Fabrication and testing of copper/gadolinium-doped ceria-based Solid Oxide Fuel Cells operating at intermediate temperature

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Abstract: Planar solid oxide fuel cells (SOFC) with CuO/gadolinium-doped ceria (GDC) supporting anode were produced and tested in H2 and in CH4/CO2 mixture at 650°C. The electrolyte densification at 900°C was promoted by compressive strains induced by larger anodic thickness. The reduction behaviour of CuO/GDC anodic powders was preliminarily evaluated. The electrochemical measurements showed an increasing power density with the anode thickness (from ≈500 μm to ≈1.4mm) reaching a maximum value of 227 mW cm⁻² at 650°C in pure H2. Power density of 29 mW cm⁻² was measured in wet CH4/CO2 biogas mixture at 650°C. Catalytic activity measurements towards methane dry reforming showed limited conversion at all investigated temperatures, this suggesting that the actual anodic reaction is the methane combustion. Scanning electron microscope observations and energy dispersive X-ray analyses of the cell tested in CH4/CO2 mixture did not show any carbon deposit, thus pointing out that the Cu/GDC cermet can be considered a stable and reliable anodic substrate for IT-SOFC fed by CH4/CO2 mixture.

Introduction

Solid oxide fuel cells represent one of the most suitable and versatile stationary devices for power applications due to their fuel flexibility and high efficiency [1]. Nevertheless, their commercialisation has been so far limited due to the high operative temperatures that can cause interdiffusion of the electrode materials to the electrolyte, which weakens the performances and reduces the lifetime [2]. Another parameter that must be taken into account is the reduction of the polarisation resistance that mainly depends on the cell design. A very typical SOFC configuration is the so-called anode-supported cell, which allows to reduce the ohmic resistance and activation polarization associated with thick electrolytes and the consequent reduction of operating temperature even below 800°C. In order to further reduce the operating temperature, some innovative electrolytic materials have been proposed in the last years. Lanthanum gallate perovskite (like (La, Sr)(Ga, Mg)O3 or LSGM) is one of the widely used material in the low or intermediate-temperature SOFC[3]. Gadolinium-doped ceria (GDC) compounds have also been intensively investigated for their high ionic conductivity in the intermediate temperature (IT) range, i.e. between 600 and 800°C [4]. GDC densification, which is usually carried out at temperature in excess to 1500°C, can be achieved at reduced temperature either by using sintering aids (like Cu, Co, Fe, Mn, Li and Zn oxides) [5] or by using nanosized GDC powders [6] or by very recently proposed field assisted and flash sintering methods [7]. In recent works, the addition of Li2O as sintering aid for GDC has been shown to be beneficial for the anode/electrolyte co-sintering process [4d, 8]. It was also reported that the electrolyte densification in GDC anode supported cells is also favoured by equi-biaxial compressive stress generated at high temperature because of the differential shrinkage rate [9]. Nickel–zirconia (Ni/YSZ) anodic cermet represents the state of the art for conventional SOFC, Ni providing both electronic conduction and catalytic effect for hydrogen oxidation. Unfortunately, Ni/YSZ anodes are not stable when exposed to hydrocarbons since Ni catalyses the formation of carbonaceous deposits that foul the anode. The catalytic properties of Ni are also reduced by sulphur impurities (in concentrations as low as 1 ppm) that are present in the most fuels [10]. Moreover, it shall be reminded also that Ni is characterized by high toxicity [11]. The mentioned drawbacks motivated the researchers towards the identification of alternative less toxic anodic catalysts which do not promote carbon deposition and are not susceptible to sulphur poisoning [12]. Among the different investigated anodic materials, Cu/GDC seems to be one of the most promising candidate [13]. The aim of the present work was the development of CuO/GDC-based cells able to perform at moderate temperature both in H2 and in CH4/CO2 mixture. The anodic substrate thickness was optimized by testing the electrochemical performance in H2. The cell performance was then investigated in CH4/CO2 mixture. Ex situ catalytic activity of the anodic powder for CH4 reforming using CO2 or O2 was also investigated to support the electrochemical results.

Results and Discussion

Powders characterisation

Figure 1 shows the XRD pattern of Cu45P and Cu45P_S powders. Both spectra reveal the presence of GDC solid solution with cubic...
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Keywords: Copper-based anode • Gadolinia-doped Ceria • planar intermediate temperature solid oxide fuel cell • co-sintering • electrochemical impedance spectroscopy