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# Electrochemical behaviour of propane-fed solid oxide fuel cells based on low Ni content anode catalysts

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ABSTRACT

Two different low Ni content (10 wt.%) anode catalysts were investigated for intermediate temperature (800 °C) operation in solid oxide fuel cells fed with dry propane. Both catalysts were prepared by the impregnation of a Ni-precursor on different oxide supports, i.e. gadolinia doped ceria (CGO) and $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ perovskite, and thermal treated at 1100 °C for 2 h. The Ni-modified perovskite catalyst was mixed with a CGO powder and deposited on a CGO electrolyte to form a composite catalytic layer with a proper triple-phase boundary. Anode reduction was carried out in-situ in $H_2$ at 800 °C for 2 h during cell conditioning. Electrochemical performance was recorded at different times during 100 h operation in dry propane. The Ni-modified perovskite showed significantly better performance than the Ni/CGO anode. A power density of about 300 mW cm$^{-2}$ was obtained for the electrolyte supported SOFC in dry propane at 800 °C. Structural investigation of the composite anode layer after SOFC operation indicated a modification of the perovskite structure and the occurrence of a $La_2NiO_4$ phase. The occurrence of metallic Ni in the Ni/CGO system caused catalyst deactivation due to the formation of carbon deposits.

## 1. Introduction

Various catalyst formulations, including $Cu/CeO_2$, Ni–Cu and various perovskites [1–5], have been investigated for the direct oxidation of hydrocarbons in intermediate temperature (500–800 °C) solid oxide fuel cells (IT-SOFCs) [6–10]. This process shows higher intrinsic efficiency with respect to internal reforming [1–3]. Steam reforming requires an excess of water injected into the stream to avoid the formation of carbon deposits in the presence of Ni-cermet anodes [11]. However, at intermediate temperatures, a high steam to carbon (S/C) ratio reduces the process efficiency and increases water-management constraints [1].

The cermets used in conventional SOFC anodes contain up to 65 vol.% of metallic Ni, as electronic conducting phase, and yttria-stabilised zirconia, as ion-conducting phase, to form a three-phase reaction zone with reactant gas [12–14]. It is well known that Ni catalyzes the cracking of hydrocarbons, causing the formation of carbon fibres that poison the anode surface [1,4].

Most efforts have focused on the direct oxidation of methane even though some attempts have addressed the direct oxidation of larger molecular weight hydrocarbons [1,6]. Propane is widely available and it can be liquefied to facilitate its storage. In liquid form, it is characterised by high energy density. Accordingly, propane is an interesting fuel for applications in portable power sources as well as for the remote and distributed generation of electrical energy. Simplicity of design for solid oxide fuel cells and their operation at intermediate temperatures appear appropriate for such applications. Thus, it is necessary to reduce the system complexity of these power sources by reducing fuel processing and water-management issues.

Although ceria-based electrolytes are characterised by partial electronic conductivity at 800 °C, they show appropriate ionic conductivity and may act as a reaction promoter. Ru in combination with ceria has been investigated for propane electro-oxidation in IT-SOFCs [6,15–17]. However, the search for cheaper catalyst formulations is mandatory. Several attempts have been made to investigate perovskite anodes for SOFCs [3,18]. The $La_{0.8}Sr_{0.2}Cr_{0.8}Mn_{0.2}O_{3-\delta}$ (LSCM) perovskite showed suitable reaction kinetics for methane but only at elevated temperatures, e.g. 950 °C [3]. Ni and Ni-doped perovskites have suitable properties as reforming catalysts whereas CGO is recognized to be an oxidation catalyst [1,2]. Thus, the electrochemical behaviour of low Ni content catalysts on these oxide supports is worthy of investigation. A highly dispersed active Ni-phase on a mixed ionic–electronic conducting oxide may provide suitable catalytic activity. However, the occurrence of carbon deposits should be avoided or, at least, significantly reduced in comparison with conventional anodic cermets containing a high Ni content. High dispersion of the Ni-phase on the oxide

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support can be achieved using low Ni-content and proper catalyst preparation procedures.

In this study, we investigated SOFC anodes based on a Ni-modified $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ perovskite combined with a gadolinia doped ceria ($Ce_{0.8}Gd_{0.2}O_{1.9}$) electrolyte and Ni supported on CGO. The $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (LSFCO) perovskite is characterised by mixed electronic and ionic conductivity. Also, CGO is a mixed ionic–electronic conductor in a reducing environment at 800 °C. These aspects favour the formation of a suitable triple-phase boundary with fuel in the porous anode. The LSFCO perovskite is characterised by poor stability under strong reducing conditions. However, previous experiments have shown that its in-situ stability can be improved in the presence of a CGO electrolyte, especially if the material is previously subjected to high temperature treatments [5].

## 2. Experimental

### 2.1. Anode catalyst preparation

An impregnation method [15] was used to prepare both Ni/CGO and Ni-modified LSFCO catalysts with a Ni content of 10 wt.%. Synthesis of the CGO powder was accomplished using a co-precipitation method described elsewhere [4]; LSFCO was supplied by Praxair.

CGO or LSFCO powders were impregnated at 50 °C with a solution of Ni nitrate in water. After drying, these powders were calcined in an oven at 500 °C for 5 h. The Ni-modified LSFCO was mixed with the CGO (70:30 wt.) in ethanol, using a ball milling procedure. Ni/CGO was used for anode preparation without any further modification. Either Ni-modified LSFCO/CGO or Ni/CGO anodes were spray coated [4] onto a CGO electrolyte (mass density, $\rho_{\text{rel}} > 95\%$) pellet (250 μm thick). A pure LSFCO layer was deposited on the other face of the electrolyte pellet to form the cathode. The electrodes were about 15 μm thick and the active area was 1 $cm^2$. A single anode layer was used. The SOFC cells were thermally treated in air at 1100 °C for 2 h before being installed in test hardware consisting of an alumina tube. A gold paste and gold wires were used as current collectors. Gold has been reported to be inert in terms of hydrocarbon cracking and/or oxidation [12].

### 2.2. Physico-chemical characterization

XRD analysis of powders and anode layers was carried out by an X'PERT Philips diffractometer with Cu Kα source. A Bragg–Brentano set-up was used for the powders whereas a grazing-angle (0.5° incidence angle) mode was adopted for the anode layer. This was necessary to study the anode layer while minimizing interference from the thick CGO electrolyte. TEM analyses of the catalysts before electrochemical testing were performed with a FEI CM12 instrument; SEM characterizations were carried out with a SEM XL30FEI instrument.

### 2.3. Electrochemical characterization

The cell was mounted on an alumina tube and sealed with ceramic adhesive (AREMCO). It was heated initially with a He stream at the anode. During heating ramp to 800 °C, the gas was switched to $H_2$ at 400 °C. At 800 °C, the anode was fed with dry propane at a 500 mV cell voltage. During polarization and steady-state measurements, the anode was fed with 100% dry propane at a high flow rate. The cathode was exposed to stationary air. Polarization and ac-impedance experiments were carried out at different times during operation.

An AUTOLAB PGSTAT30 Metrohm potentiostat/galvanostat, a frequency–response analyzer (FRA), and a 20 A booster were used for electrochemical measurements. Impedance spectra were obtained in the frequency range 10–1 MHz with an applied ac-voltage amplitude of 10 mV rms. The ohmic (series) resistance was obtained from a high frequency intercept on the real axis of the Nyquist plot. The polarization (charge transfer) resistance was derived from the difference between low frequency ($R_{\text{LF}}$) and high frequency ($R_{\text{HF}}$) intercepts on the real axis. All impedance measurements were taken at a 0.5 V cell voltage.

## 3. Results and discussion

### 3.1. Structure and morphology of the anode catalyst

The two anode catalyst powders were investigated by XRD after high temperature thermal treatments at 1100 °C (Fig. 1). Structural analysis of the anode layers was carried out after a time-study experiment (>100 h) in dry propane (Fig. 1). This allowed a comparison of the structural properties of the catalysts before and after operation. In traditional solid oxide fuel cells based on a Ni-cermet, the final anode properties are usually determined by an in-situ conditioning procedure in hydrogen that produces a chemical reduction of NiO to metallic Ni. For the anodes in this study, a similar approach was used. However, since cell was operating with dry propane, it was appropriate to evaluate the structural modifications that occurred on the anode after a reasonable operation time.

After, calcination at 1100 °C, XRD analysis of the catalysts supported on the gadolinia doped ceria and perovskite showed, essentially, typical diffraction peaks for the NiO phase (JCPDS 22-1189) and CGO or LSFCO support, respectively, without the occurrence of any specific interaction.

The formation of metallic Ni (JCPDS 4-850) on the Ni/CGO anode occurred after the time-study in propane as a consequence of the reduction of NiO. The main peaks of the cubic NiO, i.e. those with

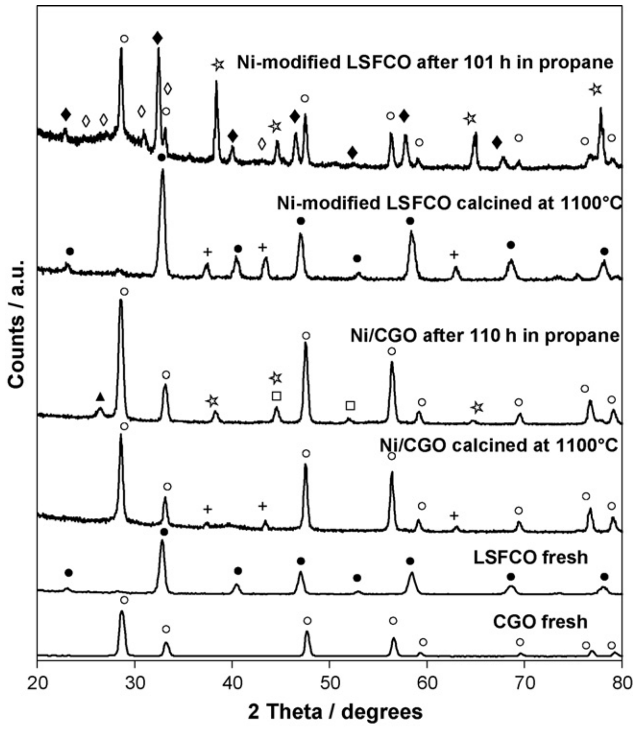

**Fig. 1.** XRD patterns of the Ni/CGO and Ni-modified LSFCO catalysts calcined at 1100 °C before and after SOFC operation (>100 h) in dry propane at 800 °C. The peaks associated to the specific phases, (◯) CGO, (●) LSFCO, (◊) $La_2NiO_4$, (♦ ) $SrFe_{1-x}Co_xO_{2.88}$, (+) NiO, (☆) Au, (□ )Ni, (▲) graphite, have been indicated.