SOFC ANODE FOR DIRECT OXIDATION OF CH₄ AT INTERMEDIATE TEMPERATURES

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ABSTRACT

A new solid oxide fuel cell cermet anode composed of Ce₀.9₀Gd₀.₁₀O₁.₉₅ and Ni₀.₅₂Cu₀.₄₈ alloy is investigated. An appropriate synthesis procedure has been developed to obtain optimal electrochemical properties. The anode is characterised by high surface area and suitable catalytic activity toward oxidation of dry methane without significant carbon deposition after prolonged operation at 800°C and 700°C.

INTRODUCTION

SOFCs offer a clean pollution-free technology for the electrochemical generation of electricity with high efficiency (1). A typical SOFC operates near 1000°C; it uses yttria-stabilised zirconia (YSZ) as an electrolyte, which exhibits oxide-ion conductivity at 1000°C of about 0.1 S cm⁻¹. Lowering the operation temperature to 700°C-800°C would enhance the reliability, lifetime, and operating cost of the cell; however, with conventional membranes of YSZ the reduction in temperature implies poor performance (2). Two approaches are being developed for operation at temperatures <800°C: reduction of the thickness of the YSZ electrolyte membrane to less than 10 μm and the use of alternative electrolytes having an oxide-ion conductivity at or below 800°C which is comparable to that of YSZ at 1000°C. Ce₁₋ₓGdₓO₂₋ₓ (CGO) is a very promising electrolyte for intermediate temperature (IT) applications. The gadolinium-doped ceria has high ionic conductivity between 500°C and 700°C (0.01 < σ < 0.04 S cm⁻¹) (3). The lower operating temperature of the CGO over traditional YSZ has a number of benefits such as use of cheaper interconnector materials, lower degradation problems, and less mismatch in terms of thermal expansion coefficient among materials (4). Another important aspect for cost reduction is the possibility of using hydrocarbons as fuel. The conventional fuels used in SOFCs are H₂ and CO produced from hydrocarbons by internal or external reforming. The reforming process increases the complexity of the whole device as well as the cost. Therefore, an important effort is under way in searching new anode electrodes with suitable catalytic activity toward the direct oxidation of dry hydrocarbons. The most important challenge for such anodes is to avoid carbon deposition during operation because this carbon reduces the efficiency of the
Recently, an anode formulation based on Cu$_{0.8}$Ni$_{0.2}$ coated on CeO$_2$-YSZ has shown suitable performance in dry methane conditions, even in the presence of carbon deposition, but without losing performance in time (at least up to 170 h of operation) (5).

In this work, a SOFC device composed of Ce$_{0.90}$Gd$_{0.10}$O$_{1.95}$ (CGO) membrane electrolyte and an alternative cermet anode based on CGO and Ni$_{0.52}$Cu$_{0.48}$ alloy (Ni-Cu) are investigated. The Ni-Cu alloy shows suitable catalytic activity to activate the methane molecules toward electrochemical oxidation and, at the same time, has good current collector properties when it is well dispersed and distributed in the anode with the presence of CGO as ionic conductor. No significant evidence of carbon deposition has been observed at least for ~ 40 h working time using dry methane at 700° and 800°C.

**EXPERIMENTAL**

The cell architecture developed in this study consists of:

- **anode**: Cermet of CGO and Ni-Cu alloy (thickness: 30 μm)
- **electrolytic membrane**: CGO (thickness: 400 μm)
- **cathode**: Composite of LSMO and CGO (thickness: 30 μm).

The synthesis of the CGO powders is made via oxalic coprecipitation described elsewhere (6). The CGO powders are activated at 1050°C for 1 h and are then compacted by uniaxial pressing (300 MPa). The green pellet is treated at 1550°C for 3 h in static air obtaining a disk-supported electrolyte membrane ($\rho_{\text{rel}}$ > 95%). The cathode electrode is deposited by slurry painting. It is composed of a composite of La$_{0.6}$Sr$_{0.4}$MnO$_{3.8}$ (Praxair) and the “homemade” CGO (6) using isopropanol as a dispersant. The deposit is then fired at 1250°C for 1 h under static air to ensure a good interface between electrode/ electrolyte membrane. The anode is also deposited by slurry painting using the same organic vehicle as for the cathode. It consists of a mixture of the CGO powders and the Ni-Cu-O amorphous oxide (50 wt%:50 wt%). First, the Ni-Cu-O amorphous oxide is prepared as described in reference (7). After painting, the deposit is dried at 150°C for 1 h for solvent evaporation. Finally, the cell is mounted on an alumina tube, sealed with quartz adhesive (AREMCO), and heated to between 500° and 800°C in air flow forming the (Ni, Cu)O crystalline oxide. The gas is switched to helium before feeding pure H$_2$, which reduces the oxide to the desired Ni-Cu alloy. A gold paste (Hereaus) is used to form the anodic current collector, and a Pt paste (Engelhard) is employed at the cathode. A Pt reference electrode is allocated on the cathodic side to investigate the electrochemical behaviour of each electrode. An Autolab electrochemical apparatus equipped with an FRA has been used for the electrochemical analysis.

The structural and compositional analyses were made by X-ray diffraction (XRD) using a Bragg-Brentano configuration with Cu-Kα (Philips Xpert, The Netherlands) and X-ray fluorescence spectroscopy (XRF) (Bruker AXS, Germany). The microstructural analysis is carried out by scanning electron microscopy (SEM) (Philips XL30, The Netherlands) and transmission electron microscopy (TEM) (Philips CM12, The Netherlands).
RESULTS AND DISCUSSION

Structural Analysis

To investigate the crystallographic phase, the composition and the morphology of the anodic cermet, XRD, XRF, SEM and TEM analyses were carried out during all steps of the synthesis process. The starting powder for making the mentioned Ni-Cu alloy consists of an amorphous oxide matrix with a small fraction of crystallised particles as could be observed by XRD in Figure 1a), which was also checked by TEM (7). The XRF analysis shows that the Ni:Cu stoichiometry is 0.58:0.42. This Ni-Cu-O amorphous oxide is heated at 500°C for 1 h in air, and a fully crystallized oxide is obtained as shown by XRD (Figure 1b). Moreover, we have obtained from that process a solid solution of (Ni,Cu)O (Figure 1b). The phase could be indexed using the NiO cubic phase with \( Fm\overline{3}m \) as space group. The crystallographic cell parameter \( a = 4.183 \) Å is slightly higher than the pure NiO \( (a = 4.1769 \text{ Å}) \) and confirms the copper introduction in the cubic NiO crystallographic lattice. The calculated particle size from the XRD pattern using the Scherrer formula (8) shows values around 4.5 nm, evidencing the nanometric nature of that crystalline precursor oxide. From the particle size, a surface area for this powder is calculated obtaining values of around 150 m\(^2\) g\(^{-1}\).

This oxide is subsequently reduced in H\(_2\) between 500 and 800°C for 0.5 to 1 h. The XRF analysis confirms the maintenance of the initial stoichiometry and the XRD shows the presence of a single phase. The single phase can be indexed (Figure 1c) using the cubic system and space group \( Fm\overline{3}m \) symmetry of the Ni or Cu. The calculated crystallographic cell parameter \( a = 3.552 \) Å is between the values of pure Ni and pure Cu (3.5238 Å and 3.60150 Å, respectively). Following the same procedure done for the (Ni,Cu)O, the particle size and the surface area of the alloy are calculated as 19 nm and 36 m\(^2\) g\(^{-1}\).

![Figure 1. XRD of several stages during the Ni-Cu alloy formation and anode synthesis: a) amorphous phase Ni-Cu-O, b) crystalline (Ni,Cu)O fired to 500°-800°C in air, c) Ni-Cu alloy formation after reduced treatment under H\(_2\) at 500°-800°C, d) synthesis of the CGO/Ni-Cu cermet where the (Ni,Cu)O is reduced together with the presence of the CGO.](image-url)
respectively. In the presence of CGO, the observed surface area for the Ni-Cu alloy phase increases up to 42 m$^2$g$^{-1}$. These values indicate suitable surface area for the Ni-Cu alloy so we could expect good catalytic properties.

**Analysis of the Catalytic Activity**

The anodic catalyst was investigated in a steam reforming operation process using a molar ration of 4 H$_2$O: 1 CH$_4$ for checking the catalytic activity of this alloy for methane activation. The catalytic activity is evidenced by the detection of H$_2$ as a gas product of the reaction [1], in the outgas side of the reactor:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2
\]  

Figure 2 shows that the onset of methane conversion occurs at about 430°C whereas a complete conversion is achieved at about 600°C. Therefore, we can assume that at the operation temperatures of 700°C–800°C the methane reaction is catalytically activated on the Ni-Cu alloy. Elemental analysis is used to determine the carbon content in the catalyst after these catalytic experiments. Analysis carried out with a CHNSO elemental analyser (Carlo Erba) revealed the absence of carbon deposition after the reforming process.

![Figure 2. Catalytic activity versus temperature diagram for methane steam reforming experiment.](image)

**Microstructural and Electrochemical Analysis**

The anode was microstructurally analysed after heating to 500°C–800°C in air when the crystalline (Ni,Cu)O is formed. It is observed to present a uniform porous morphology, as shown in the SEM image (Figure 3a). Moreover, a detailed study by TEM (Figure 3b) showed good connectivity between the CGO and (Ni,Cu)O particles that could ensure an optimal three-phase-boundary region, implying good electrochemical properties. Also, for this kind of preparation process, the CGO particles are much bigger than the (Ni,Cu)O that surround the CGO. Finally, the anode is reduced as described under Experimental. The presence of the Ni-Cu alloy with the CGO oxide without the formation of any new impurity phases is confirmed by XRD (Figure 1d). No impurity phases are detected.
The electrochemical performance of the anodic cermet is evaluated in the fuel cell device by supplying dry methane (50 cm$^3$ min$^{-1}$) as a fuel in the anodic side whereas static air was used at the cathode. The cell is conditioned in methane at 700$^\circ$C and 800$^\circ$C before recording the polarisation curves and AC-impedance spectra. Figure 4 shows the polarisation and power density curves of the cell corrected by the ohmic losses using the series resistance value ($R_S$), which is measured by the AC-impedance spectroscopy from the high-frequency intersection on the real axis of the Nyquist plot. Because we are using a thick supporting electrolyte membrane architecture, all the experimental data collected by polarisation and AC-impedance measurements are strongly affected by ohmic resistance. More studies are under way to minimize these ohmic losses using a thinner electrolyte membrane. The measured anodic overpotential (IR-free) showed values of $\eta = 0.24$ and $\eta = 0.35$ V at 0.5 A cm$^{-2}$ for working temperatures of 800$^\circ$C and 700$^\circ$C, respectively. The low open circuit voltage indicates a possible reduction of the Ce$^{4+}$ to Ce$^{3+}$ at the anode-electrolyte interface, which causes a small electronic conductivity inside the electrolyte.
Galvanostatic operation at 0.25 A cm\(^{-2}\) @ 800°C

![Graph showing galvanostatic operation]

Figure 5. a) Lifetime measurement under galvanostatic conditions at 0.25 A cm\(^{-2}\) and 800°C using dry CH\(_4\). b) Representative TEM image of the CGO/Ni-Cu anode after 35 h of working in which the absence of carbon deposition is shown.

Finally, the possibility of carbon deposition in the cermet anode is checked. The lifetime experiment is carried out under galvanostatic conditions at 0.25 A cm\(^{-2}\) in the range between 700°-800°C. Figure 5a shows the experiment recorded at 800°C. The cell is conditioned under H\(_2\) flow in the anodic side, and afterward the gas flow is switched to CH\(_4\). It is interesting to observe a slight increase in the cell performance with time (Figure 5a). The measurement was carried out doing thermal cycles to test the cell response. After 35 h of operation, no trace of carbon formation was evidenced by TEM analysis, as shown in Figure 5b. This result contrasts with that reported by Kim et al. (9), who found a significant amount of carbon deposition for the same interval of time in the presence of Ni-Cu alloy obtained by a different synthesis process.

CONCLUSIONS

A fuel cell device consisting of Ce\(_{0.90}\)Gd\(_{0.10}\)O\(_{1.95}\) (CGO) as a membrane electrolyte and anodic Ni\(_{0.52}\)Cu\(_{0.48}\) alloy/CGO cermet has been investigated. Suitable catalytic activity was observed for the cermet in the presence of dry methane as fuel. No significant carbon deposition was observed after ~40 h of operation. Therefore, this could be the proof-of-principle that the Ni-Cu alloy, obtained by appropriate preparation procedure, acts as a good methane activation catalyst with a suitable tolerance toward carbon deposition. More work is under way to vary the morphology and composition of the cermet.

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