



The electrochemical behavior of cobalt electrodeposits on 430 stainless steel as solid oxide fuel cell interconnect[☆]

Eric M. Garcia^{*}

University of São João Del Rei Campus Sete Lagoas, Km 424-BR 040, Sete Lagoas, Minas Gerais 29800-000, Brazil

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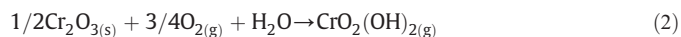
ABSTRACT

In this paper, the electrochemical reactivity between $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (LSCF) and cobalt-coated stainless steel was investigated in air at 700 °C. The cobalt electrodeposition onto ferritic stainless steel has an important role in decreasing of chromium poisoning on the cathode side of solid oxide fuel cells (SOFCs). The polarization resistance of a symmetrical cell composed by LSCF//YSZ//LSCF at 700 °C was evaluated using 430 stainless steel as electrical interconnects. The polarization resistance for cobalt-coated interconnects was 0.92 $\Omega\text{ cm}^2$ and for uncoated interconnects was 5.1 $\Omega\text{ cm}^2$. The formation of Co_3O_4 layer seems to block the chromium migration.

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1. Introduction

Metallic interconnects for solid oxide fuel cells (SOFCs) have attracted great attention in recent years. This is due to characteristics such as higher electronic and thermal conductivities, low cost and good manufacturability compared to traditional ceramic interconnects [1–5]. Many papers have been focused on ferritic stainless steel due its low cost and adequate linear thermal expansion coefficient ($11\text{--}12 \times 10^{-6}\text{ K}^{-1}$) [6,7]. However, under cathode working conditions (typically at 1123 K in air) the CrO_3 and $\text{CrO}_2(\text{OH})_2$ evaporate from Cr_2O_3 [7] causing severe degradation (Eqs. (1) and (2)). Moreover the Cr(VI) can be reduced parallel with oxygen, reducing the lifetime of SOFCs [7,8].



The interaction between metallic interconnect and cathodes as LSCF ($\text{La}_x\text{Sr}_{(1-x)}\text{Co}_y\text{Fe}_{(1-y)}\text{O}_3$) has been investigated [9]. In literature it is related to the formation of SrCr_2O_4 at LSCF/ferritic stainless steel interface [10]. The reaction to form non-conductive SrCr_2O_4 could occur between gaseous CrO_3 and a nucleation agent, namely SrO segregated on the surface of LSCF electrodes, to form Cr–Sr–O

nuclei [10]. SrCr_2O_4 is non-conductive and its formation leads to reduction of conductivity and porosity of cathode [10,11]. The deposition of reaction products showed in Eq. (3) was predicted to inhibit the cathodic oxygen reduction reaction at the three-phase boundary (TPB). To improve the surface electrical properties and reduce the amount of chromium in oxide layer, the semiconductor oxide coating has been proposed [12,13]. Cobalt oxide Co_3O_4 is a promising candidate because of its interesting conductivity (6.70 S cm^{-1}) and its adequate linear thermal expansion coefficient [14]. A good strategy to obtain the Co_3O_4 layer onto stainless steel is cobalt electrodeposition with subsequent oxidation in air at high temperatures [14].

In this paper, the 430 stainless steel surface was coated with cobalt by electrodeposition method followed by heat treatment at 700 °C for 45 h in air atmosphere. The effect of cobalt protection on LSCF polarization resistance was investigated. The technique used in this study was the electrochemical impedance spectroscopy (EIS). Indeed most of studies are focused at temperatures of 800 °C. However there is a trend to reduce the operating temperature of SOFC. A temperature range of 400–600 °C is already envisioned by the researchers [13,14]. Thus the temperature used in this paper was 700 °C.

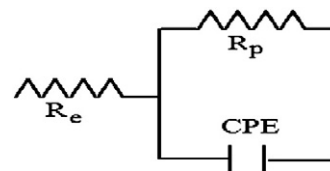


Fig. 1. Equivalent circuit between the LSCF cathode and YSZ electrolyte.

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^{*} Tel.: +55 31 3409 5714; fax: +55 31 3409 5700.

E-mail address: ericmgm@hotmail.com.

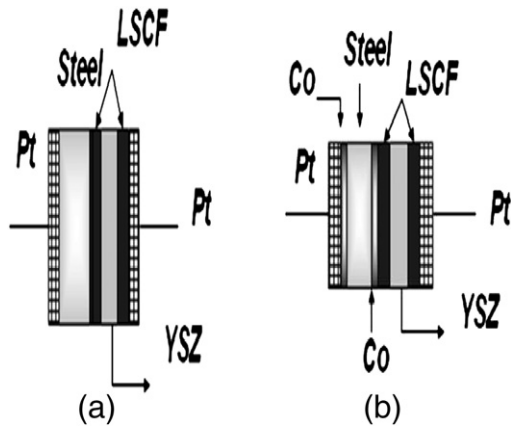


Fig. 2. (a) Cell Pt/LSCF//YSZ//LSCF/steel/Pt where the LSCF is in direct contact with metallic interconnect (430 stainless steel). (b) Cell Pt/LSCF//YSZ//LSCF/Co/steel/Co/Pt.

2. Experimental

2.1. Preparation of electrodeposition solutions

Cobalt was deposited by electroplating onto polished AISI 430 stainless steel substrates which had an area of 200 mm². The counter electrode was made of platinum, with area equal to 3.75 cm² and the reference electrode was saturated with Ag/AgCl/KCl. The electroplating bath was operated under the conditions of agitation at pH 3.0, current density of 100 mA cm⁻², temperature of 30 °C and charge density of 10.0 C cm⁻². The solution consisted of 300 g cobalt sulphate (MERCK) and 30 g of boric acid (MERCK) dissolved in 1 L of distilled water. The electrodeposited cobalt was analyzed by scanning electron microscopy and its thickness was approximately 1 μm.

2.2. Electrochemical measurements and material characterization

Electrochemical measurements were held with an AUTOLAB PGSTAT 302 with impedance module, FRA and GPES software. The electrochemical impedance spectroscopy measurements were performed in a frequency scale of 1.00 × 10⁵ to 1.00 × 10⁻³ Hz with a signal amplitude of 10.0 mV. When a sinusoidal potential excitation (Eq. (3)) is applied to the electrode/solution interface, it causes an out of phase current response with respect to the applied sinusoidal potential (Eq. (4)) [1].

$$E_{(t)} = E_0 \sin(\omega t) \tag{3}$$

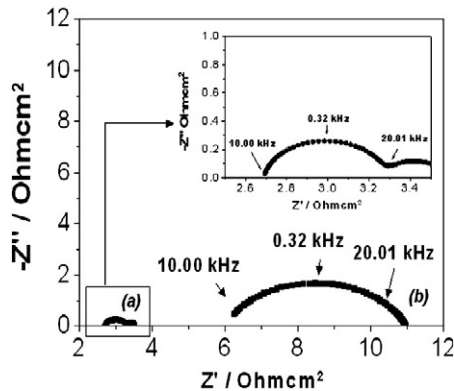


Fig. 3. Electrochemical impedance after 2 h in air at 700 °C for half-cell (a) Pt/LSCF//YSZ//LSCF/Co/steel/Co/Pt and (b) Pt/LSCF//YSZ//LSCF/steel/Pt.

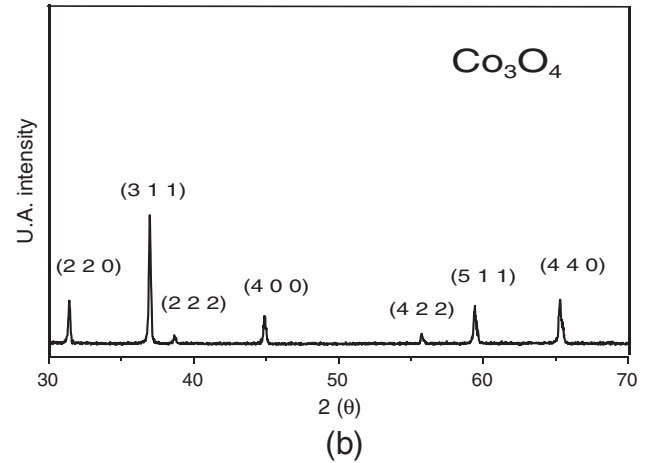
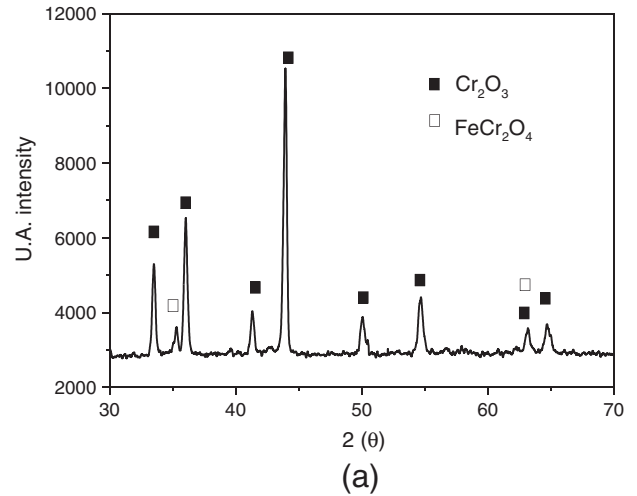


Fig. 4. The X-ray diffraction patterns of 430 stainless steel without (a) and with (b) cobalt after 45 h at 700 °C.

$$I_{(t)} = I_0 \sin(\omega t + \varphi) \tag{4}$$

Using Euler's formula, the electrochemical impedance, Z (ω), can be expressed as a real part, Z' (ω), and an imaginary part, Z'' (ω), (Eq. (5)):

$$Z_{(\omega)} = \frac{I_0 \sin(\omega t + \varphi)}{E_0 \sin(\omega t)} = Z'_{(\omega)} + iZ''_{(\omega)}. \tag{5}$$

In a system with a low contribution of mass transfer, the impedance can be predicted as the mathematical model shown in Eq. (6) [1].

$$Z_{(\omega)} = R_s + \frac{R_p}{1 - C^2 R_p^2 \omega^2} + \left[\frac{\omega C R_p^2}{1 - \omega^2 C^2 R_p^2} \right] \tag{6}$$

The mathematical model shown in Eq. (6) is equivalent to the circuit shown in Fig. 1. This figure represents the electrical interface LSCF/YSZ. In this circuit, R_e represents the electrolyte resistance, R_p represents the polarization resistance and CPE is the non-ideal capacitance of the electrical interface.

A steel plate was coated with cobalt and another plate was uncoated. These plates were subjected to a temperature of 700 °C for 45 h. The cross section of samples was analyzed by scanning electron microscopy (SEM). X-ray diffraction and energy dispersive X-ray of samples with and without cobalt were performed. The cobalt

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