50
800	71.08	18.11	6.27	1.17	3.38

Table 2. Distribution of products during life-time test at 800 °C in the presence of propane/water mixture (S/C = 2.5)

Time/min	conv.	C ₃ H ₈	CH ₄	H ₂	CO ₂	CO	C ₂ H ₄
1200	98.90	0.12	2.15	74.54	6.06	17.09	0.05
2400	99.40	0.06	2.64	74.03	6.45	16.78	0.05
3600	99.24	0.07	1.69	74.79	6.59	16.80	0.05
4800	98.39	0.15	2.21	73.88	6.70	17.00	0.05
6000	97.26	0.25	2.07	73.88	5.88	17.76	0.16
7200	98.55	0.13	2.76	72.74	5.62	18.63	0.12

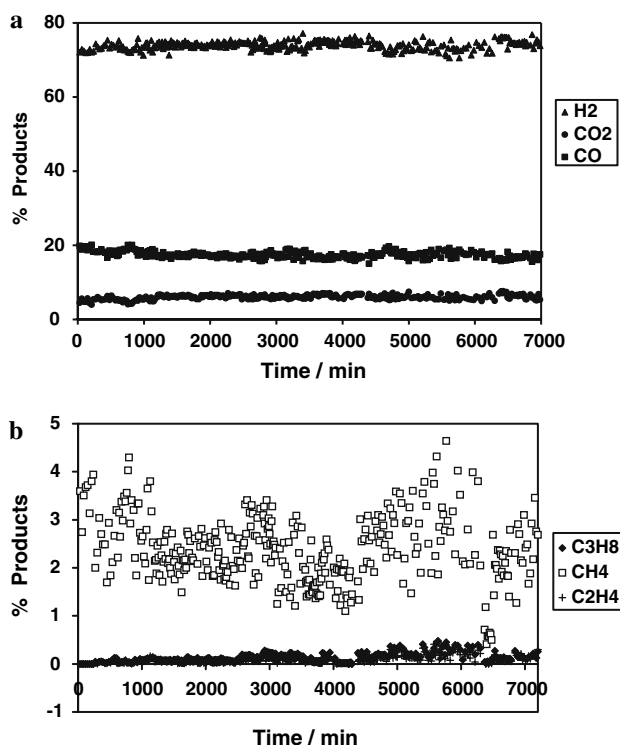


Fig. 3. (a and b) Life-time catalytic test of Ru/CGO at 800 °C in humidified propane (S/C = 2.5). Traces of C₂H₄ and C₃H₈ are detected.

significant modification in the nominal composition was observed in the XRF analysis of the anode layer after scraping it from the fired cell. This indicates that the sublimation of RuO₂ [6], as reported in the literature, does not occur with our experimental procedure. In the present process, the firing temperature is sufficiently high to promote adhesion of the anode layer to the membrane.

AC impedance analysis of the SOFC cell operating in the presence of H₂ at 750 °C (Figure 5) under open-circuit conditions, shows significant ohmic resistance (R_s), 0.615 $\Omega \text{ cm}^2$ (high frequency intercept), it de-

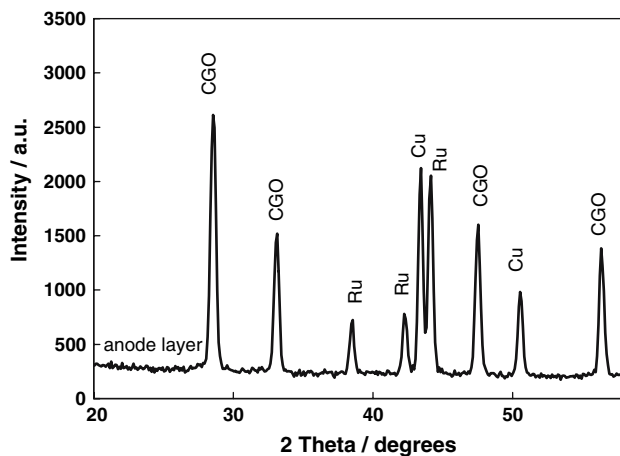


Fig. 4. X-ray diffraction patterns of the anode layer.

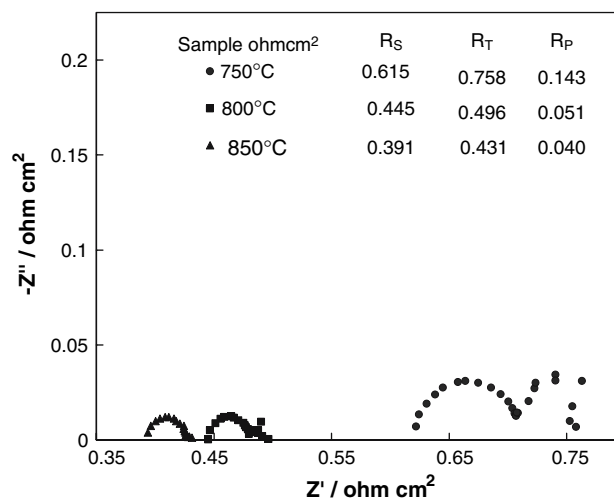


Fig. 5. AC impedance spectra for the SOFC cell operating in presence of H₂ at different temperatures under open circuit voltage.

creases to 0.445 $\Omega \text{ cm}^2$ at 800 °C (Figure 5). The observed ohmic resistance is only in part due to the supporting membrane electrolyte (about 0.3 $\Omega \text{ cm}^2$ at 800 °C). A significant contribution to the ohmic drop is also caused by the poor electrode–electrolyte interface, unoptimal adhesion and high porosity, especially in the anode. However to avoid significant loss of Ru, a low firing temperature was necessary. On the after hand, the polarization resistances (low frequency intercept) are optimal at all temperature (e.g. 0.14 $\Omega \text{ cm}^2$ at 750 °C and 0.05 $\Omega \text{ cm}^2$ at 800 °C).

Polarization curves carried out in H₂ (Figure 6) show that the maximum power density increases with temperature whereas the OCV decreases due to the electronic conduction of CGO [7]. Impedance spectra were carried out in the presence of dry propane at open circuit voltage conditions. Figure 7 shows an ohmic resistance slightly larger than that registered in H₂ at all temperatures. An increase in polarization resistance was observed, as expected, due to the slower propane oxidation reaction compared to H₂. The observed R_p

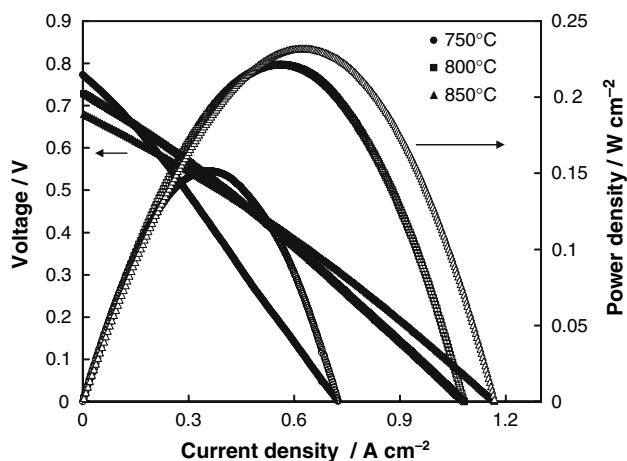


Fig. 6. Polarization curves at different temperatures in the presence H₂ feed at the anode.

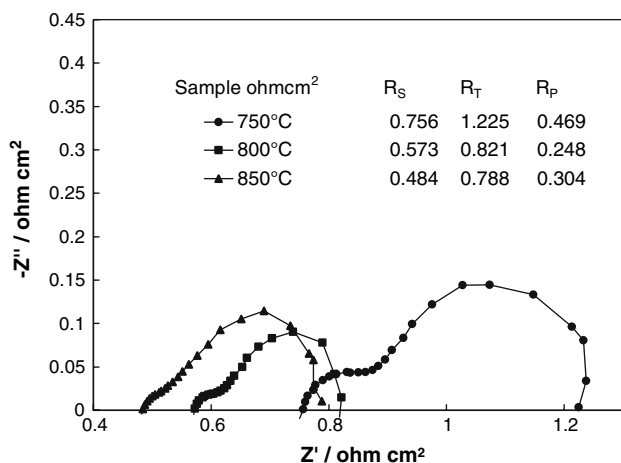


Fig. 7. AC impedance spectra for the SOFC cell operating in the presence of C_3H_8 at different temperatures and open circuit voltage.

values for propane oxidation at 750 and 800 °C are 0.469 and 0.248 $\Omega\text{ cm}^2$, respectively. An inversion of the tendency regarding the polarization resistance is observed at 850 °C. R_p slightly increases in the temperature range from 800 to 850 °C. This effect may arise from a cracking process or gas phase reaction hindering the anodic process under dry propane operation at 850 °C. No carbon deposits or tar formation were observed after cell shut down. Figure 8 shows polarization curves in dry propane feed at different temperatures. A maximum power density of about 130 mW cm^{-2} was obtained at 800 °C. Both polarization and impedance spectra indicate that the direct electro-oxidation of propane can be performed in the temperature range 750–800 °C. As observed in the impedance spectra in Figure 7, at 800 °C, the ohmic resistance is about 0.57 Ohm cm^2 , whereas the polarization resistance is about 0.25 Ohm cm^2 . Thus, the moderate output power density (130 mW cm^{-2} at 800 °C) is mainly affected by the ohmic drop and low OCV (essentially related to the electrolyte membrane).

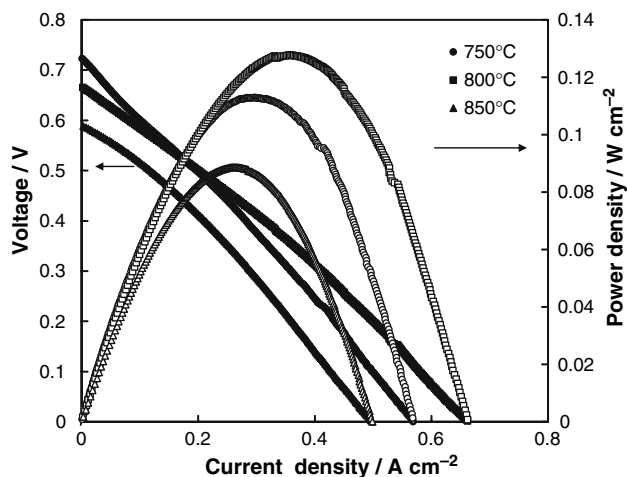


Fig. 8. Polarization curves at different temperatures in C_3H_8 fed.

In order to better evaluate the behaviour of the catalyst under SOFC operation, the internal reforming process was also investigated. Figure 9 shows a comparison of the measured fuel cell performance for the internal reforming of propane and for dry propane oxidation at 750 °C. The maximum power density measured at 750 °C decreases, passing from dry propane to wet propane, probably due to more efficient direct electro-oxidation at 750 °C as compared to steam reforming. At 750 °C, the maximum power density for the internal steam reforming ($S/C = 1$) is smaller than the dry propane oxidation process. An increase of the S/C ratio further decreases the performance; thus, we avoided investigating higher S/C ratios. Although we have used a C_3H_8 flux significantly larger than that required by the faradaic process, in the case of the dry propane a promotion of the reforming reaction on the catalyst surfaces by electrochemically produced water should not be discarded. However, it appears that the rate of C_3H_8 oxidation in the dry processes is better than in internal reforming at least at 750 °C. No carbon deposits were observed from electron microscopy and CHNS-O analyses after shut-down in propane for anodes which had operated in both direct oxidation and internal reforming modes.

3.4. Direct oxidation vs reforming

The catalyst investigated in the present study is a combination of oxidation (ceria) and reforming (Ru) promoters. Since water is formed as reaction product on the catalyst surface during oxidation of dry hydrocarbons a synergistic effect between direct oxidation and reforming would be expected. Clearly, the performance of the present SOFC may be greatly enhanced if a thin electrolyte is adopted (reduced ohmic drop) and if the CGO electrolyte membrane is replaced by electrolyte characterized by a higher ionic transport number. In fact, high ohmic drop and low OCV affect the performance of the present SOFC, whereas, charge transfer properties in dry propane were promising. As is well known, Ni promotes C–H bond scission and thus direct

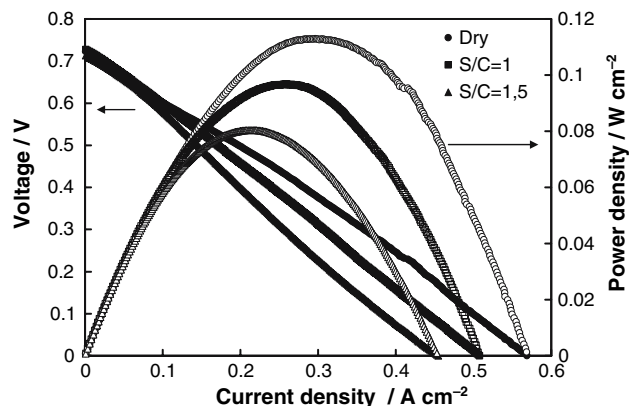


Fig. 9. Comparison of dry operation and internal reforming polarization curves at different S/C ratios at 750 °C.

oxidation; but, it also significantly increases the probability of irreversible deposition of carbon species at the surface blocking the catalytic sites with time. Breaking of the carbon–hydrogen bond is considered to be the activation step in the direct oxidation process [7] followed by removal of the adsorbed species by O^{2-} ions. Thus, higher performance is initially achieved with Ni-based catalysts; but, long-term operation of Ni-based catalysts under dry operation is affected by the growth of carbon deposits. On the other hand, CGO has been identified as a suitable oxidation catalyst for both H_2 and methane oxidation [8]. The rate-determining step on this oxide catalyst presently appears to be related to the scission of the C–H bond. Ru promotes this reaction step whereas ceria accelerates the oxidation to CO_2 . Although the performance achieved in our direct oxidation process is lower than that reported by Zhan and Barnett [9] using a propane–air mixture at the anode, the direct propane oxidation is characterized by a high intrinsic efficiency. Further enhancement of the electrode microstructure and cell configuration is necessary to achieve the desirable oxidation rates during SOFC operation.

4. Conclusions

Direct oxidation and internal reforming processes of propane at a Cu–Ru/CGO electro-catalyst have been investigated at intermediate temperatures (750C–800 °C) in a CGO electrolyte-supported cell. The measured electrochemical performance was affected by significant ohmic resistance and low OCV and polarization resistances were recorded, especially at high temperatures. Although, out-of-cell catalytic steam reforming tests indicate that propane conversion to syngas reached 80–90% under these conditions, the

measured power densities in hydrogen were more than twice those recorded in the internal reforming process of C_3H_8 . Interestingly, the SOFC performance recorded for the dry C_3H_8 operation was larger than that for internal reforming at 750 °C. It appears that further optimization of the anode structure is necessary for better utilization of the Ru/CGO catalyst.

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