PROPALE CONVERSION ON Ru/CGO CATALYSTS FOR APPLICATION IN INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

Massimiliano Lo Faro, Giuseppe Monforte, Vincenzo Antonucci, Antonino Salvatore Aricó
CNR-ITAE Institute, Via Salita S. Lucia sopra Contesse, 5-98126 Messina, Italy
Vincenza Modafferi, Sebastiano Candamano, Pierluigi Antonucci
Department of Mechanics and Materials, University of Reggio Calabria, Italy

ABSTRACT

A Ru/CGO electrocatalyst 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. Comparable electrochemical power densities for both direct oxidation and internal reforming have been measured at 750°C. The electrochemical performance in the presence of propane was significantly affected by the polarization resistance which is about four times larger than that obtained for the SOFC fed with hydrogen. However, out-of-cell steam reforming tests showed a C₃H₈ conversion to syngas approaching 90% at 800°C. Thus, it is observed that significant enhancements may be achieved by properly optimizing the anode structure. No formation of carbon deposits was observed for operation of the anode both in the direct oxidation and the internal reforming processes at 750°C.

INTRODUCTION

The direct oxidation of hydrocarbons in intermediate temperature solid oxide fuel cells (IT-SOFCs) has been intensively investigated in the last few years due to the high intrinsic efficiency of the direct electrochemical oxidation process. A 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.

Some attempts have been addressed to the direct oxidation of larger molecular weight hydrocarbons (1). It has been observed that the kinetics of direct electrochemical oxidation of propane is lower than methane and, moreover, it is more affected by the cracking process producing carbon fibers poisoning 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. Accordingly, it appears necessary to investigate alternative catalysts for both direct electro-oxidation and steam reforming of propane in IT-SOFCs.

We have focused our efforts on the investigation of Ru/Ce₀.₈Gd₀.₂O₁.₉ (CGO) system since both Ru and CGO are known as suitable promoters for oxidation reactions. 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.

EXPERIMENTAL

Catalysts Preparation and Characterization

The Ru/CGO catalyst was prepared by the incipient wetness method (4). 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 hours (heating rate, 1°C/min; cooling rate, 2°C/min). Reduction was carried out in 5:95 H₂/Ar flow at 400°C. The resulting Ru content was about 18% (wt/wt), as determined by X-ray fluorescence analysis (XRF Explorer, Bruker). 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 depositing a drop of suspension on carbon-coated grids. A Carlo Erba CHNS-O elemental analyzer was used to determine the amount of deposited carbon on the catalysts after steam reforming and electrochemical operation.

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 properly calibrated mass flow controllers (Brooks 5850S) after purification by Deoxo Gas Clean Filters (Chrompack) and molecular sieve trap.

The steam to carbon (S/C) inlet flow was adjusted to 2.5. The total inlet flow was fixed at 150 cc/min, using nitrogen as balance. Reaction product gases were analyzed using a Varian micro gas chromatograph (GC). The catalytic activity results were generally taken 90 min after the setting of the reaction conditions, when reproducible data were obtained for at least 60 min.

SOFC Cell Characterization

The cell architecture developed in this study consists of:

Anode: Ru-CGO catalyst (30%wt) and CuO (70%wt) (thickness: 15 μm)
Electrolytic membrane: CGO (thickness: 150 μm)
Cathode: Composite of LSMO and CGO (thickness: 15 μm)
Copper was selected as a suitable current collector. 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.

The synthesis of the CGO powders was made by a co-precipitation method described elsewhere in ref. (5). The CGO powders were compacted by uniaxial pressing (300MPa). The green pellet was treated at 1550°C for 3 h in static air obtaining a disk supporting electrolyte membrane (ρrel > 95%) The cathode was deposited by slurry painting using isopropanol as dispersant. It was composed of La0.6Sr0.4Fe0.8Co0.2O3-δ (Praxair). The deposit was then fired at 1100°C for 2 h under static air to ensure a good interface between electrode/electrolyte membrane. The anode was also deposited by slurry painting using the same organic vehicle as for the cathode and thermal treated at 600°C for 6 hours. A low firing temperature for the anode is selected to avoid loss of RuO2 by evaporation. Finally, the cell was mounted on an alumina tube and sealed with quartz adhesive (AREMCO) and heated between 500 and 750°C in diluted H2 stream. At 750°C the gas was switched to dry propane or propane-water mixture to evaluate direct oxidation or reforming process.

An HPLC pump was used to feed precise amounts of water. Electrochemical impedance measurements were performed on electrolyte supported single cells at 750°C by using an AUTOLAB PGSTAT30 Metrohm frequency-response analyzer. Gold wires were used as current collectors for the cell. A thermocouple was positioned close to the cell. Impedance spectra were obtained in the frequency range from 10 mHz to 1 MHz with applied ac-voltage amplitude of 10 mV rms. All impedance measurements were taken under open-circuit conditions.

RESULTS AND DISCUSSION

The XRD patterns of fresh and used catalysts are shown in Fig. 1. 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 pattern of the catalyst after the steam reforming process 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 process. No evidence of carbon deposits was observed from TEM and CHNS-O analyses.

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. The effect of temperature on the 20 wt% Ru/CGO catalyst was investigated. Conversions and products distribution are presented in Table 1.

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

| T (°C) | H2   | CO   | CO2  | CH4  | 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|
An 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. On the contrary, both CO2 and CH4 in the outlet stream decreased with temperature.

AC impedance analysis of the SOFC cell operating at 750°C (Fig. 2) shows significant ohmic resistance (high frequency intercept) for both H2 (0.64 Ω·cm²) and C3H8 (0.832 Ω·cm²). However the series resistance is comparable for both fuels and it is ascribed to unoptimised anode-electrolyte interface characteristics. In fact, to avoid loss of Ru, a low
The polarization resistance in the presence of propane (2.15 Ω·cm²) is significantly larger than for H₂ (0.53 Ω·cm²) as expected. Although, the impedance spectra indicate that the direct electro-oxidation of propane can be performed at these temperatures, proper optimization of the electrode structure is necessary to achieve practical electrochemical oxidation rates.

IR-free polarization curves (Figs. 3 and 4) indicate that the maximum power density in H₂ is more than twice as large as in propane. Yet, in the presence of a thin film electrolyte configuration, a performance approaching 80 mW·cm⁻² is possible with dry propane.

![Figure 3. Raw and IR free polarization curves for hydrogen oxidation at 750°C in a CGO electrolyte supported SOFC.](image)

![Figure 4. Raw and IR free polarization curves for dry propane oxidation at 750°C in an electrolyte supported SOFC.](image)
Fig. 5 shows the measured fuel cell performances for the internal reforming of propane. It is observed that the maximum power density does not vary significantly with the S/C ratio in the range of S/C from 1 to 2.5.

![Graph showing measured fuel cell performances](image)

Figure 5. Internal reforming polarization curves at different S/C ratios at 750 °C.

The measured maximum power density is in the case of the internal reforming (41-45 mW·cm⁻²) comparable to that observed with dry propane (46 mW·cm⁻²). Although we have used in the case of dry propane a C₃H₈ flux significantly larger than that required by the faradaic process, a promotion of the reforming reaction on the catalyst surfaces by the electrochemically produced water should not be discarded. Otherwise, it is hypothesised that the kinetics of internal reforming and direct oxidation processes are comparable under these conditions (750°C).

A decrease in performance is observed for a S/C=3 due to a dilution effect of water. No carbon deposits were observed by electron microscopy and CHNS-O analyses after shut-down in propane for the anodes which have operated in both direct oxidation and internal reforming modes.

Finally, some transmission electron microscopy images of the Ru-CGO catalyst are presented in Fig. 6. These show a distribution of fine spherical Ru particles of about 20 nm on large irregular shape CGO particle support. Further optimization of the anode requires a proper distribution of the Ru promoter at the Triple-Phase Boundary (TPB).

CONCLUSIONS

Direct oxidation and internal reforming processes of propane at a Cu-Ru/CGO electrocatalyst have been investigated at 750°C in a CGO electrolyte supported cell. The measured electrochemical performances were affected by significant ohmic and polarization resistances. Although, propane conversion to syngas reached 80-90% under these conditions, the measured power densities in hydrogen were more than twice those recorded with C₃H₈. It appears that further optimization of the electrode structure is necessary for a better utilization of the Ru promoter.
Figure 6. TEM micrographs of the Ru/CGO catalyst.

ACKNOWLEDGMENTS

The authors are grateful to the Italian Ministry of Education and research (MIUR) for the financial support through the FISR Project (Fondo integrativo speciale per la Ricerca. "Sviluppo di SOFC planari con elettrodo supportante ad elevata area geometrica" Decreto 16.10.2000 G.U. n. 278 28.11.2000).

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