Glycerol oxidation in solid oxide fuel cells based on a Ni-perovskite electrocatalyst

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ABSTRACT

An investigation of the electrochemical oxidation of glycerol as alternative to hydrogen and methane in solid oxide fuel cells (SOFCs) based on a noble metal-free anode catalyst was carried out. The anode electrocatalyst consisted of a Ni-modified $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (LSFCO) perovskite. After thermal activation, air treatment at $1100\,°C$ followed by reduction at $800\,°C$ in H_2, Ni was mainly present as ultrafine La_2NiO_4 particles homogeneously dispersed on the perovskite surface. The thermal activation also caused a modification of perovskite into a lanthanum depleted structure. The thermal reduction at $800\,°C$ determined the occurrence of metallic Ni on the surface. These results were corroborated by X-ray photo-electron spectroscopy (XPS), transmission electron microscopy (TEM) and X-ray diffraction (XRD). A suitable power density ($327\,mW\,cm^{-2}$) was achieved for the electrolyte supported SOFC fed with chemical-grade glycerol in almost dry condition, i.e. steam to carbon ratio (S/C) of 0.2. The highest electrical efficiency (voltage efficiency) approached 50% at the peak power under mild humidification (S/C = 0.2). Whereas an increase of water to glycerol ratio, caused a progressive decrease of voltage efficiency at the peak power down to 44% for S/C = 2.

1. Introduction

Conventional energy resources like petroleum, natural gas, and coal presently fulfill the major energy demand. Hydrocarbons-based fuels are characterized by limited reserves concentrated in certain regions of the world [1]. Thus, the most feasible way to meet the growing demand of energy is to utilize alternative fuels that can be obtained from renewable sources [2—8].

Bio-diesel is considered to be an attractive alternative to conventional fuels [5,9—11] because it is a carbon-neutral fuel and it is characterized by low sulphur content [12]. Thus, its increasing use as alternative to fossil fuels would reduce our generation of carbon dioxide [13,14]. Glycerol is obtained as a by-product when biodiesel and fatty acid methyl ester are produced [9,10]. Currently, glycerol is used as a raw material in cosmetic, pharmaceutics, food, and tobacco industries [4].

At the present, the production of 1000 kg of biodiesel causes the occurrence of 100 kg of glycerol as by-product. Therefore, it is inferred that the availability of glycerol could exceed the demand as consequence of the biodiesel production [9]. Various routes for utilization of the surplus of glycerol have been suggested. Glycerol is non-toxic, non-flammable, and non-volatile. It is ideal for a wide variety of power applications. It has also a high energy density ($6.26\,kWh\,l^{-1}$ pure liquid) if compared to hydrogen ($0.76\,kWh\,l^{-1}$ at 34.5 MPa) and methane ($3.19\,kWh\,l^{-1}$ at 34.5 MPa) commonly used in Solid Oxide Fuel Cells (SOFCs), making it a very attractive fuel. In fact, glycerol can be used at suitable conversion efficiency in SOFCs. Solid oxide fuel cells operating at $800\,°C$ are quite

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resistant to fuel poisoning and furthermore can run on several fuels [15–18]. Crude glycerol derived from biodiesel production is affected by variable content of impurities depending on the preparation process [19]. A purification stage is needed; as example, an ion exchange resin is typically used [20,21]. A heterogeneous catalyst is generally used during transesterification reactions [22]. Desulfurization is also appropriate before fuel feed to SOFCs [12].

One of the main advantages of a SOFC is its capability to tolerate significant amount of water contents in the fuel without degradation of the performance. The excess of water, besides promoting internal reforming to H_2 and CO, also reduces the occurrence of carbon deposits formation on stainless-steel pipelines and on the anode catalyst surface [23].

The technology of solid oxide fuel cells has now reached a proper level of maturity to address problems connected to the remote and distributed generation of electric power. Currently, SOFCs are an appropriate choice for small and medium distributed generation systems (0.5–50 electrical kW) [24–30]. SOFCs can be fed with various kinds of fuels, especially those widely available and/or characterized by low cost [2,3]. The need of sustainable energy systems has stimulated the investigation of alternative fuels in SOFCs, growing interest to use by-products of potential large-scale industrial processes. Accordingly, the oxidation of glycerol in solid oxide fuel cells (SOFCs) is of significant interest because glycerol is widely available and obtainable from renewable sources. Yet, only recently, studies concerning with the direct feed of glycerol to SOFCs have been carried out [31,32]. In a first work of our group, we have reported a preliminary investigation of the feasibility of direct glycerol feed in a SOFC [32]. However, no detailed analysis of catalytic activity, catalyst properties, conversion efficiency and effect of steam to carbon ratio was carried out. In a work of another group, the authors specifically investigated glycerol internal reforming in a conventional tubular SOFC based on a Ni/YSZ anode without considering the possibility of using dry glycerol or low values of S/C [33]. The use of an internal reforming (typically S/C = 2.5) requires an excess of water to be fed to the SOFC anode to avoid carbon deposits and to promote the reaction at the Ni-cermet. Alternatively, there were a few studies concerning the conversion of glycerol to syngas in a reformer and the subsequent utilization of the produced gas in SOFCs operating at 850 °C [34]. The direct utilization of dry glycerol in SOFCs may represent an alternative approach due to the high intrinsic efficiency of the direct oxidation process.

In this paper, we report about a new Ni-modified perovskite electrocatalyst as alternative to Ni/YSZ cermet for the direct utilization of glycerol in SOFCs. Perovskite materials as electrocatalyst support are characterized by mixed electronic and ionic conductivity and appear appropriate for intermediate temperature operation [35] whereas Ni acts as promoter for the catalytic activity. In this work Ni is not present in catalytic layer as bulk form as in a classical cermet, but, it is highly dispersed on the perovskite support; moreover, we have used a composite catalytic layer of Ni/perovskite-gadolinia doped ceria (CGO) to enhance ionic percolation in the anode and promote fuel coxidation by the O^{2-} ions. The electrochemical investigation concerns with the effect of water addition to the anode stream on the cell performance and the

direct utilization of dry glycerol. To promote O^{2-} ions flow from the cathode to the anode, gadolinia-doped ceria was also used as ceramic electrolyte. A SOFC operation temperature of 800 °C was used since this is the targeted temperature for internal reforming of methane for state-of-the-art anode supported SOFCs [36].

2. Experimental

2.1. Anode catalyst preparation

The Ni/LSFCO-CGO catalyst was prepared by the incipient wetness method. The LSFCO powder (11.19 m^2 g^{-1}, Praxair) was impregnated for 2 h with continuous magnetic stirring at 50 °C with a solution 1 M of Ni nitrate (Aldrich) in water. The powder was first dried and then calcined in air at 500 °C for 5 h (heating rate, 2 °C/min; cooling rate: 2 °C/min). The resulting Ni content was 10% on LSFCO (wt/wt). Afterwards, Ni-modified LSFCO catalyst and $Ce_{0.9}Gd_{0.1}O_2$ electrolyte (CGO, 18.80 m^2 g^{-1}, Praxair) powders in a weight ratio of 70:30 were ball milled for 20 h in ethanol, for the anode layer preparation. Hereafter, this composite ceramic catalyst and electrolyte powder will be referred to as "fresh electrocatalyst". The fresh catalyst powder was deposited onto one face of a CGO pellet. It was first thermal treated at 1100 °C in air (2 h) and subsequently in-situ reduced at 800 °C in hydrogen (2 h) to obtain the activated anode electrocatalyst for SOFC (see below). The first step favoured the adhesion of the catalytic layer to the ceramic electrolyte membrane. The second step allowed to stabilize the catalyst for operation in a reducing environment and favoured formation of metallic Ni sites.

To allow for a proper ex-situ characterization, the fresh electrocatalyst powder was also activated out of cell according to the manufacturing and conditioning procedure of the SOFC cell i.e. a thermal treatment at 1100 °C for 2 h in air and subsequently reduction at 800 °C in hydrogen for 2 h. Hereafter this will be referred to as "activated anode electrocatalyst".

2.2. Physico-chemical characterization of the anode catalyst

X-ray photoelectron spectroscopy (XPS) measurements were performed on Ni-modified and unmodified support by using a Physical Electronics (PHI) 5800-01 spectrometer to investigate the presence of Ni on the catalyst surface. A monochromatic Al/Kα X-ray source was used at a power of 350 W. The pressure in the analysis chamber of the spectrometer was 133 nPa during the measurements. To compensate for surface-charging effects, the calibration of the binding energy (B.E.) scale was made with reference to the B.E. at 284.6 eV of the adventitious carbon.

The structural properties of the powders were investigated by X-ray diffraction (X'PERT Philips) with Cu Kα source. The crystallographic phases were identified by using the JCPDS (Joint Committee of Powder Diffraction Standards) database. A Bragg-Brentano set-up was used. Transmission electron microscopy (TEM) analysis was carried out by FEI CM12-EDX instrument operating at 120 kV and equipped with LaB$_6$ filament. The sample was dispersed in ethanol in an ultrasonic