



Short communication

LaCrO₃-based coatings deposited by high-energy micro-arc alloying process on a ferritic stainless steel interconnect material

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ABSTRACT

Currently used ferritic stainless steel interconnects are unsuitable for practical applications in solid oxide fuel cells operated at intermediate temperatures due to chromium volatility, poisoning of the cathode material, rapidly decreasing electrical conductivity and a low oxidation resistance. To overcome these problems, a novel, simple and cost-effective high-energy micro-arc alloying (HEMAA) process is proposed to prepare LaCrO₃-based coatings for the type 430 stainless steel interconnects. However, it is much difficult to deposit an oxide coating by HEMAA than a metallic coating due to the high brittleness of oxide electrodes for deposition. Therefore, a Cr-alloying layer is firstly obtained on the alloy surface by HEMAA using a Cr electrode rod, followed by a LaCrO₃-based coating using an electrode rod of LaCrO₃-20 wt.%Ni, with a metallurgical bonding between the coating and the substrate. The preliminary oxidation tests at 850 °C in air indicate that the LaCrO₃-based coatings showed a three-layered microstructure with a NiFe₂O₄ outer layer, a thick LaCrO₃ sub-layer and a thin Cr₂O₃-rich inner layer, which thereby possesses an excellent protectiveness to the substrate alloy and a low electrical contact resistance.

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1. Introduction

Solid oxide fuel cells (SOFCs) are energy generation systems which convert electrochemically chemical energy of fuel and oxidant gases into electricity, with the advantages of high efficiency and reduced emissions [1]. Unlike lower temperature fuel cells, SOFCs can use a variety of fuels such as hydrogen, carbon monoxide, or even natural gases. Thus, over the past years, SOFCs have received increased attention around the world. Although significant progresses have been achieved, SOFCs are still facing great obstacles to their commercialization, mainly relating to cell materials issues [2,3]. As one of the critical components of a planar SOFC stack, interconnects connect individual cells in series, perform as current conductors between cells, and separate the anodic and the cathodic gases. The reduction of SOFCs operating temperatures from around 1000 °C to 600–800 °C has made it possible to use metallic materials as interconnects materials to replace ceramics such as LaCrO₃ [4]. Differing from doped LaCrO₃ ceramics, metallic materials have the advantages of low cost, higher mechanical strength and higher thermal conductivity. Moreover, metals are easy to be fabricated into complex shapes. However, metals can be oxidized to form an oxide scale at the operating temperatures of SOFCs, leading to the increase in electrical contact resistance, and thus to the deteriora-

tion of the long-term cell performances. This kind of oxidation restricts the use of many of commercial Fe-based and Ni-based alloys as interconnect materials. Of the commercial high temperature alloys, Cr₂O₃-forming alloys are the leading candidates, among which ferritic stainless steels are the most promising materials for SOFC interconnects, due to their good mechanic properties and electronic conductivity, good thermal compatibility with other cell components, ease fabrication and low cost. In the relatively high-operating temperatures of SOFCs, ferritic stainless steels usually form a scale composed of two layers, a Mn–Cr spinel outer layer and a chromia subscale [5]. The growth of chromia scale leads to a high contact resistance, while volatile Cr species from the chromia scale may form in the presence of water vapor, giving rise to the contamination of the cathode or the cathode–electrolyte interface [6,7]. Two different methods have been attempted to solve these problems. One is to modify the composition of alloys for interconnects, by which more conductive and more thermodynamically stable oxides are formed [8] (for example Crofer 22 APU and ZMG232 alloys). However, the Cr evaporation remains high enough to affect cell performances. The other measure is to add thin layers of surface dopants [9,10] such as Y, La, and Ce that can improve the adhesion and growth kinetics of the oxide scale, or to apply a conductive and protective coating on the stainless steel interconnect, such as a Mn–Co spinel protective layer and perovskite coatings [11,12]. Perovskite oxides, such as (La,Cr)CrO₃ and (La,Sr)MnO₃, have been extensively investigated as protective coatings for ferritic stainless steels interconnect due to their high electrical conductivity,

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thermal compatibility and stability in the oxidizing environments [12–20]. Numerous techniques have been developed to deposit perovskite coatings on stainless steel substrate, such as sputtering [16], screen-printing [17], sol-gel [18], electrodeposition [19] and plasma spraying [20]. Among these techniques, sputtering has the advantages of precise composition control and low deposition temperature, but the deposition rates are relatively low and equipment is expensive. Screen-printing is economic and can produce thick coatings, but the coatings are usually porous. The sol-gel route exhibits the advantages of good homogeneity and composition control, low sintering temperature and low cost, but is usually for thin film deposition. Electrodeposition is economic and can produce thick coatings, but the coatings are usually composed of a metallic layer incorporated with some conductive particles. Plasma spraying has been widely used to prepare high temperature coatings. However, equipment for this technique is relatively expensive, and the deposition process of coatings usually produces high noise.

In this study, a novel, simple and cost-effective process based on high-energy micro-arc alloying (HEMAA) has been considered to deposit compact LaCrO_3 -based coatings on ferrite stainless steels. HEMAA is a microwelding technique using short-duration, high-current electrical pulses to deposit an electrode material on a metallic substrate, and thus normally can produce high-quality diffusion coatings at a lower cost, with a minimal thermal distortion or microstructural changes of the substrate due to low energy transfer involved in the HEMAA process.

2. Experimental

Type 430 ferritic stainless steel was used as the substrate alloy for the present work. The steel plates were cut into specimens with the size of $10\text{ mm} \times 10\text{ mm} \times 1.5\text{ mm}$, followed by grinding with 150-grit SiC paper, and degreasing with acetone. The preparation of LaCrO_3 -based coatings on all sides of the specimens is as follows. A Cr-alloying layer was firstly obtained on the specimen surface by HEMAA using a Cr electrode rod, with a succession of pulse discharge depositing operation under the conditions of middle voltage and middle frequency. To avoid heating and oxidation during deposition, the substrate area was kept at room temperature by a strong jet of argon gas. Then, LaCrO_3 -based coatings were deposited on the surface of the Cr-alloying layer by HEMAA. Due to the high brittleness of pure LaCrO_3 electrodes, a sintered rod of LaCrO_3 -20%Ni (in weight percent), prepared by mixing LaCrO_3 powders with Ni powders, cold-pressing, and then sintering at high

temperature in vacuum, was used as the electrode for the deposition of LaCrO_3 -based coatings, with a succession of pulse discharge depositing operation under the conditions of low voltage and middle frequency.

The oxidation of the uncovered and covered 430SS was conducted in a high temperature furnace at 850°C in air. The samples were weighed every 20 h.

The electrical contact resistances of the uncovered and coated steels were measured preliminarily using a setup described elsewhere [21]. Both surfaces of the samples were covered by platinum paste, and then platinum foils were placed on top of the pastes as current collectors.

X-ray diffraction (XRD) and scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectrometer were used to examine the oxidized specimens.

3. Results and discussion

3.1. Characterizations of LaCrO_3 coatings

Fig. 1 shows the XRD pattern of the sintered LaCrO_3 -20%Ni electrode. The electrode is composed of perovskite oxide LaCrO_3 and metallic Ni. Ni powder as a binder can increase the electric conductivity of LaCrO_3 electrode at room temperature to meet the demands for HEMAA deposition.

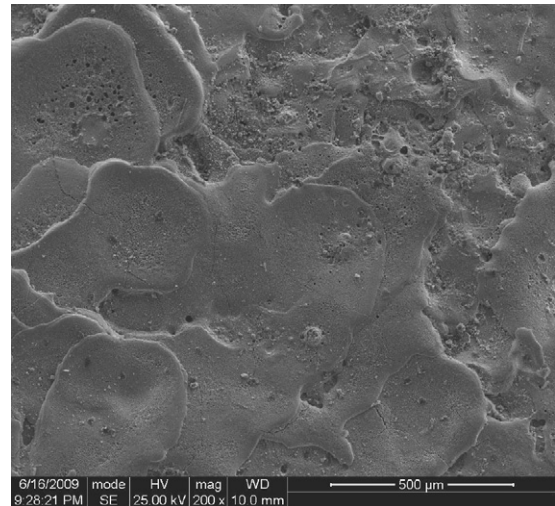


Fig. 2. Surface morphology of LaCrO_3 coating.

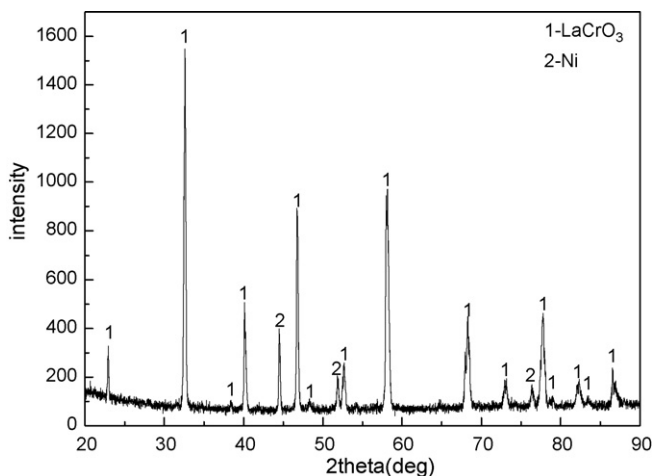


Fig. 1. X-ray diffraction pattern for the sintered LaCrO_3 -Ni electrode.

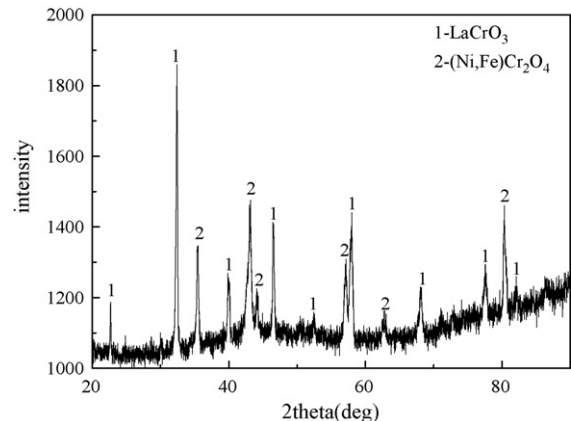


Fig. 3. XRD pattern of LaCrO_3 coating deposited on type 430 stainless steel.

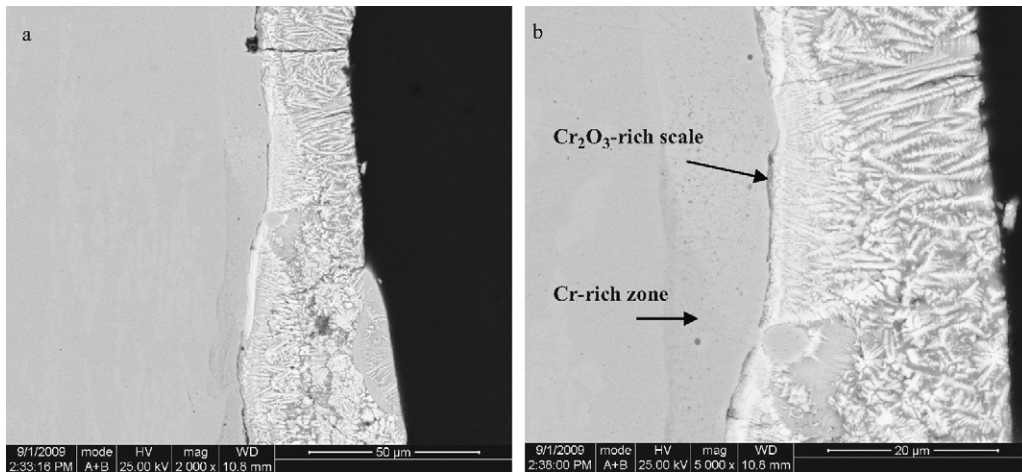


Fig. 4. Cross-sectional morphologies of LaCrO_3 coating deposited on type 430 stainless steel. (a) General view; (b) amplified view of (a).

Fig. 2 shows the typical surface morphology of LaCrO_3 coating deposited on the alloy surface. The coating surface exhibits a molten appearance which is the characteristics of HEMA process. Meanwhile, some small cracks were also observed, due to high cooling rates in argon and relatively inherent high brittleness of LaCrO_3 -based coatings. Fig. 3 shows the X-ray diffraction of the coating deposited on 430SS. The coating is mainly composed of LaCrO_3 and $(\text{Ni,Fe})\text{Cr}_2\text{O}_4$. During HEMA deposition, mass transfer occurs, i.e. LaCrO_3 and Ni transfer from the LaCrO_3 -Ni electrode to the alloy surface, and some elements such as Cr and Fe from the substrate alloy to the coating. $(\text{Ni,Fe})\text{Cr}_2\text{O}_4$ results from high temperature reaction during HEMA process.

Fig. 4 shows the cross-sectional morphology of the coating. The coating is composed of a thick external layer mainly consisting of bright phase LaCrO_3 with some gray phases $(\text{Ni,Fe})\text{Cr}_2\text{O}_4$, a very thin Cr_2O_3 -rich middle layer, and a Cr-rich alloying layer. Meanwhile, cracks were observed partly across the coating and along the scale layer/Cr-rich layer interface.

3.2. Oxidation behavior

Fig. 5 shows the oxidation kinetics of the uncoated and the coated 430SS at 850°C in air. The mass for the coated steel increased sharply in the initial stage, followed by a very low increase, while the bare steel followed an approximate parabolic oxidation law with a much lower mass gain.

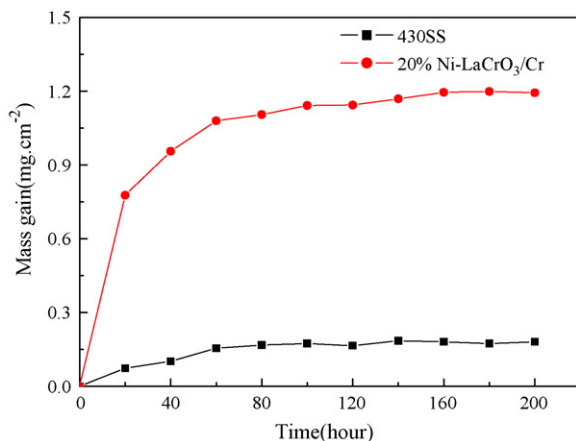


Fig. 5. Oxidation kinetics for the uncoated and LaCrO_3 coated 430 stainless steel at 850°C in air.

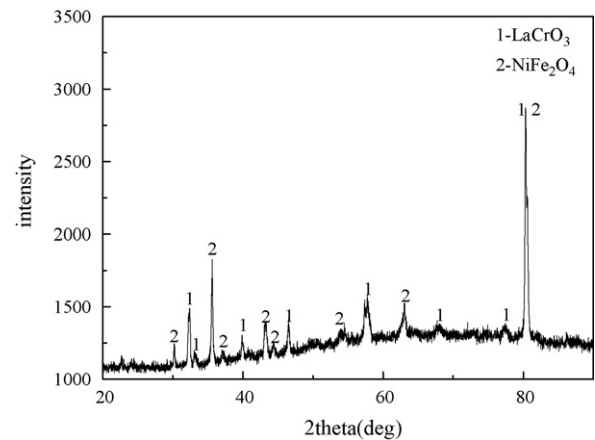


Fig. 6. XRD pattern for the coated 430SS after oxidation at 850°C in air for 200 h.

steel in the initial stage can be expected and is ascribed to that Fe and Ni existing in the LaCrO_3 layer diffuse outward to form Fe and Ni oxides over the LaCrO_3 coating. XRD analysis confirmed the presence of Ni and Fe oxides, as shown in Fig. 6. The decrease in the Ni content of LaCrO_3 -Ni electrodes and the increase of

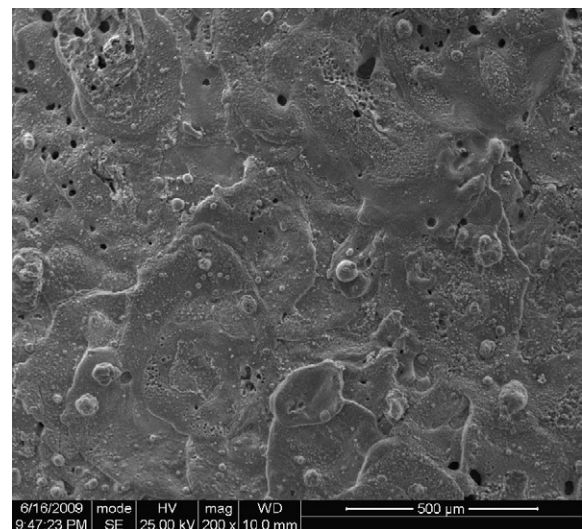


Fig. 7. Surface morphology of the coated steel after oxidation at 850°C in air for 200 h.

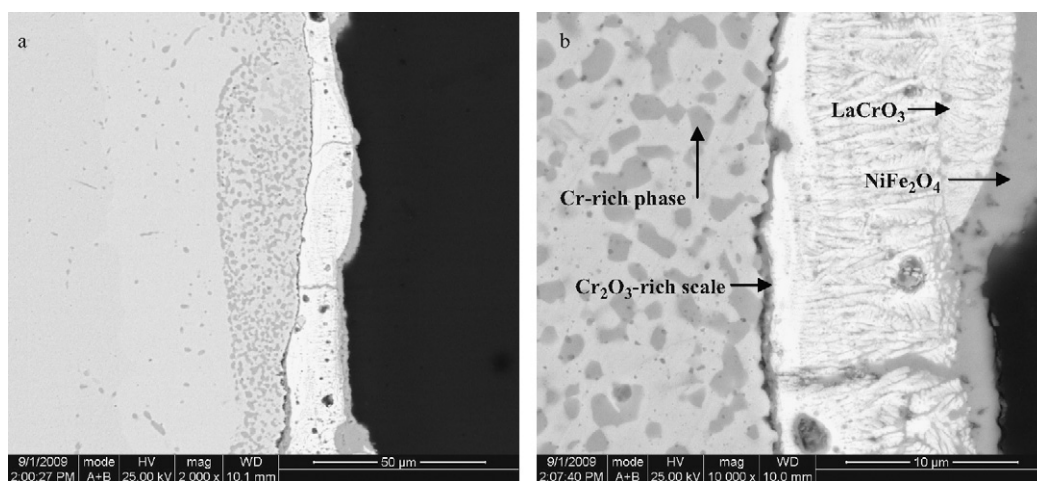


Fig. 8. Cross-sectional morphologies of the coated steel after oxidation at 850 °C in air for 200 h. (a) General view; (b) amplified view of (a).

coating's compactness help to reduce the formation of Ni and Fe oxides.

Fig. 7 shows the surface morphology of the coated steel after oxidation at 850 °C in air for 200 h. Though some nodules were observed, the molten appearance of the original coating was retained to a certain extent. Fig. 8 shows the cross-sectional morphologies of the coated steel after oxidation at 850 °C for 200 h. The oxide scale consists of three layers, a gray external layer of NiFe_2O_4 , a thick bright LaCrO_3 sub-layer incorporated with small amounts of fine Cr-rich oxides, and a thin Cr_2O_3 -rich inner layer. HEMAA process can induce the mass transfer of some elements such as Fe and Cr from the substrate alloy into the LaCrO_3 layer. As a result, Ni and Fe from the coating can diffuse outward to form an external NiFe_2O_4 layer over the LaCrO_3 layer during oxidation at 850 °C, with a fast oxidation mass gain as observed. The consumption of Ni and Fe in the coating and the formation of a Cr_2O_3 -rich inner layer give rise to the decrease in the oxidation rate. Beneath the scale is a Cr-enriched substrate alloy layer where many gray Cr-rich particles containing around 73 at.%Cr are distributed over the bright substrate alloy with a Cr content of around 23 at.% still higher than the as-received substrate alloy. The presence of a Cr-rich layer is helpful to the formation of a Cr_2O_3 -rich scale at the substrate/ LaCrO_3 layer interface, thus further improving the oxidation resistance of alloy. It is noted that some micro-pores are present at the substrate/ Cr_2O_3 -rich layer interface, which bring harms to the adhesion of LaCrO_3 coatings. It was found that if LaCrO_3 -Ni composite coatings were applied directly onto the alloy surface without a Cr-alloying treatment, the coatings exhibit poor adhesion, and cannot offer good protection to the alloy. Therefore, Cr-alloying by HEMAA is an important pretreatment to obtain a protective LaCrO_3 -Ni composite coating. Recently, Shaigan et al. [19,22] developed novel and electrodeposited composite Ni- LaCrO_3 and Co- LaCrO_3 [23] coatings for AISI 430 stainless steel, respectively. The oxide scale, which forms on the surface of Ni- LaCrO_3 coated steel, consists of a LaCrO_3 -filled chromia-rich subscale and an outer layer of Ni-Fe mixed spinel [19,22], while that for the Co- LaCrO_3 coated steel is composed of two layers of cobalt containing spinel, a Co-Fe spinel as the mid-layer containing LaCrO_3 particles and Co_3O_4 as the top layer, and a chromia-rich inner layer also containing LaCrO_3 particles [23]. Moreover, these coatings exhibit a low area-specific resistance (ASR) after oxidation at 800 °C in air, due to the presence of conductive LaCrO_3 particles in the chromia-rich subscale and good adhesion. For the present study, the protection of the composite coatings is offered by the compact LaCrO_3 sub-layer plus

Cr_2O_3 -rich inner layer. It is also expected that the external Ni/Fe-rich complex spinel can act as an effective barrier against chromium evaporation in the presence of water vapor. However, cavities form along the substrate alloy/scale interface during oxidation, which is detrimental to the oxidation resistance and the electrical contact resistance of the coated steel.

Preliminary electrical contact resistance measurements by electrochemical impedance spectroscopy indicated that the area-specific resistance for the LaCrO_3 coated steel was increased from around 0.035 to 0.055 Ωcm^2 at 850 °C after oxidation for 50 and 100 h, respectively, and then changed little with time up to 200 h. These values are obviously smaller than the value of around 0.1 Ωcm^2 for the bare steel after oxidation at 850 °C for 100 h. The increase in ASR for the coated steel is related to the formation of an outer Ni/Fe complex spinel layer, an inner Cr_2O_3 -rich scale, and cavities along the substrate/scale interface. Much work is still needed to improve the adhesion of LaCrO_3 -based coatings.

4. Conclusions

A compact LaCrO_3 -Ni composite coating has been deposited successfully on the type 430 stainless steel by high-energy micro-arc alloying process using a LaCrO_3 -20 wt.%Ni electrode, with a metallurgical bonding between the coating and the substrate. The as-received coating was mainly composed of LaCrO_3 with some (Ni,Fe) Cr_2O_4 . The coated steel suffered from a fast mass gain at the initial oxidation stage at 850 °C in air, followed by a low oxidation rate. The oxide scale on the coated steel after oxidation consisted of three layers, an external NiFe_2O_4 layer, a thick LaCrO_3 middle layer incorporated with some small Cr-rich oxides and a thin Cr_2O_3 -rich inner layer. The fast oxidation of the coated steel at the initial stage is related to that Ni and Fe existing in the coating diffuse outward to form Ni and Fe oxides over the LaCrO_3 coating. The area-specific resistance for the coated steel increased from around 0.035 Ωcm^2 after oxidation at 850 °C in air for 50 h to 0.055 Ωcm^2 for 100 h, which is obviously lower than the value for the uncovered steel. The preliminary results indicate that HEMAA exhibits application potential for preparing LaCrO_3 -based coatings on ferritic stainless steels. More work is still needed to improve the quality of coatings, namely to optimize the deposition parameters and to construct coatings with a composition gradient so as to produce coatings with excellent protectiveness and thermal compatibility to the substrate alloys.

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References

- [1] S.C. Singhal, *Solid State Ionics* 152–153 (1–4) (2002) 405–410.
- [2] H. Tu, U. Stimming, *J. Power Sources* 127 (2004) 284–293.
- [3] S.P.S. Badwal, *Solid State Ionics* 143 (2001) 39–46.
- [4] W.Z. Zhu, S.C. Deevi, *Mater. Sci. Eng. A* 348 (2003) 227–243.
- [5] Z. Yang, *Int. Mater. Rev.* 53 (2008) 39–54.
- [6] S.P.S. Badwal, R. Deller, K. Foger, Y. Ramprakash, J.P. Zhang, *Solid State Ionics* 99 (1997) 297–310.
- [7] Y. Matsuzaki, I. Yasuda, *Solid State Ionics* 132 (2000) 271–278.
- [8] T. Horata, Y. Xiong, K. Yamaji, N. Sakai, H. Yokokawa, *Fuel Cells* 2 (2–30) (2002) 189–194.
- [9] P.Y. Hou, J. Stringer, *Mater. Sci. Eng. A* 202 (1995) 1–10.
- [10] S. Chevalier, J.P. Larpin, *Acta Mater.* 50 (2002) 3105–3114.
- [11] J.W. Wu, C.D. Johnson, R.S. Gemmen, X.B. Liu, *J. Power Sources* 189 (2009) 1106–1113.
- [12] S. Linderoth, *Surf. Coat. Technol.* 80 (1996) 185.
- [13] C. Johnson, R. Gemmen, N. Orlovskaya, *Composite B* 35 (2004) 167–172.
- [14] Y.D. Zhen, S.P. Jiang, S. Zhang, V. Tan, *J. Eur. Ceram. Soc.* 26 (2006) 3253–3264.
- [15] C. Johnson, N. Orlovskaya, A. Coratolo, C. Cross, J.W. Wu, R. Gemmen, X.B. Liu, *Int. J. Hydrogen Energy* 34 (2009) 2408–2415.
- [16] Z. Yang, G. Xia, G.D. Maupin, J.W. Stevenson, *J. Electrochem. Soc.* 153 (2006) A1852.
- [17] T. Brylewski, K. Przybylski, J. Morgiel, *Mater. Chem. Phys.* 81 (2003) 434.
- [18] J.H. Zhu, Y. Zhang, A. Basu, Z.G. Lu, M. Parathaman, D.F. Lee, E.A. Payzant, *Surf. Coat. Technol.* 177 (2004) 65.
- [19] N. Shaigan, D.G. Ivey, W. Chen, *J. Electrochem. Soc.* 155 (2008) D278–D284.
- [20] H.W. Nie, T.L. Wen, H.Y. Tu, *Mater. Res. Bull.* 38 (2003) 1531.
- [21] K.P. Huang, P.Y. Hou, J.B. Goodenough, *Solid State Ionics* 129 (2000) 237–250.
- [22] N. Shaigan, D.G. Ivey, W.X. Chen, *J. Power Sources* 183 (2008) 651–659.
- [23] N. Shaigan, D.G. Ivey, W.X. Chen, *J. Power Sources* 185 (2008) 331–337.