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$LaNi_{0.6}Co_{0.4}O_{3-\delta}$ dip-coated on Fe–Cr mesh as a composite cathode contact material on intermediate solid oxide fuel cells

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HIGHLIGHTS

- After 1000 h at 800 °C LNC/Fe–Cr mesh still present adequate mechanical integrity.
- ASR value for LNC/Fe–Cr mesh with interconnect was 5.40 ± 0.01 mΩ cm^2 at 800 °C.
- Cr deposition under the channel is higher than under the rib of the interconnect.

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ABSTRACT

The feasibility of using Crofer22APU mesh dip coated with $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ (LNC) ceramic paste as a uniform contact layer on a Crofer22APU channeled interconnect was studied. The control of LNC dip coating thickness on Fe–Cr mesh was carried out by rheological measurements of the suspension. SEM cross-section of formed composite contact material showed good adherence between ceramic and metallic components. The measured area specific resistance (ASR) value at 800 °C was 0.46 ± 0.01 mΩ cm^2, indicating low contact resistance itself. The long term stability of metallic/ceramic composite was also studied. The contact resistance, when composite contact material was adhered to channeled Crofer22APU interconnect, was 5.40 ± 0.01 mΩ cm^2, which is a suitable value for the performance of IT-SOFC stack. The stability of the system after treating at 800 °C for 1000 h was characterized using X-ray Micro-Diffraction (XRMD), Scanning Electron Microscope equipped with an Energy Dispersive X-ray analyzer (SEM-EDX) and X-ray Photoelectron Spectroscopy (XPS) techniques. The oxidation rate of the alloy and Fe_3O_4 phase formation were enhanced on the channels of the interconnect. Thus, the formation of CrO_3 (g) and $CrO_2(OH)_2$ (g) species was accelerated on the composite surface under the channel. Through XRMD and XPS analysis the coexistence of two perovskite phases (initial LNC and Cr-perovskite) was observed.

1. Introduction

Global warming and its detrimental climatological, ecological and sociological effects have led to an increasing interest in more efficient and clean power systems [1]. High temperature solid oxide fuel cells (HT-SOFCs, operating in the range of 800–1000 °C) have a good potential for being used as stationary stand-alone power generation systems [2]. For these applications, chemical to electrical efficiency of HT-SOFC is in the range of 45–65% [3]. For smaller scale applications, such as micro combined heat and power (micro-CHP), small auxiliary power units (APUs) and small electrical generators [4], there is a need to lower operation temperatures, into the intermediate temperatures (IT) range of 500–800 °C. Lower temperature operation affords more rapid start-up and shutdown.

A single SOFC cell produces ~0.6–0.7 V under normal working conditions [3]. Therefore, in order to obtain the desired electric power output, single cells are connected and fabricated together to form a stack using interconnect and sealing materials [5]. In HT-

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SOFCs, the bond between the cell and the $LaCrO_3$ interconnect is typically realized by sintering at 1300 °C. A solid bond with good electrical contact is obtained and no other contact material is then required. However, for IT-SOFC chromium-containing ferritic stainless steels are generally used as interconnect [6,7] and, contact materials are needed to provide a homogeneous bonding between interconnect and electrode to avoid power losses [8]. Previous studies [9,10], based on the effect of contact between electrode and current collector on the performance of SOFCs, concluded that when the contact area of the current collector increased from 4.6% to 27.2%, the cell resistance decreased from 1.43 to 0.19 Ω cm^2 at 800 °C.

The oxide scale formed on the surface of Fe–Cr alloys, after long exposure in the SOFC environment, results in volatile chromium (Cr) species such as CrO_3 and $Cr_2(OH)_2$ (in presence of vapor) [3]. These species can cause rapid performance deterioration in SOFCs due to the deposition of Cr at the bulk electrode and at the electrolyte/electrode interface regions [11]. The cathode contact materials can act as a barrier to the migration of chromium from the metallic to the cathode and further minimize the area specific resistance (ASR) between both materials [12–14].

The cathode contact materials compositions should fulfill the following requirements [15,16]: i) high electrical conductivity and appropriate sintering activity to minimize the resistance of the contact layer itself and to protect the steel substrate from excessive oxidation, ii) chemically compatible and appropriate thermal expansion behavior with adjacent materials and, iii) high thermo-chemical and structural stability in the oxidizing cathode environment. The materials used as contact layers include: i) noble metals (Ag) or noble metal-perovskite composites (Ag-$(La_{0.6}Sr_{0.4})(Co_{0.8}Fe_{0.2})O_3$, Ag–$La_{0.8}Sr_{0.2}MnO_3$), ii) conventional perovskite cathode materials (such as, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$, $La_{0.8}Sr_{0.2}FeO_3$), iii) oxides with a spinel structure, M_3O_4 (M = Ni, Mn, Co, Cu, Fe), or iv) recently developed oxides like $Ni_{0.33}Co_{0.67}O$. Despite the interactions of these kind of materials which formed oxide scale on metal surface, due to their susceptibility to form phases like Ag_2CrO_4, $AgCrO_2$, $SrCrO_4$, Cr-spinels or Cr-perovskites, the use of those materials, in most cases, are quite effective for improving the electrical contact between the cathodes and metallic interconnects [17–25]. In addition, these materials can reduce the oxidation rate of the steel and minimize the formation of new phases arising from the oxidation of metal itself such as, Fe_2O_3 and Fe_3O_4 [26]. In this study, $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ (LNC) ceramic composition was selected, due to the adequate sintering activity, electrical conductivity and thermal expansion coefficient (TEC) [17], coupled with ferritic stainless steel Crofer22APU mesh to form a ceramic/metallic composite contact material. Crofer22APU was developed to increase the electrical conductivity of the scale and to reduce the chromium vaporization. This is achieved by adding 0.5% Mn in its composition which facilities the $(Cr,Mn)_3O_4$ spinel formation [3]. The use of a high conductivity perovskite type material in conjunction with stainless steel mesh is expected to improve current collection. At the same time, it achieves a continuous contact on the ribs without sacrificing the flow of the air through the channels. Taking into account our previous studies [17,27] the use of this composite material between Crofer22APU interconnect and $La_{0.6}Sr_{0.4}FeO_3$ cathode in flow channel configuration, can offer an adequate mechanical integrity and low reactivity between the applied layers without compromising the contact resistance of the system.

The goal of this work is to develop a metallic/ceramic composite contact material achieving a good bonding between this contact material and the channeled metallic interconnect. An adequate formulation of the LNC ceramic slurry was set and then dip coated [28,29] on Crofer22APU mesh. The electrical resistance, chemical compatibility and adherence between ceramic and metallic parts of the composite material, under long term IT-SOFC operating conditions, were determined. Results of electrical performance of the contact material/interconnect system are presented. In addition, long term contact stability of the metallic/ceramic composite material under the rib (direct contact) and channel (indirect contact) of the interconnect was analyzed.

In order to understand the interactions between the Crofer22-APU alloy and the LNC ceramic material the following issues were considered [3,30]: i) the preoxidized alloys form protective and semi-conductive chromia oxide and a dense and stable $(Cr,Mn)_3O_4$ spinel on the surface of the alloy, which is effective to reduce the generation of volatile Cr species ii) the reason for the Cr volatility is the thermodynamic instability of chromia scales formed on the alloy, forming gaseous species (CrO_x (x = 1,2,3)); and iii) the deposition process of Cr species at the ceramic coating, under SOFC operation conditions, can be described by the nucleation deposition theory.

2. Experimental

The formulation of ceramic powder used in this study was $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ (LNC) (NexTech, Fuel Cell Materials). To obtain metallic/ceramic contact composite, Crofer22APU stainless steel mesh (Fiaxell SOFC Technologies), with mesh opening of about 175 μm and a thickness of 250 μm, was cut into 10 × 10 mm squares, cleaned with acetone in an ultrasonic bath and dried. The squared-meshes squares were preoxidized at 600 °C for 10 h and then dip coated with an LNC ceramic paste (dip coating rate = 4.5 mm s^{-1}). The chemical composition of the steel, as given by the supplier, is listed in Table 1. The ceramic slurry was composed of ceramic powder (LNC), dispersant (Dolapix, Zschimmer & Schwarz, Chemische Fabriken), binder (PVB, polyvinyl butyral, Solutia Solutions) and solvent (ethanol, Panreac). The paste composition was based on the formulation shown in Table 2. Particle size distribution of the ceramic powder was carried out using a Mastersizer particle size analyzer (Malvern Instruments). Rheology of the suspensions was analyzed using a rheometer (HAAKE MARS II) at shear rates from 0.1 s^{-1} to 1000 s^{-1}, and at room temperature. Ceramic/metallic material was sintered at 1050 °C for 2 h [9] and then treated at 800 °C for 1000 h, in open air.

The composite contact material was bonded to a Crofer22APU channeled interconnect (ThyssenKrupp VDM). The channels of substrate are 2 mm width, 0.5 mm depth, 10 mm length and the distance between neighboring is 2 mm (Fig. 1). The substrate was cut into 10 × 10 mm and 1 mm thick pieces, polished using #800 grit SiC paper and then, cleaned with acetone in an ultrasonic bath and dried. Subsequently, they were preoxidized at 800 °C for 100 h. An additional layer of LNC was coated on the ribs of the interconnect substrate by colloidal spray technique [31]. The composite contact material was directly adhered to the interconnect, sintered at 1050 °C for 2 h and then treated at 800 °C for 1000 h. The reactivity between the contact material and the rib and channel of the Fe–Cr interconnect, after long term heated at 800 °C in open air, was characterized according to the scheme shown in Fig. 1. All the experiments were performed in open air so the moisture level in the incoming air stream can be establish considering that the water vapor (H_2O) in air is around 0.001–5% by volume. However, these

Table 1
Composition of the Crofer22APU steel in wt%.

	Cr	Fe	Mn	Ti	Si	Al	La	Others
Crofer22APU	22	Bal.[a]	0.5	0.1	0.25	0.25	0.15	0.28

[a] Balance.