Short communication

Open- and closed-circuit study of an intermediate temperature SOFC directly fueled with simulated biogas mixtures

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Abstract

An intermediate temperature solid oxide fuel cell (SOFC) based on a gadolinia doped ceria (GDC) solid electrolyte, a Ni(Au)-GDC cermet anode and a $La_{0.54}Sr_{0.46}MnO_3$ perovskite cathode was tested at 600 and 640 °C on direct feed of simulated biogas mixtures. The catalytic (open-circuit) rate of the methane dry (CO_2)-reforming reaction over Ni(Au)-GDC anode was found to be maximized at about equimolar CH_4/CO_2 feed ratio. Cell power density up to 60 mW cm^{-2}, at a cell voltage of 445 mV and a current density of 135 mA cm^{-2} at 640 °C, has been obtained under closed-circuit cell operation at this optimal feed ratio. Carbon deposition was found not to downgrade cell output characteristics under closed-circuit conditions at constant external loads for ~120 h, preceded by open- or closed-circuit operation for ~100 additional hours.
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1. Introduction

Methane and CO_2 are the main constituents of biogas [1–4], extensively produced today in an indigenous local base by anaerobic biological waste treatment. Biogas composition usually lies within the following ranges: $CH_4 = 50–70\%$, $CO_2 = 25–50\%$, $H_2 = 1–5\%$ and $N_2 = 0.3–3\%$ with various minor impurities, notably NH_3, H_2S and halides [1].

Hydrogen, carbon monoxide or $H_2 + CO$ mixtures, produced by steam or CO_2-reforming of methane, can be used as efficient fuels for high temperature solid oxide fuel cells (SOFCs) to produce electricity [5,6]. Hence, in order to utilize methane, fuel cells usually employ an external fuel reforming process where readily available fuels are converted to CO and H_2, before these gases are supplied to the fuel cell compartment of the plant. Alternatively, the internal reforming concept has been considered as a more attractive and advantageous design. In this concept, the reforming reaction takes place directly – without the necessity of an external reformer – on the anodic electrode of the fuel cell, simultaneously with the charge transfer reactions, i.e., H_2 and CO oxidations by O^{2-}. Since sulfur impurities can cause deactivation of most methane reforming catalysts or solid oxide fuel cell anodes, both in the case of external or internal reforming, they have to be removed from biogas feedstock before its use in fuel cell stacks. Ammonia impurity is not practically a problem in SOFC feeds, since it can be easily oxidized to N_2 and H_2O.

The kinetics of methane CO_2-reforming reaction, as well as of H_2 and CO oxidations by O^{2-}, are fast at the operating temperatures of most SOFCs. Furthermore, the reforming reaction is endothermic and can cause severe cooling of the anode. Such cooling can have a strong adverse effect on cell performance but it can, in principle, be balanced by a portion of the heat produced by the parallel highly exothermic H_2 and CO oxidation reactions; the rest of the free energy change associated with these reactions determines the electrical energy produced by the cell.

It is also known that reactions which lead to carbon formation, such as CH_4 cracking and Boudouard reaction can occur on Ni catalysts [6,7]. Graphitic carbon deposition onto the anode can cause significant inhibition of its catalytic performance [8–19]. Recent experimental studies have shown that the incorporation of Au into the Ni-cermet composites promotes the formation of carbidic and adsorbed carbon, at the expense of graphite [15,16]—the former are readily oxidized by O_2 or O^{2-} [15,16], and thus do not have a negative influence on cell performance.

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A number of investigations on fuel cells operating under internal reforming of methane have been reported [17–22]. Although methane reforming can be performed by steam or CO_2, most internal reforming investigations have used steam as the reforming agent [17–21], while only a few preliminary studies have addressed fuel cells operating under CO_2-reforming conditions [22]. Other studies have shown that CeO_2-based solid electrolytes can be successfully used for intermediate temperature (500–650 °C) fuel cells, conditions under which gadolinia or samaria doped CeO_2 exhibit very high O^{2-} conductivity [23–25]. Fuel cells operating at intermediate temperatures offer several advantages compared to those based on YSZ and operated at much higher temperatures ($\geq$900 °C) [25].

Here we report the performance of a SOFC based on gadolinia doped ceria (GDC) solid electrolyte, a Ni(Au)-GDC cermet anode and a $La_{0.54}Sr_{0.46}MnO_3$ perovskite cathode. The aim was to investigate the feasibility of operating this device directly with simulated biogas ($CH_4 + CO_2$) feeds at intermediate temperatures, where the CO_2-reforming of methane can be catalyzed internally on the Ni(Au)-GDC anode. Au was used as a component of the Ni-cermet anode to inhibit graphitic carbon deposition, as noted above.

2. Experimental

The fuel cell reactor consisted of a 6.5 cm long GDC tube closed at one end, internal diameter 1.2 cm and wall thickness 1.1 mm. This was prepared by a slip casting method using a calcium sulfate tubular matrix and an aqueous suspension of GDC powder (Gd/Ce = 10/90 molar ratio, Rhodia) with ammonium polymethacrylate (Darvan C, R.T. Vanderbilt Co. Inc.) as dispersant. The amounts of water and dispersant in the suspension were 25 and 1 wt% of the amount of the GDC powder, respectively. The resulting GDC tube was sintered in air up to 1350 °C according to the following temperature program: $25\,°C \xrightarrow{2\,°C\,min^{-1}} 140\,°C\,(2\,h) \xrightarrow{2\,°C\,min^{-1}} 1350\,°C\,(2\,h) \xrightarrow{5\,°C\,min^{-1}} 25\,°C$. A size reduction of about 25% was observed after the sintering procedure. SEM (JEOL 6300: 20kV) images of the fired GDC electrolyte revealed spheroidal CeO_2-Gd_2O_3 particles with a narrow size distribution (0.4–0.7 μm).

The $La_{0.54}Sr_{0.46}MnO_3$ ceramic composite electrode was prepared by the citrate method [26,27], using high purity La_2O_3, $MnCO_3$ and $SrCO_3$ (Aldrich). The resulting gel was slowly (2 °C min^{-1}) heated in air, kept for 1 h at 350 °C, and then calcinated at 700 °C for 24 h in order to form the perovskite phase. In order to produce a thin (~20 μm) electrode film on the outer wall of the GDC tube, the perovskite powder was ball milled to $\leq$5 μm, dispersed in alcohol, coated onto the electrolyte outer wall, sintered in air up to 1000 °C at 5 °C min^{-1} and kept at 1000 °C for 6 h.

The porous Ni(Au)-GDC cermet anode was prepared by the combustion synthesis method using urea as fuel and $Ni(NO_3)_2 6H_2O$ (Merck), $Ce(NO_3)_3 6H_2O$ (Aldrich), $Gd(NO_3)_3 6H_2O$ (Aldrich) as metal precursors. Appropriate amounts of these nitrates were mixed with urea and a small amount of ethanol to yield a 65 wt% Ni-GDC cermet with Gd/Ce = 10/90. The required amounts of $HAuCl_4 3H_2O$ and NH_4NO_3 were then added to achieve the desired Au/Ni atomic ratio of 0.002. The mixture was stirred at 80 °C until a sol was formed and the Ni(Au)-GDC electrode deposited by coating this sol onto the inner wall of the GDC tube followed by progressive heating in air to 650 °C. Three subsequent coatings were necessary in order to produce an electrode film of suitable thickness (10–20 μm). The film had a Ni content of 60 wt% with Gd/Ce and Au/Ni molar ratios of 0.106 and 0.002 as determined by ED-XRF analysis (PGT Model LS 30143; 150 eV resolution at 5.9 keV). These values are close to those expected based on the stoichiometry of the preparation procedure. After reducing the film (10% H_2 in He; 650 °C/30 min) SEM indicated a porous microstructure consisting of spheroidal particles of uniform grain size (0.5–0.8 μm), the Ni(Au) and CeO_2-Gd_2O_3 phases being indistinguishable. The total mass of the anodic catalyst electrode was 30 mg with a superficial surface area of ~1 cm^2.

The open end of the GDC tube was clamped to a stainless-steel cap which had provisions for inlet and outlet gas lines, an Au connecting lead and a K-thermocouple with electrical isolation by means of α-Al_2O_3 tubing. The Au wire established electrical contact with the inner Ni(Au)-GDC catalyst electrode via a spirally shaped end and the thermocouple junction was located ~1 mm away from the electrode. The electrical circuit was achieved by a second Au lead connected to the perovskite electrode via a Pt-mesh pressed onto the cathode. Residence time distribution measurements showed that the 6 cm^3 cell behaved as a well mixed reactor over a wide range of flow rates (10–300 cm^3 min^{-1}).

Reactant gases were delivered by mass flow meters (MKS-247) with analysis by on-line gas chromatography (Shimadzu 14B; MS-5A and PN columns operated at 80 °C) and mass spectroscopy (Pfeiffer-Vacuum, Omnistar Prisma). The reactants were Messer Hellas certified standard CO_2 (99.6%) and CH_4 (99.5%); ultra pure He, H_2 and 20% O_2 in He were used for in situ treatment of the anodic electrode when necessary. Before acquisition of kinetic or fuel cell operation data, the anode was reduced in 10% H_2/He at 650 °C for 30 min. This activated the electrode for catalytic dry-reforming and also rendered it electrically conducting.

3. Results and discussion

3.1. Open-circuit measurements (methane CO_2-reforming kinetics)

A recent kinetic study of the CO_2-reforming of methane over a Ni-YSZ cermet catalyst provided strong evidence for competitive adsorption of CH_4 and CO_2 on the Ni surface [28]. Characteristic rate maxima located at equimolar CH_4/CO_2 reactant composition were observed, implying that the kinetics of CO_2-reforming of CH_4 on Ni catalyst can be modeled within the framework of classical Langmuir–Hinshelwood kinetics. Open-circuit kinetic data (Fig. 1) showed that with the novel Ni(Au)-GDC catalyst reforming activity is also maximized at around equimolar CH_4/CO_2. This implies that the mechanism
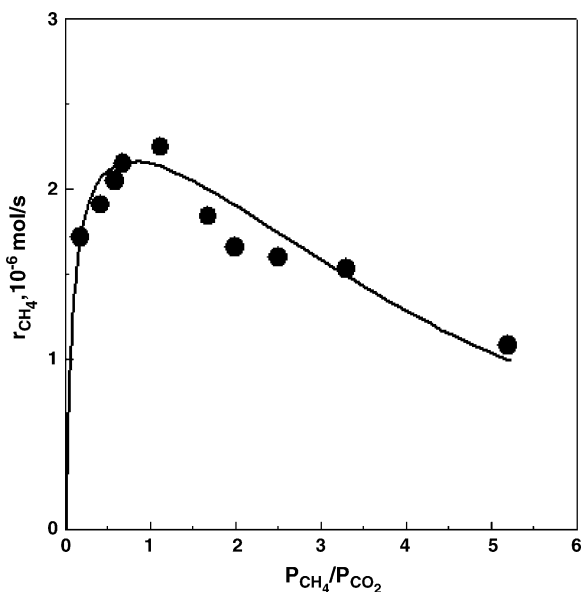
Fig. 1. CH$_4$ consumption rate during the internal dry-reforming reaction over the Ni(Au)-GDC catalyst electrode as a function of the CH$_4$/CO$_2$ molar feed ratio. $T = 600\,°C$. Total flow rate $F = 100\,cm^3\,min^{-1}$.

of the reforming reaction is essentially unaffected by changing the carrier to GDC and by the inclusion of Au; it is known that the CeO$_2$ component can promote the Ni-catalysed dry reforming of methane [13,29,30].

Under open-circuit conditions the maximum in the methane consumption rate coincides with the maxima in the rates of CO and H$_2$ production. This implies that under these conditions the anode is exposed to substantial concentrations of H$_2$ and CO. Because the charge transfer reactions of H$_2$ and CO with O^{2-} taking place at the anode three phase boundaries are related to the electrical energy produced, high concentrations of H$_2$ and CO are expected to have a beneficial effect on the rates of these electrochemical steps and consequently on electrical power generation.

3.2. Closed-circuit measurements (fuel cell operation)

The electrical efficiency of the cell was tested using an equimolar CH$_4$/CO$_2$ feed and Fig. 2 shows typical voltage–current (Fig. 2a) and power output–current (Fig. 2b) data. The results in Fig. 2a show a clear linear dependence of cell voltage on current density: *this demonstrates that ohmic polarization is the only source of polarization*. The slopes of the voltage–current curves are the ohmic resistance of the cell, a significant part of which is due to the O^{2-} transport resistance of the thick (1.1 mm) solid electrolyte. The absence of activation and concentration polarizations under biogas fueling appears very promising and implies that anodic and cathodic charge transfer reactions are fast on the anodic and cathodic materials employed over the temperature interval investigated. Equally, mass transfer or diffusion limitations involving the electrode pores, which would cause concentration overpotential, are insignificant. Clearly, substantial improvements in power output could be obtained by using thinner GDC components or by
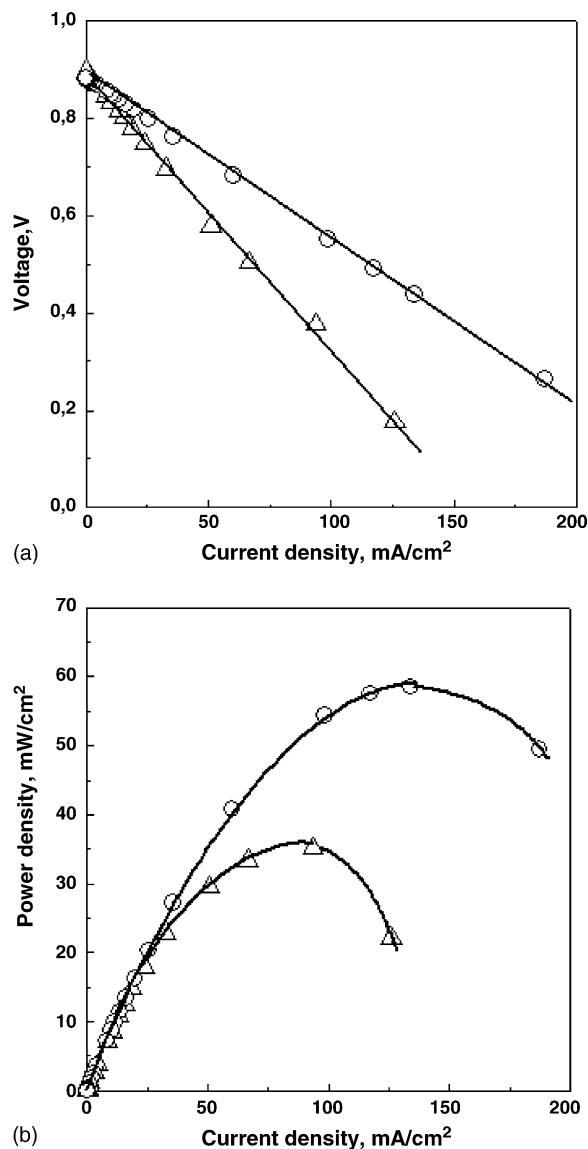

Fig. 2. Voltage–current (a) and power–current (b) behavior of the biogas fueled fuel cell under equimolar 50% CH$_4$/50% CO$_2$ feed ratio. Total flow rate $F = 20\,cm^3\,min^{-1}$. ($\triangle$) $T = 600\,°C$ and ($\bigcirc$) $T = 640\,°C$.

increasing operation temperature: both would lead to a reduction in ohmic resistance. The power density ($\sim$60 mW cm^{-2}) achieved is also very encouraging in view of the thickness of the electrolyte (1.1 mm). This value compares favorably with that of $\sim$90 mW cm^{-2} reported for GDC-SOFCs with electrolyte thickness of 280 μm, operating at similar temperatures and with wet 10% H$_2$/N$_2$ feed [25].

Visible blackening of the anode due to a very thin layer of carbon deposited seems not to downgrade cell performance after more than $\sim$120 h of operation at constant external loads (Fig. 3) preceded by open- or closed-circuit operation for $\sim$100 additional hours. This implies that extensive carbon deposition is not a significant factor in determining electrochemical performance under closed-circuit operation. It is possible that under such conditions electro-oxidation reactions of carbon at the anode (e.g. C(s) + O^{2-} → CO + 2e$^-$ and C(s) + 2O^{2-} → CO$_2$ + 4e$^-$),
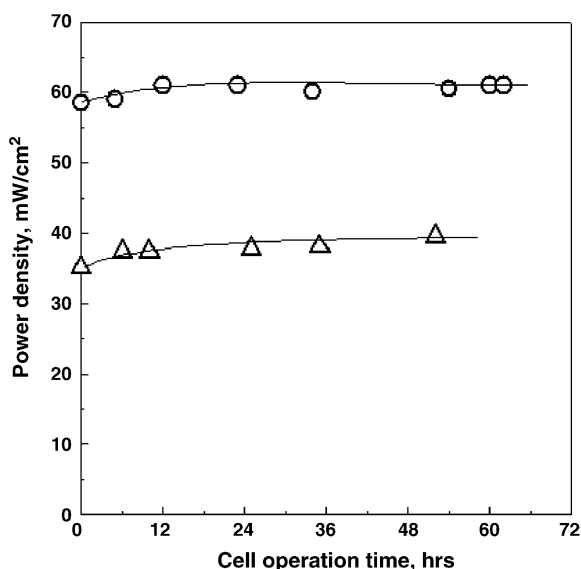
Fig. 3. Time dependence of cell power density output for two different temperatures, at equimolar 50% CH_4/50% CO_2 feed composition, flow rate $F = 20\,cm^3\,min^{-1}$ and constant external resistance loads. ($\triangle$) $T = 600\,°C$ and ($\bigcirc$) $T = 640\,°C$.

which also contribute to electrical power generation, effectively inhibit carbon accumulation. This explanation is supported by the results of recent work on internal CO_2-reforming of methane in a NiO-MgO/YSZ/(La, Sr)MnO$_3$ fuel cell where it was found that carbon deposition did not occur at the anode under closed-circuit conditions, whereas substantial deposition did occur under open-circuit cell conditions [18]. Similar effects have been reported in the case of internal steam-reforming at a Ni-ScSZ anode [19]—increased cell current resulted in decreased carbon deposition.

4. Conclusions

1. Intermediate temperature GDC-SOFCs with Ni(Au)-GDC cermet anodes operated with simulated biogas appear to be promising for electrical energy production. Long-term experiments (>1000 h) are required to assess their practical potential.
2. An equimolar CH_4/CO_2 feed ratio maximizes the rate of the dry internal reforming reaction of methane and consequently the electrical energy output characteristics of the cell.
3. Over the time scale of these experiments carbon deposition on the Ni(Au)-GDC anode had no measurable effect on the power output characteristics of the cell, likely due to the countering effect of carbon electro-oxidation reactions by O^{2-}. Possible adverse effects on long-term mechanical robustness remain to be investigated.

Acknowledgements

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