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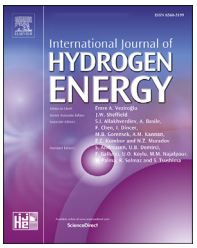

Lanthanum chromite based composite anodes for dry reforming of methane

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ABSTRACT

Composite anodes containing $La_{0.6}Sr_{0.4}CrO_{3-\delta}$ (LSCr) and $Ce_{0.9}Gd_{0.1}O_2$ (GDC) infiltrated with 5 or 10 wt% Ni were investigated as potential catalysts for dry reforming of methane (DRM) reaction in methane rich mixtures. Powders were characterized and tested as catalysts for DRM reaction. Ni-infiltrated composite anodes were used for fuel cell tests and compared to Ni-free anodes. Electrochemical tests were performed in different gas mixtures to evaluate the anodic performance in externally reformed biogas (external reforming mode). The design of an external layer of composite anode achieved the internal DMR reaction (internal reforming mode).

Introduction

Solid oxide fuel cells (SOFCs) keep attracting great attention mainly for their capability of being powered by methane or biogas [1]. Among the different routes for methane-syngas conversion, dry reforming of methane (DRM) reported in eq. (1) shows advantages, combining syngas production and CO_2 utilization.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad (\Delta H^0 = 247\ kJ\ mol^{-1})\ (DMR) \qquad (1)$$

DRM is an extremely endothermic reaction and requires temperatures as high as those of operating SOFC to attain reasonable yield of syngas. SOFCs can simultaneously perform DRM reactions in their anode sides (internal reforming mode) and, partly compensate the energy necessary for the reforming with the heat released during the electro-oxidation [1–4]. Alternately, SOFCs can be fuelled by biogas reformed in an external reactor (external reforming mode) [5–8]. In both cases, performing anodes are highly required because conventional Ni–YSZ electro-catalysts show severe instability due to carbonaceous deposits and sulphur impurities that deactivate the active sites [9,10].

In this work, composite anodes based on perovskite oxide and small amount of Ni were investigated. Among perovskite oxides, lanthanum chromite ($LaCrO_3$) was chosen for its

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structural stability and good electrical conductivity [11–15]. Commonly, alkaline earth (AE)-doped lanthanum chromites have been used as interconnectors because of their p-type conductivity in air and phase stability in hydrogen [16]. Lower valence elements, such as Sr, act as electron acceptors on the trivalent lanthanum or chromium sites, increasing p-type conduction by polaron hopping conduction mechanism [17–20]. Increasing the strontium content resulted in increased conductivity keeping the single phase stable for a strontium concentration up to 0.4 mol% [21].

Strontium doped lanthanum chromites as novel anodic materials for direct methane oxidation and/or reforming were only rarely investigated [22–24], while $La_{1-x}Sr_xCr_{1-y}M_yO_{3-\delta}$ with M = Fe, Co, Ni, and Mn were widely reported in literature [25–27]. Although the electrochemical properties of some lanthanum chromite-based oxides were relevant, they do not show proper catalytic properties for methane reforming [24,28]. In our work, Sr doping of lanthanum chromite was increased to achieve high electrical conductivity, then infiltration of a small amount of Ni catalyst was added to promote methane reforming. Composite anodes containing 70 wt% $La_{0.6}Sr_{0.4}CrO_{3-\delta}$ impregnated with 5 or 10 wt% Ni, and 30 wt% $Ce_{0.9}Gd_{0.1}O_2$ (GDC) were investigated as potential catalysts for DRM reaction in methane rich mixtures. The addition of GDC was evaluated to improve the anodic conductivity, the carbon resistance and the adhesion with the electrolyte, while the proper Ni amount (5 wt%) was assessed to reduce the carbon formation caused by methane cracking. Both LSCr+5 wt% Ni+30 wt%GDC and LSCr+10 wt%Ni+30 wt%GDC composite anodes were used for fuel cell tests and compared to LSCr+30 wt%GDC Ni-free anode. Electrochemical tests were performed in different gas mixtures to evaluate the anodic performance in externally reformed biogas (external reforming mode) and as electro-catalyst for DRM reaction (internal reforming mode). The design of the anodic side of the single cell was optimized by adding a second external layer to improve the internal DMR reaction and thus the overall electrochemical performance in presence of biogas.

Experimental

Materials and cell fabrication

$La_{0.6}Sr_{0.4}CrO_{3-\delta}$ was synthesized by citrate auto-combustion method using corresponding metal nitrates as precursors: $(La(NO_3)_3{\cdot}6H_2O$ (99%, Sigma-Aldrich), $Sr(NO_3)_2$ (99.5%, Alfa Aesar), and $Cr(NO_3)_3{\cdot}9H_2O$ (99.9%, Sigma-Aldrich)) [29,30]. The powder was ball milled for 5 h at 350 rpm and calcined in 1000–1400 °C temperature range. The phase composition of resulting powders was investigated by X-ray diffraction using a Scintag X1 diffractometer equipped with a Cu Kα (λ = 1.5418 Å) source and the Brag-Brentano θ–θ configuration in the 20–80 2θ range, with 0.05° step size and 3s acquisition time.

Wet impregnation with aqueous solution of $Ni(NO_3)_2$ achieved different Ni loading (5 or 10 wt% Ni). The powders were then dried and calcined at 500 °C to remove the nitrates. Composites containing 30 wt% $Ce_{0.9}Gd_{0.1}O_2$ (GDC) and 5 wt% or 10 wt% Ni infiltrated $La_{0.6}Sr_{0.4}CrO_{3-\delta}$ powders were ball milled for 3 h at 350 rpm. Samples labels and compositions are reported in Table 1.

Specific surface area values were measured by the Brunauer–Emmett–Teller (BET) method using a Micromeritics Gemini V apparatus and the measured values are reported in Table 1.

Electrolyte supported cells were prepared using $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) powders purchased by Praxair. Dense pellets were obtained as reported elsewhere [29,30] and they were approximately 0.5 mm thick with a relative density of 99.8%. $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSFCo) (Praxair) powder was used as cathode. To get a controlled thickness, both electrodes were deposited by spin coating technique. The cathode layer was spinned at 1000 rpm for 4 min by using a suspension of 0.1 g of LSFCo powder in 0.2 Ml of serigraphic oil (based on terpineol and ethanol). Likewise, the anode was fabricated by spinning 3 layers of 0.05 g of anodic cermet in 0.4 mL of serigraphic oil at 1500 rpm for 20 s. The electrode microstructure was investigated by field emission gun scanning electron microscope (FEG–SEM SUPRA™ 35, Carl Zeiss SMT, Oberkochen, Germany). Electrodes were covered with a diluted Au paste (Heraeus, C5755A) to obtain a uniform and porous current collector.

Electrical characterization

The electrical conductivity of LSCr pellets was measured by standard four-probe DC method both in synthetic air and 5% H_2/Ar in the 350–850 °C range [29]. The probes were placed in a linear configuration with a 2 mm tip spacing and gold was used for contacts and wires. To get fully dense pellets, LSCr powders were uniaxially pressed at 270 MPa and sintered at 1600 °C for 10 h.

H_2-TPR

ThermoScientific TPDRO1100 flow apparatus was used for temperature programmed reduction measurements (H_2-TPR). The sample (0.025 g) was treated in 5% O_2/He mixture (50 cm^3 min^{-1}) at 300 °C for 1 h then reduced in 5% H_2/Ar flowing mixture (30 cm^3 min^{-1}) up to 800 °C, holding the temperature at 800 °C for 1 h. H_2 consumption was measured by a TCD detector removing the H_2O generated in the reduction by a trap [31].

Catalytic activity

The catalytic activity was measured in a fixed-bed quartz reactor using a mixture of CH_4:CO_2:Ar = 48:32:20 vol% and a

Table 1 – Composite anode powders and relative specific surface area values.

Label	Composition	BET[m^2/g]
LSCr	$La_{0.6}$ $Sr_{0.4}$ CrO_3	14.5
LSCr + GDC	$La_{0.6}$ $Sr_{0.4}$ CrO_3+ 30 wt% GDC	21,3
LSCr+5Ni + GDC	$La_{0.6}$ $Sr_{0.4}$ CrO_3+5 wt% Ni + 30 wt% GDC	22.3
LSCr+10Ni + GDC	$La_{0.6}$ $Sr_{0.4}$ CrO_3+10 wt% Ni + 30 wt% GDC	23.6

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