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Mn_{1.5}Co_{1.5}O₄ SPINEL CONDUCTING COATINGS ON AL453 FERRITIC STEEL WITH REGARD TO THEIR APPLICATION AS INTERCONNECTS IN IT-SOFC

PRZEWODZĄCE POWŁOKI SPINELU Mn_{1.5}Co_{1.5}O₄ NA STALI FERRYTYCZNEJ AL453 Z PRZEZNACZENIEM NA INTERKONEKTORY DO OGNIW PALIWOWYCH TYPU IT-SOFC

The ferritic AL453 steel is one of potential metallic interconnect materials for intermediate-temperature solid oxide fuel cells. However, the evaporation of chromium from the chromia scale formed on this steel and the increasing thickness of this scale result in the slow deterioration in the electrical properties of the interconnect's elements. In order to improve fuel cell efficiency, the surface of the interconnect material was modified by applying a protective-conducting Mn_{1.5}Co_{1.5}O₄ spinel coating. Thermal and electrical tests of the La_{0.8}Sr_{0.2}FeO₃ cathode - AL453/Mn_{1.5}Co_{1.5}O₄ interconnect system at 1073 K for 200 hrs in air confirmed the effectiveness of the spinel layers as a means of stopping chromium diffusion from the AL453 steel and inhibiting oxidation, while at the same time promoting electrical contact and minimizing cathode-interconnect interfacial resistance.

Keywords: Interconnect, Ferritic Stainless Steel, Spinel-based coatings, Microstructure, Electrical resistance

Jednym z potencjalnych materiałów na metaliczne interkonektory do stałotlenkowych ogniw paliwowych typu IT-SOFC jest stal ferrytyczna AL453. W związku z parowaniem chromu z powierzchni ochronnej zgorzeliny tlenku chromu oraz wzrostem jej grubości następuje pogorszenie właściwości elektrycznych interkonektora. W celu poprawy wydajności ogniwa paliwowego, stosuje się modyfikację interkonektora polegającą na nakładaniu na jego powierzchni ochronno-przewodzącej powłoki spinelu Mn_{1.5}Co_{1.5}O₄. Przeprowadzone testy termiczne i elektryczne układu katoda La_{0.8}Sr_{0.2}FeO₃ – interkonektor AL453/Mn_{1.5}Co_{1.5}O₄ w 1073 K przez 200 godz. w powietrzu potwierdziły wysoką efektywność powłoki spinelowej jako bariery zaporowej dla dyfuzji chromu ze stali AL453 oraz jej utleniania co w efekcie prowadzi do spadku oporu elektrycznego na interfejsach układu katoda-interkonektor.

1. Introduction

In an era of growing demand for electricity, Intermediate-Temperature Solid Oxide Fuel Cells (IT-SOFCs) appear to be a superior alternative to conventional energy sources due to their high performance, very limited environmental impact, and low costs of production and utilization [1-2]. Currently one of the challenges in improving physico-chemical properties, performance and cost-effectiveness of this type of fuel cell is the development of suitable interconnect materials. Interconnects significantly affect the conductive and corrosion properties, as well as the durability of entire fuel cell [1-2]. These elements are in contact with both the anode and the cathode, and thus must be compatible with both electrode materials and stable in oxidizing and reducing environments. This is why these materials must meet many requirements, such as: stability, gas-tightness (needed to prevent the direct combination of the oxidant and the fuel during operation), a thermal expansion coefficient close to that of the electrolyte material and, most significantly, low electrical resistance [1-3].

The reduction of IT-SOFC operating temperatures to 1073 K enables the use of cheaper metallic interconnects such as chromia-forming ferritic steels. These metals are less brittle and easier to shape compared to traditional ceramic interconnects applied thus far, mainly doped lanthanum chromite [1-3]. However, ferritic steels react with corrosive gases and form protective chromia layers that generally exhibit high electrical resistance due to their growing thickness, which increases with oxidation time [3-5]. The second problem encountered with chromia is the evaporation of chromium from the chromia scales formed on these steels, which leads to the possibility of poisoning the cathode material and the subsequent degradation in the performance of the cell [6]. Thus the corrosion of ferritic steel interconnects poses a great hindrance in a working IT-SOFC stack. In order to improve the overall oxidation resistance and the electrical conductivity of the interconnect, the surface of the ferritic steel was modified by applying a spinel coating. Several papers [7-14] found that the Mn_{1.5}Co_{1.5}O₄ manganese cobaltite spinel, which belongs to the Mn_xCo_{3-x}O₄ (with 0 ≤ x ≤ 3) family, is the closest TEC match to ferritic

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steels, and it has very low oxygen diffusion coefficients and exhibits relatively high conductivity. Therefore, this spinel is a promising candidate for use as a protective-conducting coating.

In the present study the ferritic steel AL453 was coated with an $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ coating via screen-printing combined with the appropriate thermal treatment. Thermal and electrical tests of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ cathode-AL453/ $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ interconnect system to be applied in IT-SOFCs and of the reference system ($\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ cathode – AL453 interconnect) were carried out for 200 hrs of oxidation in air at 1073 K.

2. Experimental part

2.1. Preparation of steel samples

The AL453 stainless steel from Allegheny Ludlum was used, with the chemical composition of: Fe (Bal.), Cr (22.0 mass%), Mn (0.3 mass%), Ce (0.1 mass%), Ti (0.02 mass%), Si (0.08 mass%), Al (0.6 mass%), P (0.02 mass%), S (0.03 mass%) and C (0.03 mass%). Steel sheets were cut into circular samples with a diameter of 15 mm and ground with SiC paper grade no. 600, ultrasonically degreased and finally washed in ethanol.

2.2. Preparation of powders and screen-printing pastes

$\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ (referred to as MC), $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ (referred to as LSF) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (referred to as LSCM) powders were synthesized by means of EDTA gel processes. A detailed description of this procedure together with the evidence for its effectiveness may be found in [15].

Manganese(II) nitrate tetrahydrate $\text{Mn}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ (SIGMA-ALDRICH, $\geq 97.0\%$), cobalt(II) nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ (SIGMA-ALDRICH, 99.999% trace metals basis), lanthanum(III) nitrate hexahydrate $\text{La}(\text{NO}_3)_3 \times 6\text{H}_2\text{O}$ (FLUKA, puriss. p.a., $\geq 99.0\%$), strontium nitrate $\text{Sr}(\text{NO}_3)_2$ (SIGMA-ALDRICH, puriss., $\geq 98\%$) and iron(III) nitrate nonahydrate $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ (ALDRICH, 99.99% trace metals basis) were used as starting materials, while ethylenediaminetetraacetic acid – EDTA ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, ALDRICH, 99.995%) – and an ammonium hydroxide solution (28% NH_3 in H_2O , SIGMA-ALDRICH, 99.99% trace metals basis) were used as chelating agents, as received from the suppliers. The above-mentioned salts were used for the preparation of 1.0 M Mn, Co, La, Sr and Fe nitrate solutions, which were subsequently mixed in the appropriate ratio to yield the desired stoichiometry. To obtain gel precursors, the nitrate solutions were mixed with 0.1 M EDTA acid, the volume of which was determined from the ratio of 1 mole EDTA acid : 1 mole metal cation. A constant pH = 8 was maintained via drop-wise addition of ammonia. The aqueous solutions containing appropriate cation complexes were heated for several hours at 363 K and simultaneously stirred with a magnetic stirrer. The solutions became highly viscous and finally gelled to a transparent resin with a plum hue. The gels were then pyrolyzed for 1 hr at 873 K, crushed, and calcinated for 10 hrs in air at 1073 K. After heat-treatment, the powders were ground in a rotary-vibratory mill in dry ethanol for 5 hrs and, finally, dried at room temperature.

The resulting fine and homogeneous $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_3$ powders with the desired phase and chemical compositions were fabricated into pastes. The pastes were prepared by mixing the afore-mentioned powders and a 5 wt.% solution of ethyl cellulose (Fluka, pure powders) in anhydrous terpineol (ALDRICH, purum, mixture of isomers). The mixtures, which contained ca. 17 wt.% of organic binder, were homogenized for 10 hrs using a three-roll mill.

2.3. Preparation of the cathode-interconnect system and oxidizing procedure

To measure the area specific resistance ASR defined as the product of resistance and the nominal contact surface area of the oxide and steel, the setup shown in Fig. 1, which simulates the cathode-interconnect structure in IT-SOFC stacks, was constructed, as proposed by Yang *et al.* [9]. Thick, porous layers of LSF representing the cathode were deposited on both sides of the bulk LSF substrate using screen-printing, and this complex structure was then treated thermally for 10 hrs in air at 1423 K. In order to obtain the dense substrate cathode in the form of a disc with a diameter of 10 mm and a thickness of 1 mm, the LSF powder was isostatically pressed at 300 MPa into pellets, which were then sintered for 2 hrs in air at 1623 K. Once prepared, the LSF substrate together with the porous LSF layers was squeezed between two circular AL453 steel samples, as demonstrated in Fig. 1.

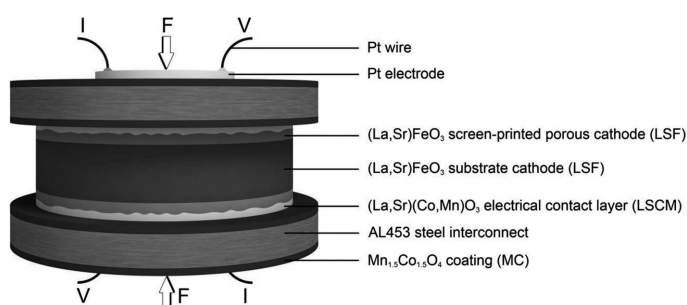


Fig. 1. Test setup for the evaluation of ASR at the cathode-interconnect interface [8]

An LSCM conducting paste was applied between the cathode and the interconnects to ensure electrical conduction. LSCM was selected due to the fact that at 1073 K its electrical conductivity is higher than that of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ ($175 \text{ S}\cdot\text{cm}^{-1}$ [13] and $90 \text{ S}\cdot\text{cm}^{-1}$ [16], respectively).

In the present study the following two types of cathode-interconnect systems were investigated: I – AL453/ Cr_2O_3 /LSCM/LSF/LSCM/ Cr_2O_3 /AL453 and II – AL453/MC/LSCM/LSF/LSCM/MC/AL453. In the former case, uncoated AL453 steel pre-oxidized for 100 hrs in air at 1073 K was studied, while the latter case involved steel with a $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ coating. This coating was prepared using a procedure in which a $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ paste was first deposited on the appropriately prepared surface of the steel via screen-printing, and then dried at 353 K for two hours. All organic components were removed from the paste by 30 min of thermal treatment in air at 873 K. The heat-treatment of the coated steel samples involved two stages. During the first stage the samples were heated for 12 hrs at 1023 K in an

Ar-H₂-H₂O gas mixture with p(H₂)/p(H₂O)=94/6 using the setup described in [17]. Then, during the second stage, the samples were oxidized for 48 hrs in air at 1073 K. The thickness of the obtained coating on the AL453 steel substrate ranged from 10 to 20 μm.

2.4. Methodology

The phase composition of the powders, bulk samples and metal-ceramics composites was analyzed by means of the X'Pert XRD diffractometer (Panalytical) using CuK_α radiation. Scanning electron microscopy (FEI Nova NanoSEM 200) coupled with an EDAX Genesis XM X-ray microanalysis system was used to examine the morphology and chemical composition of the studied samples. The electrical resistance of coated and uncoated steel in the cathode-interconnect interface setup was measured using the *dc* 2-probe 4-point technique with a constant current of 10 mA. For this purpose, both sides of each cathode-interconnect systems were coated with a Pt paste using screen-printing. The apparatus and the methods used for measuring electrical resistance are described in [18]. Electrical measurements were carried out in air at 1073 K as a function of time for a period of 200 hrs. Due to the symmetrical design of the test the area specific resistance, ASR, of the samples was calculated based on the obtained resistance values, using the following formula:

$$ASR = \frac{R \cdot A}{2} \quad (1)$$

where: R – electrical resistance [Ω], and A – surface area of the Pt layer [cm²].

3. Results and discussion

3.1. Morphology and composition of products of AL453/Cr₂O₃/LSCM/LSF/LSCM/Cr₂O₃/AL453 oxidation

Fig. 2 shows the SEM microphotograph of the polished cross section of the AL453/Cr₂O₃/LSCM/LSF/LSCM/Cr₂O₃/AL453 system obtained after 200 hrs of oxidation at 1073 K in air and the EDS line scan analysis of the elements: Co, Fe, Mn, Cr, La, Sr, Al and O (Fig. 2.b) along the line in Fig. 2a. As this microphotograph demonstrates, this system is compact and is composed of three original layers (LSF, LSCM, and Cr₂O₃), each with a different thickness and porosity. The LSF cathode layer adheres well to the sinter and exhibits a porous microstructure with a well-developed surface. This is important, because this element serves as a catalyst of oxygen reduction on the cathode side of the IT-SOFC. The second, LSCM conducting layer exhibits low porosity and is in close contact with the afore-mentioned LSF layer and the third layer, i.e. the scale which is the oxidation product of the AL453 steel. EDS line scan runs performed along the line of the AL453/LSCM interfacial region visible in Fig. 2b indicated that the scale had been enriched with Cr and O due to the formation of Cr₂O₃. The chromia scale is dense, with a thickness of approximately 2 μm. This scale is significantly thinner compared to that formed on the uncoated AL453 steel oxidized in

the same conditions, but in the absence of the cathode system [19]. In addition, at the steel/scale interface and within the metallic core, SiO₂ and Al₂O₃ precipitates may be observed. These oxides had formed as a result of internal oxidation of silicon and aluminum.

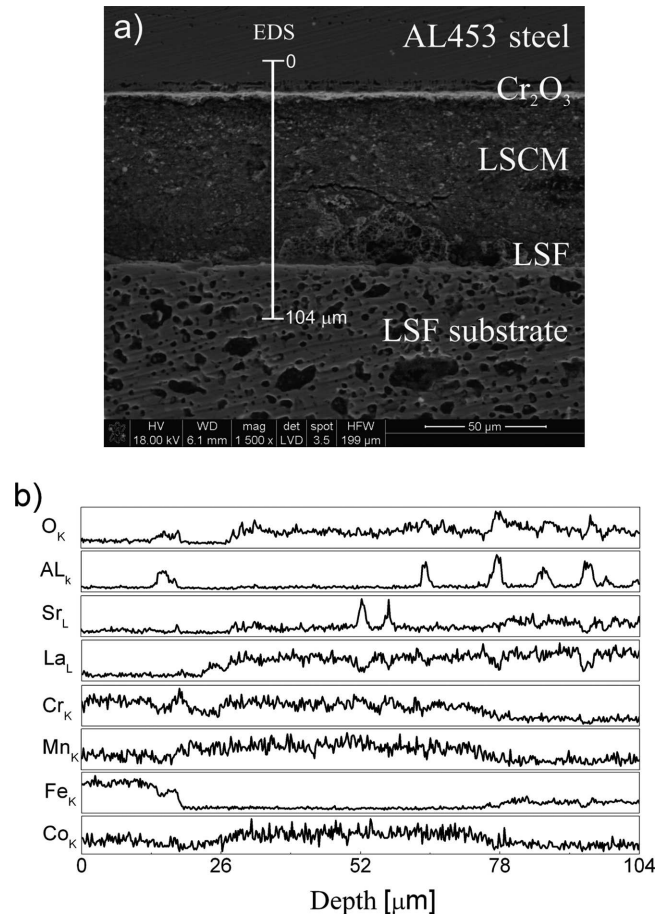


Fig. 2. Microstructure of the AL453/Cr₂O₃/LSCM/LSF/LSCM/Cr₂O₃/AL453 system after 200 hrs of oxidation in air at 1073 K: a) SEM microphotograph of the polished cross-section and b) EDS line scan analysis

As can also be seen from the EDS line scan profile, the growth of the Cr₂O₃ scale on the AL453 steel in the AL453/Cr₂O₃/LSCM/LSF/LSCM/Cr₂O₃/AL453 system promotes the diffusion of chromium from the substrate metal and in the direction of the cathode material. This phenomenon leads to the loss of the scale's protective properties and the contamination of the cathode material, and the subsequent degradation in the electrochemical performance of the IT-SOFC cell. Due to the substantial activity of chromium along the analyzed cross-section of the samples, some SrCrO₄ and (Mn,Cr)₂O₃ precipitates had formed at the LSF/LSCM and Cr₂O₃/LSCM interfaces, respectively. The existence of these oxide phases was confirmed by means of XRD and EDS analyses.

3.2. Morphology and composition of products of AL453/MC/LSCM/LSF/LSCM/MC/AL453 oxidation

Fig. 3 shows the SEM polished cross-section microphotograph and EDS line scan analysis run across the AL453/MC/LSCM/LSF/LSCM/MC/AL453 system obtained

after 200 hrs of oxidation in air at 1073 K. This system is very similar to the previously discussed one – it is compact and consists of three different original layers: LSF, LSCM and MC (Fig. 3a). The spinel layer with the composition of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ that had deposited on the surface of the interconnect steel is approximately $10\ \mu\text{m}$ thick and exhibits good adhesion to the substrate metal. This coating is relatively dense and has a small amount of isolated spherical pores (Fig. 3a).

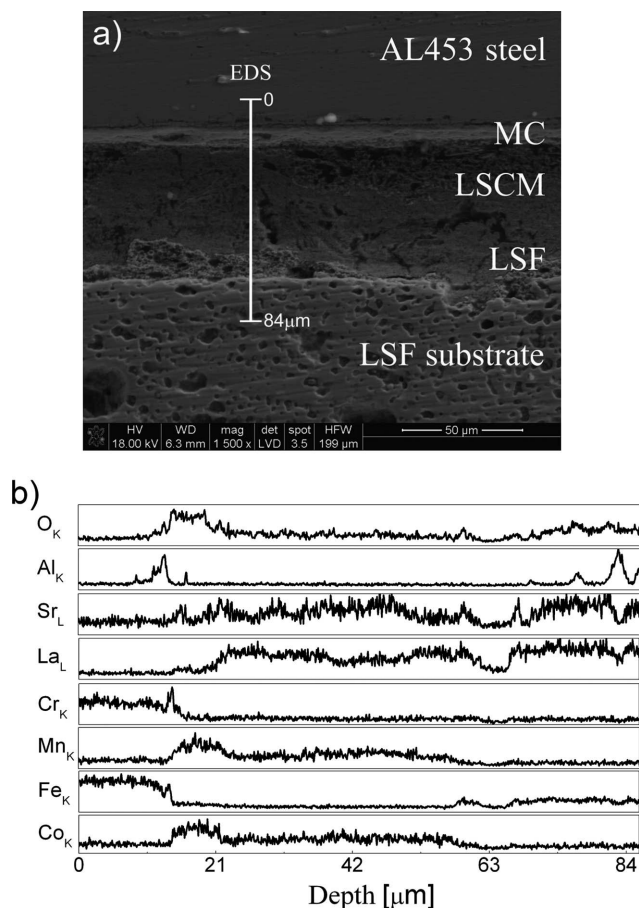


Fig. 3. Microstructure of the AL453/MC/LSCM/LSF/LSCM/MC/AL453 system after 200 hrs of oxidation in air at 1073 K: a) SEM microphotograph of the polished cross-section and b) EDS line scan analysis

Detailed cross-sectional SEM-EDS investigations of the microstructure and composition of the oxidized AL453/MC/LSCM/LSF/LSCM/MC/AL453 system revealed the presence of an intermediate spinel reaction layer of $(\text{Mn},\text{Co},\text{Cr})_3\text{O}_4$ with a thickness of about $0.5\ \mu\text{m}$ at the MC coating/AL453 steel interface. This compound was the product of the chemical reaction between $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ and Cr_2O_3 at 1073 K induced by the diffusion of manganese and cobalt from the MC coating toward the chromia sublayer, which had formed on the surface of the AL453 steel during the initial stage of the oxidation process. Moreover, the EDS line scan analysis of chromium distribution in the MC coating indicated a significant decrease in concentration when moving away from the metallic substrate and in the direction of the LSCM/LSF interfacial zone (Fig. 3b). Thus the $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ (MC) ceramic coating may play the role of an effective barrier against outward chromium diffusion from the AL453 steel and, therefore, protect the cathode material from the negative ef-

fects of the formation of volatile Cr vapors within the chromia subscale.

3.3. Interfacial resistance of the cathode-interconnect systems

In order to determine the electrical functionality and evaluate the usefulness of the elaborated procedure for the fabrication of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ cathode-AL453/ $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ interconnect system used in the construction of the IT-SOFC, their area specific resistance was measured. Fig. 4 shows the in-situ ASR values vs time for the AL453 steel with the scale formed after its oxidation in the AL453/ Cr_2O_3 /LSCM/LSF/LSCM/ Cr_2O_3 /AL453 system and the AL453 steel coated with $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ in the AL453/MC/LSCM/LSF/LSCM/MC/AL453 system during exposure to air at 1073 K. The average ASR value for the system based on the surface of the AL453 steel modified with the manganese cobaltite spinel coating (MC) was approximately $0.023\ \Omega\cdot\text{cm}^2$ and remains practically constant throughout the measurements. This value is significantly lower than the ASR level of $0.1\ \Omega\cdot\text{cm}^2$ that forms one of the requirements for IT-SOFC interconnect materials [20] and indicates that the $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ coating may minimize electrical resistance at the cathode-interconnect interface. On the other hand, the oxidation of the AL453/ Cr_2O_3 /LSCM/LSF/LSCM/ Cr_2O_3 /AL453 system, in which uncoated ferritic stainless AL453 was used, leads to a monotonic increase in the ASR resistance, up to approximately $0.22\ \Omega\cdot\text{cm}^2$.

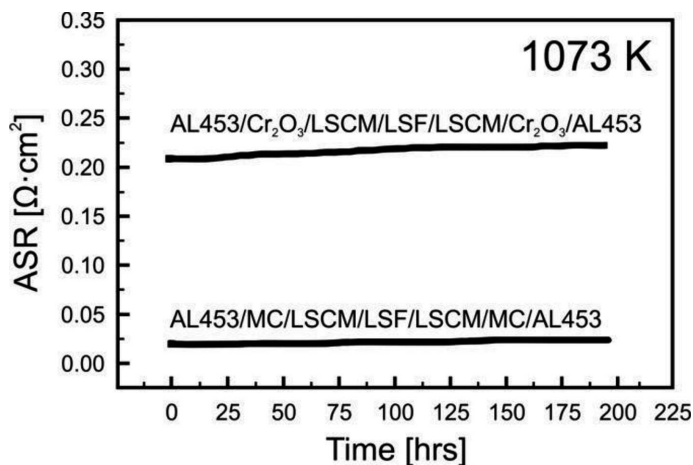


Fig. 4. Time dependence of ASR for AL453 steel with the scale in the AL453/ Cr_2O_3 /LSCM/LSF/LSCM/ Cr_2O_3 /AL453 system and AL453 steel coated with $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ in the AL453/MC/LSCM/LSF/LSCM/MC/AL453 system during oxidation at 1073 K in air

The ASR of the AL453/MC/LSCM/LSF/LSCM/MC/AL453 system is thus about one order of magnitude lower than that of the AL453/ Cr_2O_3 /LSCM/LSF/LSCM/ Cr_2O_3 /AL453 system. The significantly lower ASR resistance level of the AL453/MC/LSCM/LSF/LSCM/MC/AL453 system may be explained by the electrical conductivity of the $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ coating, which is higher than that of Cr_2O_3 [5] and improved adhesion of the intermediate reactive $(\text{Mn},\text{Co},\text{Cr})_3\text{O}_4$ spinel layer to the steel core and to the ceramic coating. Similar results were reported by the authors of [9], who registered a

decrease in ASR to the value of approximately $0.0114 \Omega\text{-cm}^2$ during nearly 500 hrs of oxidation at 1073 K in air in a similar system to the one studied in the present paper, but featuring the ferritic Crofer 22APU steel covered with the $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ coating deposited using screen-printing.

The observed results prove that the studied protective-conducting $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ coating may effectively prevent chromium migration from the AL453 steel interconnect into the cathode space and also significantly improves the electrical properties of the cathode-interconnect system during long-term oxidation.

4. Conclusions

Two types of cathode-interconnect systems, namely AL453/ Cr_2O_3 /LSCM/LSF/LSCM/ Cr_2O_3 /AL453 and AL453/MC/LSCM/LSF/LSCM/MC/AL453, were investigated, and one of them featured the AL453 steel covered with $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ (MC) paste deposited using screen-printing. The tested cathode-interconnect multilayer systems were compact. The SEM-EDS study of the AL453/MC/LSCM/LSF/LSCM/MC/AL453 system after 200 hrs of oxidation in air at 1073 K showed a decrease in the content of chromium at steel/coating interface, which implies that the $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ has a chromium-getter barrier. A long-term study of the electrical resistance of the cathode-interconnect systems revealed a significant decrease in ASR values for the system featuring the AL453 steel modified with thick films of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ spinel in comparison to the uncoated steel. After 200 hrs of oxidation in air at 1073 K, the ASR of the AL453/MC/LSCM/LSF/LSCM/MC/AL453 system reached a level of about $0.023 \Omega\text{-cm}^2$; this value is significantly lower than the upper ASR limit for IT-SOFC interconnect materials and indicates that the $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ coating may minimize electrical resistance at the cathode-interconnect interface.

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REFERENCES

- [1] N.Q. Minh, T. Takahashi, Science and Technology of Ceramic Fuel Cells. Elsevier, Amsterdam 1995.
- [2] M. Mosiałek, M. Dudek, J. Wojewoda-Budka, Arch. Metall. Mater. **58**, 275 (2013).
- [3] J.W. Fergus, Mater. Sci. Eng. A **397**, 271 (2005).
- [4] W.J. Quadackers, J. Piron-Abellan, V. Shemet, L. Singheiser, Mater. High Temp. **20**, 115 (2003).
- [5] T. Brylewski, M. Nanko, T. Maruyama, K. Przybylski, Solid State Ionics **143**, 131 (2001).
- [6] K. Hilpert, D. Das, M. Miller, D.H. Peck, R. Weiß, J. Electrochem. Soc. **143**, 3642 (1996).
- [7] X. Chen, P.Y. Hou, C.P. Jacobson, S.J. Visco, L.C. DeJonghe, Solid State Ionics **176**, 425 (2005).
- [8] Z. Yang, G. Xia, S.P. Simner, J.W. Stevenson, J. Electrochem. Soc. **152**, A1896 (2005).
- [9] Z. Yang, G. Xia, J.W. Stevenson, Electrochem. Solid-State Lett. **8**, A168 (2005).
- [10] B. Hua, J. Pu, W. Gong, J. Zhang, F. Lu, L. Jian, J. Power Sources **185**, 419 (2008).
- [11] Z. Yang, G.G. Xia, X.H. Li, J.W. Stevenson, Int. J. Hydrogen Energy **32**, 3648 (2007).
- [12] A. Petric, H. Ling, J. Am. Ceram. Soc. **90**, 1515 (2007).
- [13] N. Shaigan, W. Qu, D.G. Ivey, W. Chen, J. Power Sources **195**, 1529 (2010).
- [14] K. Wang, Y. Liu, J.W. Fergus, J. Am. Ceram. Soc. **94**, 4490 (2011).
- [15] M. Kakihana, J. Sol-Gel Sci. Technol. **6**, 7 (1996).
- [16] Z. Yang, G. Xia, Z. Nie, J. Templeton, J.W. Stevenson, Electrochem. Solid State **11**, B140 (2008).
- [17] K. Przybylski, T. Brylewski, J. Prazuch, Schriften des Forschungszentrums Jülich, Reihe Energietechnik/Energy Technology (Germany) **15**, Part II, 741 (2008).
- [18] S. Chevalier, G. Caboche, K. Przybylski, T. Brylewski, J. Appl. Electrochem. **39**, 529 (2009).
- [19] A. Kruk, M. Stygar, T. Brylewski, K. Przybylski, in: R. Bjørge, F.J.H. Ehlers and R. Holmestad (Eds.), 7th International Conference on the Physical Properties and Application of Advanced Materials (ICPMAT 2012), NTNU – Trondheim Norwegian University of Science and Technology, p.140 (2012).
- [20] W.Z. Zhu, S.C. Deevi, Mater. Res. Bull. **38**, 957 (2003).