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Thin film perovskite coatings and their application for SOFC ferritic steel interconnects

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Abstract

High electrical contact resistance and Cr evaporation are two well recognised technical issues in reliable long-term use of ferritic stainless steel interconnects in solid oxide fuel cells (SOFCs). They have a crucial negative impact on the cell performance and stability, if not adequately addressed. During the last years, many types of conductive ceramic oxides with either a spinel or perovskite lattice structure have been investigated as protective oxide layers for SOFC interconnect applications. For example perovskites show sufficiently high electronic conductivity, good matching of the thermal expansion coefficient (TEC), chemical stability in SOFC-operating environments and low cation mobility. Nevertheless, their performance has been often reported to be below expectations due to poor adherence and higher difficulty in obtaining densely sintered layers in comparison to spinel coatings. As a new attempt to address such aspects, a novel chemical conversion process has been developed for producing dense thin films (below 1 μm) of LaFeO₃-based perovskite coatings on ferritic stainless steel surfaces, under relatively low temperature conditions. Commercially available ferritic 22Cr steels (Crofer 22H and Sanergy HT steels) have been used to evaluate electrical contact resistance, corrosion stability and Cr evaporation of the perovskite-modified stainless steel surfaces in medium-term tests at 700°C. X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (SEM-EDX) have been used to characterise the materials before and after testing. Results show that a stable electrical contact resistance is obtained at 700°C, well below the target value of 0.05 Ωcm² at this temperature, for both coated steels. Coated Sanergy HT steel show a somewhat better Cr retention, although not to a fully satisfactory degree. Further efforts are still required for obtaining improved Cr barrier performance on 22Cr steels.
Introduction

Metallic interconnects made of special-purpose 22Cr ferritic steel alloys such as Sanergy HT and Crofer 22H have gained increased popularity in recent years for the application in planar Solid Oxide Fuel Cell (SOFC) technology due to their optimal combination of oxidation resistance and mechanical strength at the typical SOFC-service conditions (i.e., 600-850°C). Although 22Cr steels form a unique protective scale composed of a (Mn,Cr) oxide top layer and a chromia sublayer that significantly reduce the oxidation rate with respect to common 18Cr ferritic steels, a protection ceramic coating that prevents formation of surface resistive layers and Cr cathode poisoning is still required for a stable and long-term interconnect performance [1]. Ceramic coatings must be dense, adherent and have electronic conductivity, matching thermal expansion properties, chemical stability in oxidizing atmospheres along with chemical compatibility with the adjacent cell components, which restricts the choice of coating materials essentially to mixed oxide ceramics belonging to either spinel or perovskite crystal structure family.

Over the past years, considerable attention has been paid to various lanthanum-based LaBO$_3$ perovskite coatings that contain Co, Mn and Fe in the B site and that are fairly similar in composition to those used as cathode materials [2]. However, most studies report that Co- and Mn-based perovskites become highly unstable when deposited directly on steel substrates and provide unsatisfactory results in terms of Cr retention, thus allowing rapid Cr diffusion through the perovskite coatings and formation of interfacial reaction layers with high electrical resistance [2-4]. On the other hand, it has recently been found that Fe-based perovskites may offer a better diffusion barrier protection against Cr evaporation due to their high chemical stability when in direct contact with chromia or Cr-containing species [5]. More recently, the tolerance of lanthanum ferrite perovskites towards chromia has been studied at various temperatures by using a highly conductive Ni-substituted LaNi$_{0.6}$Fe$_{0.4}$O$_3$ (LNF) composition as an example [6,7]. It has been demonstrated that reactivity of LNF strongly depends on temperature. Lowering temperature below 800°C resulted in a very low chemical reactivity, which seems promising for use of pure or substituted lanthanum ferrite as a Cr-tolerant coating, especially under Intermediate Temperature SOFC (IT-SOFC) operating conditions [7].

At the same time, the practical application of perovskite coatings has been impeded for the poor adhesion and low sintering density in comparison to spinel coatings [8,9]. To improve these limitations, we have recently developed a novel and simple lanthanum surface conversion treatment, which is based on lanthanum chemical conversion reactions with the iron in stainless steel and other high temperature alloys to produce dense and adherent LaFeO$_3$ perovskite coating layers [10-12]. The surface treatment is carried out in a specially-formulated molten carbonate salt bath, under relatively low temperature conditions (i.e., at around 600°C). The high versatility of the molten salt process results in the formation of perovskite coating layers with thickness ranging from sub-micron to a few microns.

This novel conversion coating process is currently being investigated within the FCH-JU funded project SCORED 2:0 (full title: Steel Coatings for Reducing Degradation). One main purpose of the SCORED 2:0 project is to develop advanced surface treatments and coatings for improving the surface functional properties of commercial ferritic stainless steels of metallic interconnects for IT-SOFC applications, on a cost-effective basis.

1. Scientific Approach

As part of the research activities in the project, the purpose of this work is to examine the feasibility of a LaFeO$_3$ perovskite conversion coating approach to improve the functional surface properties of two 22Cr ferritic steels (Crofer 22H and Sanergy HT). To our
knowledge, there are no reports in literature describing the perovskite coating behavior at lowered SOFC temperatures. Consequently, thin, dense layers of LaFeO$_3$-based coatings have been prepared using the perovskite conversion process and investigated in terms of microstructure, electrical conductivity, Cr diffusion and oxidation resistance of the coated 22Cr steels after operation, under relevant IT-SOFC oxidizing conditions.

### 2. Experiments

Ferritic stainless steel samples of Crofer 22H and Sanergy HT were received from ThyssenKrupp VDM and Sandvik Materials Technology, respectively. Their nominal chemical composition are reported in Table 1.

#### Table 1 – Nominal chemical composition (wt %) of Crofer 22H and Sanergy HT ferritic stainless steels, according to the available manufacturer analysis.

<table>
<thead>
<tr>
<th>steel</th>
<th>element</th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>W</th>
<th>Nb</th>
<th>Ti</th>
<th>La</th>
<th>P</th>
<th>Ni</th>
<th>Cu</th>
<th>Mo</th>
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<tbody>
<tr>
<td>Crofer 22H</td>
<td>min</td>
<td>0.03</td>
<td>0.80</td>
<td>0.60</td>
<td>0.10</td>
<td>1.0</td>
<td>0.20</td>
<td>0.02</td>
<td>0.04</td>
<td>24</td>
<td>0.03</td>
<td>0.60</td>
<td>0.10</td>
<td>1.0</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>20</td>
<td>bal.</td>
<td>0.10</td>
<td>0.02</td>
<td>0.20</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>21.2</td>
<td>bal.</td>
<td>0.04</td>
<td>0.30</td>
<td>0.12</td>
<td>0.017</td>
</tr>
</tbody>
</table>

Thin foils of 0.3 mm thickness for Crofer 22H and of 0.2 mm for Sanergy HT steel were used in this work. All the samples were received and tested in a standard BA (Bright Annealed) surface finish condition.

Perovskite conversion coatings were grown according to reaction conditions and procedures already described in our recent work [12]. In essence, the molten carbonate bath consisted of an eutectic binary mixture of Li$_2$CO$_3$ and Na$_2$CO$_3$ salts (53%Li$_2$CO$_3$-47%Na$_2$CO$_3$) to which La$_2$O$_3$ and other minor soluble additives were added to control melt basicity and coating thickness. The steel samples were immersed in the bath for 48 hours at 595°C under a CO$_2$ gas blanketing atmosphere. After the coating treatment, a prolonged cleaning treatment in boiling deionized water for about 6 hours was required in order to completely remove any residual salt from the sample metallic surfaces [12].

Oxidation experiments were conducted in a moistened ambient air at 700°C for 1000 h by placing coated steel samples in a quartz tube furnace in which the air flow rate was set at 1Nl/min. The moisture content of the air was 3 % in terms of relative humidity.

A novel characterization method was specifically developed in this project to evaluate Area Specific Resistance (ASR) and Cr retention properties in simultaneous testing. The method simulates the interface of interconnect and cathode in a SOFC stack by placing a coated steel sample in contact with a palladium plated coated with a cathode material paste (lanthanum strontium cobaltite, LSC). Testing was conducted at 700°C for 1000 h in a 3 % RH ambient air. Active area of the coated steel samples was 1 cm$^2$ and the ASR was continuously recorded during the test under 0.4 A/cm$^2$ current load and 0.4 MPa compressing pressure conditions [13].

X-Ray Diffraction (XRD) and Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDX) were used for post-test analysis of the coated steel samples. Further, SEM/EDX analysis on LSC layer was used to measure the Cr released from the coated steel.
3. Results

Results of SEM and XRD analysis of the coated steels are reported in Figure 1. From morphological analysis, it can be observed that the molten carbonate process produces a smooth coating layer on the surface of both 22Cr steels, although larger perovskite grains are visible on the coating of Sanergy HT sample. XRD patterns show that in both cases the main component of the coating layer is a LaFeO$_3$ perovskite phase. In the case of the Sanergy HT sample, small peaks ascribed to a Fe-Cr rich cubic spinel are also observed.

Figure 1: SEM image (a) and XRD patterns (b) of the Sanergy HT and Crofer 22H samples after the surface perovskite conversion process.

Figure 2 shows results of SEM and XRD analysis of the coated steel samples after air exposure experiments at 700°C for 1000 h. Significant structural evolution is observed on both samples. In the case of the Sanergy HT the initial crystalline coating structure changed into a more smooth surface layer. Small brighter (La,Si)-rich oxide particles are present on the top surface, according to SEM analysis. In contrast, a more significant growth of La-Si particles with a platelet morphology takes place on the Crofer 22H steel. The findings may be expected in consideration of the fact that Crofer 22H contains a higher Si content than Sanergy HT steel (see Table 1). The surface enrichment of Si clearly suggests that this element can be selectively removed from the near surface regions of stainless steels during the molten carbonate process, as previously reported [12]. Development of low-Si stainless steels is recognized as an important factor to avoid formation of resistive silica layers at the scale/metal interface. Consequently, these findings indicate that the molten carbonate surface treatment is also useful to remove Si from the steel interior during perovskite coating formation, which could be highly promising for enhanced electrical functionality of SOFC steel interconnects. XRD analysis shows in both cases some growth of spinel and hematite phases combined with a decrease of LaFeO$_3$ perovskite peak, which is more distinct on the Crofer 22H steel. Regarding the Crofer 22H pattern, the appearance of a peak at 2Θ~47° could be ascribed to the presence of a Cr$_2$SiO$_4$ –rich phase, most likely to be related with the formation of the Si-rich platelet particles on the top surface.
The results of long-term ASR experiments are reported in Figure 3. Two coated samples of each steel were tested for reproducibility. It can be observed that, after an initial sharp resistance decrease, the Sanergy HT samples show a gradual ASR increase up to 350 h, followed by a steady decrease trend with a final ASR value in the 0.02-0.04 Ω·cm² range. The Crofer 22H sample exhibits a continuous decrease in the ASR with final values in the 0.015-0.025 Ω·cm² range. It is worthy of consideration that the measured ASR values of both the coated steels are significantly lower than the target limit of 0.05 Ω·cm², at 700°C. Furthermore, ASR results seem not to be adversely influenced by the above-mentioned presence of La-Si or Cr-Si oxide particles on the top surface. Even more remarkable is the fact that best electrical results have been obtained with the coated Crofer steel in spite of formation of higher amounts Si-rich oxide particles on the coating top surface.

In Figure 4 the SEM cross-section images of the steel-cathode assembly after the ASR experiments are reported. Structure of the initial perovskite coating is not clearly observed due to its evolution into a more complex reaction layer with the cathode material. The overall reaction layer thickness is rather narrow with values lesser than 5µm in the Sanergy HT case and lesser than 3µm for the Crofer 22H sample. Only in the case of the Crofer steel, the position of La is still clearly observable. The cross-section image indicates that La is being confined in a very thin layer of about 100-200 nm, suggesting that a submicron perovskite coating layer would have formed on the Crofer steel surface under the chosen coating synthesis conditions. Formation of a very thin perovskite coating layer is also in agreement with the highly smoothed coating surface as reported in Figure 1. All these findings could therefore explain the better electrical performance of the coated Crofer 22H samples during the ASR test. In both cases, however, some diffusion of Cr, Mn...
and Co cations through the perovskite coating and the reaction with the cathode material has been also observed.

![SEM images of the coating cross section at the cathode side.](image1.png)

**Figure 4:** SEM images of the coating cross section at the cathode side.

Limiting to the Cr diffusion analysis, the results of the EDX analysis on the cathode material after the ASR experiment are illustrated in Figure 5. In both cases, a reaction layer is evident at the coating-cathode interface, with the formation of a Cr-rich dense phase. Increasing the distance from the Sanergy HT steel interface, the chromium content is reduced significantly, with values of 1-2%, approximately. In the case of the Crofer 22H, Cr content remains high through all the cathode section, suggesting that the thickness of La-Fe perovskite coating formed on Crofer 22H was probably too thin to effectively prevent chromium diffusion from the steel.

![SEM images of the cathode cross section with overimposed EDX results related to chromium detection in the cathode layer.](image2.png)

**Figure 5:** SEM images of the cathode cross section with overimposed EDX results related to chromium detection in the cathode layer

### 4. Conclusions

A molten carbonate perovskite conversion process was applied on two 22Cr ferritic stainless steels to produce thin and dense LaFeO₃ perovskite coating layers. Selective removal of silicon from the near surface region of the stainless steels during the perovskite coating formation is an additional and positive effect of the molten carbonate process. The steel composition influences the growth process: the difference in morphology and phase
composition is evident on the two different steels indicating larger crystals and somewhat thicker perovskite coating layers in the Sanergy HT samples. During the 1000 h air exposure test, significant evolution including growth of spinel, hematite and silicate phases was observed on the coatings, being much more evident on the thinner perovskite coated Crofer 22H steel. Despite the formation of Si-rich particles on the top surface of perovskite coating layers, the ASR values are excellent (<0.05 Ω·cm²) through the whole examined period, with a decreasing trend in both cases. The Crofer 22H is characterized by the best results (0.015-0.025 Ω·cm² after 1000 h, at 700°C). Regarding chromium retention properties, there is the evidence that Cr diffuses into the cathode layer. Cr diffusion is significantly higher on the Crofer 22H coated steel probably due to its thinner perovskite coating layer.

The results of this work clearly indicate that thin LaFeO₃-based perovskite layers undergo a significant evolution of structure, phase and morphology when in contact with SOFC cathode materials, under IT-SOFC operation condition exposure at 700°C. However, this does not prevent from obtaining excellent and stable surface electrical functional properties in long-term testing. On the other hand, the chromium retention property of such thin LaFeO₃ perovskite coatings is less satisfactory suggesting that better Cr barrier properties could be obtained with somewhat thicker LaFeO₃ perovskite coatings. These aspects are being actively studied within the framework of the SCoReD project with the purpose of developing LaFeO₃ perovskite conversion coatings with a sufficiently low ASR combined with high Cr retention properties on 22Cr ferritic steels.

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References


