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Electrocatalytic performance and carbon tolerance of ternary Au-Mo-Ni/GDC SOFC anodes under CH₄-rich Internal Steam Reforming conditions

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ABSTRACT

The present work examines the effect of Au-Mo modification on the electrocatalytic performance and carbon tolerance of Ni/GDC for the internal CH₄ steam reforming reaction. Comparative electrocatalytic measurements are presented between cells that comprise Ni/GDC and 3Au-3Mo-Ni/GDC as anodes under CH₄-rich feed (S/C = 0.3), without dilution in a carrier gas. Complementary electrochemical and physicochemical characterization was performed to investigate the possible modifications on the electrochemical and structural properties of the electrodes. In brief, the cell with Ni/GDC was more active catalytically, but exhibited worst electrocatalytic performance and operated for significantly shorter period with a degradation rate 5.5 mV/h. The main degradation factor was the higher carbon formation rate, which increased gradually and affected the polarization resistance of the electrode. The cell with 3Au-3Mo-Ni/GDC was moderately active catalytically, but performed better and lasted for the double operating period with a degradation rate 2.6 mV/h. In the latter case the carbon formation rate was almost negligible and degradation was attributed to the gradual re-oxidation of nickel, which affected the ohmic resistance of the electrode.

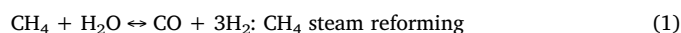
1. Introduction

Solid Oxide fuel Cells (SOFCs) represent an attractive and viable high temperature fuel cell technology for the generation of clean power, by converting chemical energy directly into electricity. Their main advantages are: (i) high electrical efficiency due to the enhanced reaction kinetics within the wide range of operating temperature (500–1000 °C), (ii) fuel flexibility and (iii) production of high quality waste heat [1,2]. Specifically, SOFCs can operate directly with various hydrocarbon (H/C) fuels, without the need of an external reformer. This mode of operation, known as Internal Reforming (I.R.), is one of the competitive advantages for the commercialization of SOFCs, in both stationary and mobile applications, since it improves and simplifies the whole system's integration. Indicatively, I.R. is based on the catalytic activity of the fuel electrode and has the benefit that part of the generated heat in the cell, can be directly used for the endothermic reforming reactions [1–3]. In this respect, various types of H/C fuels can be considered as candidates, including biogas and Natural Gas (N.G.). However, the basic drawback is that such feeds comprise carbon components and sulfur impurities, which deactivate the State of the Art (SoA) SOFC anodes [1,4].

Ni-containing ceramic – metal composites with Yttria-Stabilized

Zirconia (YSZ), Scandia-Stabilized Zirconia (ScSZ) and Gadolinia-Doped Ceria (GDC) are currently the most commonly used anode materials. This is mainly because, at the operating conditions of SOFCs, Ni-based electrodes exhibit very good activity and electronic conductivity for the electrochemical oxidation and/or reforming reactions, high gas diffusivity and excellent mechanical/structural integrity. Furthermore, the commercial interest on the I.R. mode of operation urged the SOFCs research community to focus on these materials, due to their close relation with the typical nickel-containing reforming catalysts [1]. However, SOFCs comprising Ni-based anodes face some critical degradations issues. Indicatively: (i) they are prone to carbon deposition, formed by decomposition of e.g. CH₄ [Reaction (4)] and/or by CO disproportionation [Reaction (5)], (ii) the deposited carbon causes further corrosion of Ni, leading to direct structural damage of the anode and loss of conductivity [2,5], (iii) they exhibit poor redox stability and (iv) Ni forms agglomerates, after prolonged fuel cell operation [6].

The internal steam reforming of methane is an endothermic process towards the production of H₂, CO and CO₂. It is generally considered [7–9] as a mixture of the following catalytic and electrochemical reactions, which proceed in parallel and/or in series:

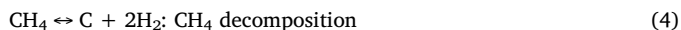
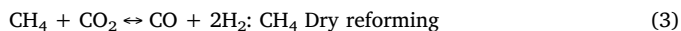
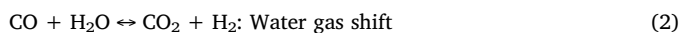


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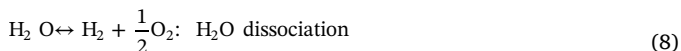
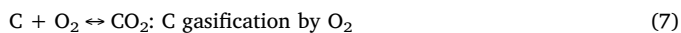
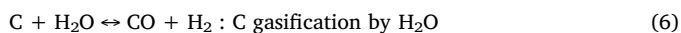
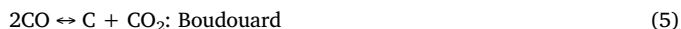
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At temperatures, typically below 700 °C, the produced CO can undergo disproportionation [Reaction (5)] and form carbon.



In regards to the electrochemical reactions, H₂ and CO can be oxidized at the solid electrolyte/metal/gas three-phase boundaries (tpb) to form H₂O and CO₂.



Moreover, CH₄ can be partially oxidized electrochemically towards the production of H₂ and CO [10,11]



Taking into account the above, carbon formation may occur through the Reactions (4), (5) and the reverse of (6). On the other hand, carbon can be removed by Reactions (6), (7) and the reverse of (5). Overall, carbon accumulation takes place in the case where the rate of carbon forming reactions exceeds the rate of carbon removal reactions [2].

Therefore, in order for SOFCs to operate on I.R. mode it is suggested [1,12] that the anode electrode should be moderately active for the reforming reactions and tolerant against carbon formation. The latter property is rather difficult for Ni-based materials and especially for Ni/YSZ, which is the SoA anode in both electrolyte and electrode-supported cells. One approach for ensuring limited carbon formation and long-term operation of Ni/YSZ anodes, is to increase the steam content in the fuel and to maintain a steam/carbon (S/C) ratio equal to 2 or higher. However, such S/C ratios have been proven to be too high to be practical in SOFCs. Indicatively, there is significant decrease in the Nernst potential value [Eq. (3)], resulting in lower cell efficiency, while there is enhancement of the anode's re-oxidation causing the failure of the cell [3].

Another alternative is the development of efficient and carbon tolerant anodes, aiming to replace Ni/YSZ. In this direction CeO_{2-δ} – based formulations have been considered as quite promising materials. This is because the reduced form of ceria exhibits a substantial mixed oxygen ionic and n-type electronic conductivity. Furthermore, the high oxygen storage capacity (OSC) and the sufficient mechanical and thermal stability properties of ceria in combination with the catalytic activity for combustion and hydrocarbon oxidation reactions [1,13] are important characteristics for a SOFC electrode, especially for internal reforming operation. In this category GDC [CeO₂(Gd₂O₃)] is one of the most frequently used substitutes of YSZ. It is known to suppress coke formation and for its catalytic behavior in the steam reforming of methane [1,12,14]. However, the electrocatalytic activity of GDC without any additives is insufficient and mixing with nickel oxide forms Ni/GDC as a potential electrode for CH₄ fueled SOFCs.

Ni/GDC has been investigated as anode in H/C fueled SOFCs and it has been reported that it can be further improved through modification with several transition non noble – metal catalysts or noble-metal catalysts [1]. In this direction our research group with collaborators [7,9,15–18] attempted to study and modify commercial NiO/GDC powder with Au and/or Mo nano-particles. These modifications

resulted in electrodes with high tolerance and improved electrocatalytic activity under both carbon forming and sulfur poisoning conditions. The investigation started [7,15] by studying the effect of the applied Au and/or Mo doping on the physicochemical and catalytic properties of Ni/GDC for the reactions of catalytic methane dissociation and steam reforming. One of the main findings was the induced structural modification on nickel through the formation of a trimetallic Au–Mo–Ni solid solution in the ternary sample. Furthermore, the powders have been examined [17] as anode electrodes for their sulfur tolerance in the reaction of internal methane steam reforming, under high and low H₂O/CH₄ ratios, including 10 ppm H₂S. So far in these studies the fuel feed was diluted in helium carrier gas, which was the predominant constituent of the reaction mixture, and the main conclusion was that the 3Au-3Mo-Ni/GDC sample proved to be the most sulfur tolerant electrode, compared to Ni/GDC and the binary 3Au-Ni/GDC and 3Mo-Ni/GDC. The superior performance of the ternary electrode was attributed to a synergistic interaction of the trimetallic Au-Mo-Ni solid solution that seems to partly protect nickel against sulfur poisoning.

The present study is a continuation of our research with complementary characterization and electrocatalytic measurements. The main objective was to further examine the effect of the Au-Mo modification on the behavior of the ternary electrocatalyst and to perform comparative electrocatalytic stability measurements, but by applying this time harsh reaction conditions without dilution of the reactants in a carrier gas. The comparison is between Ni/GDC and 3Au-3Mo-Ni/GDC anodes for the internal methane steam reforming reaction under CH₄-rich fuel feed. In particular, there is focus on some catalytic and electrochemical performance indicators through time, including the production rates of H₂, CO, CO₂, the formation of carbon deposits and the evolution of the ohmic and polarization resistances as a reflection of the operating potential.

2. Experimental

2.1. Preparation of electrocatalysts

Commercial NiO/GDC powder (Marion Technologies) was used as the non-modified “blank” sample and as the support for the preparation of the modified electrocatalysts. A binary Au – NiO/GDC sample with nominal loading 3 wt.% of Au was prepared via the deposition-precipitation (D.P.) method. Moreover, a ternary Au-Mo-NiO/GDC sample with nominal loading 3 wt.% of Au and 3 wt.% of Mo was prepared with the Deposition co-Precipitation (D.CP) method. Details for the preparation of these samples are reported in a previous study [7]. After filtering, the precipitate was dried at 110 °C for 24 h and one part of the batch was calcined at 600 °C for 90 min, while another part at 1100 °C for 75 min. The former batch was used for the preparation of pastes for the screen printing technique, which is described below. The batch at 1100 °C was used for the characterization of the samples. In this way the powders have been subjected to similar thermal stress like the calcined Solid Oxide electrolyte-supported cells. In the presented study the prepared powders were physicochemically characterized with *in situ* XRD in CH₄/N₂ and SEM.

2.2. Preparation of solid oxide electrolyte-supported cells

The electrolyte-supported cells consisted of circular shaped planar 8YSZ electrolytes manufactured by Kerafol with a diameter of 25 mm and 300 μm thick. The anode and cathode electrodes were deposited by means of the screen printing technique. In particular for the anode electrode, a paste (solids loading 60 wt.%) was prepared by using an amount of NiO/GDC (Marion Technologies) anode powder (modified with Au, Mo and Au-Mo), terpineol (Sigma-Aldrich) as the dispersant and PVB (polyvinylbutyral, Sigma-Aldrich) as binder. Similarly the cathode electrode was prepared by using a paste of YSZ/LSM (Lanthanum Strontium Manganite: LSM) (provided by SOLIDpower).

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