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Research Paper

Solid oxide fuel cells fed with dry ethanol: The effect of a perovskite protective anodic layer containing dispersed Ni-alloy @ FeOx core-shell nanoparticles

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ABSTRACT

Solid oxide fuel cells (SOFCs) based on conventional nickel-yttria stabilised zirconia (Ni-YSZ) anodes can not be fed directly with organic fuels because of the associated formation of carbon deposits. This work explores a simple approach to solve such relevant limiting factor that affects the direct utilization of conventional dry hydrocarbons in SOFCs. The approach consists in depositing a composite multifunctional electrocatalyst layer on the SOFC anode to work as an internal integrated fuel processor. This study investigates the direct oxidation of dry ethanol in the modified SOFC and provides an evaluation of cell performance. A protective layer based on a composite made of Ni-modified perovskite and gadolinia-doped ceria is coated on a conventional SOFC anode based on Ni-YSZ. Besides the oxygen storage properties of ceria, the composite electrocatalyst is characterized by the presence of dispersed Ni-alloy @ FeOx core-shell nanoparticles in the outer layers and surface basicity properties. Efficient dehydrogenation of ethanol, carbon deposition-free cracking reactions and internal reforming assisted by a H_2/H_2O “shuttle mechanism” appear as the key steps involved in the direct oxidation of the organic fuel at the modified SOFC anode. The best performance achieved for the dry ethanol-fed SOFC is about 0.65 W cm^{-2} at 0.6 V and 800 °C. No carbon deposition is observed both on the Ni-YSZ supporting layer and protective Ni-doped perovskite layer after a durability test of more than 100 h.

1. Introduction

The market penetration of advanced technologies for distributed energy generation can be significantly enhanced by the development of highly efficient and reliable conversion devices such as fuel cells mainly fed with bio-alcohols [1,2]. Although Solid Oxide Fuel Cells (SOFCs) have the potentialities to be part of this new market, the present systems still suffer from relevant issues [3].

SOFCs are currently based on anode-supported planar cells made of Ni-YSZ supporting cermets [4]. This cell structure offers good robustness and reliability for operation with syngas and methane internal reforming [5]. External fuel processing to syngas is instead required for larger molecular weight hydrocarbons, and an upstream desulphurisation process is needed for natural gas and other fuels of practical interest. However, this configuration is affected by several constraints [6]. In particular, i) a poor redox stability with an associated risk of electrode delamination from the electrolyte layer due to the dimensional mismatch between metallic nickel and Ni-oxide during the Ni^0/NiO redox cycle, ii) a very poor flexibility for the direct utilization of dry hydrocarbons which is replaced by fuel processing through external reforming/partial oxidation, iii) internal reforming is only possible in the case of pure methane and not for natural gas, iv) limited tolerance to sulphur contaminants (few ppm); this requires the use of a large desulphurizer. Although several new materials have been demonstrated to be appropriate for application in SOFCs [5,7,8], in the short-period, the replacement of the Ni-YSZ based anode appears not feasible

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due to the high industrial risk associated with a new production chain for novel materials-based cells which have not yet shown proper mechanical robustness. A possible strategy to overcome the limitations of commercial cells is regarding the anode coating with a protective layer, which is active towards catalytic conversion of the organic fuel and more tolerant to sulphur contaminants while avoiding to introduce relevant ohmic drop. Previous studies carried out in our laboratory on bimetallic cermets, used as a protective layer, have already shown a significant influence on improving the stability of the SOFC cells towards the direct utilization of ethanol [9]. However, still some formation of carbon nanofibers on bimetallic alloys, during prolonged operation with dry hydrocarbons, can compromise the long-term stability of these devices. Whereas, oxide-layers containing encapsulated Ni particles on the surface are in principle less affected by carbon deposition [8,10]. In this work, the utilization of a low Ni content modified perovskite in combination with gadolinia doped ceria (CGO) is investigated as a protective layer for the anode of a commercial-type cell fed with ethanol.

The use of perovskite anodes in SOFCs has been the focus of several studies [11–15]. Different approaches have been proposed including i) perovskite formulations that are chemically stable under reducing conditions [16], but require high operating temperatures (>800 °C) or ii) perovskites characterized by high electronic or ionic conduction allowing to work at intermediate temperatures (650 °C–800 °C) but requiring modification or stabilization treatments [17]. Moreover, redox stable perovskites containing exsolved metal particles on the surface from B-site doping have recently attracted relevant interest as anode materials [18–25].

The investigated approach in this study differs from the above mentioned configurations since the perovskite structure, based on a strontium doped lanthanum ferrite-cobaltite, is decorated on the surface with Ni nanoparticles and successively stabilised by specific thermal treatments corresponding to the pre-conditioning treatments of a SOFC operating at 800 °C (i.e. static air up to 800 °C and then diluted H_2 at the same temperature). In particular, a ceramic composite made of Ni-modified perovskite and CGO is coated on the supporting anode of a conventional cell. Therefore, the composite of Ni-modified perovskite and CGO is used as catalytic layer in order to convert the alcohol in syngas or other reaction intermediates to minimize the risk of carbon formation. We show that such simple modification of the SOFC cell can provide significantly enhanced activity towards the direct utilization of dry ethanol without the relevant occurrence of carbon deposits.

2. Experimental

Low Ni content modified perovskite mixed to CGO has been prepared by an incipient wetness method at 50 °C using $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ PRAXAIR raw powders (11.19 $m^2\,gr^{-1}$) and 10 wt.% of Ni as Ni-nitrate (Aldrich) solution (0.5 M) in water. The wet raw powders were dried at 110 °C for 2 h and then calcined in air at 500 °C for 5 h. The resulting raw powders were grinded for 20 h with $Gd_{0.1}Ce_{0.9}O_{2\text{-}\delta}$ (CGO, Praxair, 38.92 $m^2\,gr^{-1}$) with a weight ratio of 70:30 in the presence of ethanol. This composite material was spray-coated onto a Ni-YSZ anode surface of a conventional SOFC cell. This was thermally treated at 800 °C in air and thereafter in hydrogen during cell conditioning. Hereafter this composite layer (Ni-modified perovskite and $Gd_{0.1}Ce_{0.9}O_{2\text{-}\delta}$) will be referred as "protective layer" or "pre-layer". Ni-modified perovskite powders, treated under conditions similar to the protective layer that is applied on the anode, were characterized by X-ray diffraction (XRD – PANalytical X'Pert), Electron Transmission Microscopy (TEM – FEI) equipped with Energy dispersive X-ray analyser (EDX), and X-ray photoelectron spectroscopy (XPS – PHI 5800-1).

The composition of the nanostructure was investigated by scanning transmission electron microscopy (STEM) carried out in a Cs corrected microscope CF-ARM Jeol operated at 200 kV, equipped with a SSD Jeol EDX spectrometer.

The electrochemical behaviour of a commercial SOFC coated with the protective layer and fed directly with absolute ethanol (≥99.5 vol.%) was investigated. Electrochemical experiments were carried out in a set-up including a furnace for high temperature tests, syringe pump for liquid ethanol and mass flow controller for the gases (hydrogen and inert gas) used during the cell pre-conditioning and as carrier during the operation with liquid ethanol. The cell used for the electrochemical experiment consisted of button cell (2 cm^2) laser-cut from a large area anode-supported cell (100 cm^2) and with the architecture and composition referred to Ni-YSZ/YDC/YSZ/LSFC; YDC refers to Yttria doped Ceria and the other components were defined above. Gold wires were attached to the anode by using a gold paste and thermally treated at 450 °C for curing and subsequent annealing the electrical contacts. The anode was spray coated with the protective layer powders to obtain a deposit of approximately 4 μm thick. Then, the cell was sealed onto an alumina tube with the anode exposed to the inner part of tube and the cathode exposed to the external static air. Gold wires were thus attached to the cathode side and thermally treated as above described for the anode. The sealing was assured by a ceramic paste (AREMCO 516) that was annealed with a specific thermal treatment procedure suggested by the manufacturer in the presence of inert gas fed into the anode. The cell temperature was measured by a thermocouple in contact with the cathode. After reaching the operating temperature (800 °C) in the presence of air, the cell was initially fed at the anode with N_2 and then with an N_2/H_2 mixture with a gradual transition to pure H_2. This procedure allowed to reduce both the Ni nanoparticles decorated on the perovskite surface and the NiO of the supporting SOFC anode. The electrochemical experiments were carried out by feeding a constant flow of ethanol. This was set at 4.5 cc min^{-1} or at 6.4 cc min^{-1} ethanol vapour, that was in excess to the amount required by the faradaic reaction. The sealing properties were checked by a thermocamera [26]. An AUTOLAB PGSTAT30 Metrohm potentiostat equipped with a 20 A booster and a frequency–response analyser module for impedance spectroscopy was used for the electrochemical investigation. The polarization curves were carried out from OCV to 0.5 V. EIS spectra were obtained at 0.7 V in the frequency range from 10 mHz to 1 MHz with an applied AC-voltage amplitude of 10 mV rms. The outlet stream was collected in a cold ice trap and then analysed by GC–MS spectrometry (AGILENT 7890A + 5975C) equipped with a column DB-WAXETR (Agilent). The gas stream after the condenser was also analysed by using micro-GC (Varian – CP4900) and Mass spectroscopy (Pfeiffer – ThermoStar GSD 320 T). The morphology of the cell was then studied by scanning electron microscopy (LEO 440 SEM-EDX system (Leica-Zeiss, Cambridge, England)).

3. Results

3.1. *Ex-situ physico-chemical analysis of the protective layer electrocatalyst*

Fig. 1 shows a comparison between the X-ray diffraction of the LSFCO precursor and the Ni-modified perovskite after specific thermal treatments (calcination at 500 °C and subsequent reduction at 800 °C). Two new phases ascribed to a Co- and Fe-partially depleted perovskite based on a $SrFeLaO_4$–type structure showing a Ruddelsden-Popper phase (i.e. K_2NiF_4-type oxides [27,28]) and to an $\alpha\text{-}Fe_{100\text{-}y\text{-}z}Co_yNi_zO_x$ oxide compound containing an excess of Fe [29–31], were formed as consequence of the thermal treatments. These caused quite significant exsolution of Co and partial exsolu-