Facile route for reactive coating of $LaCrO_3$ on high-chromium steels as protective layer for solid oxide fuel cell applications

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Abstract:

In this study, we present a facile route for the production of thin $LaCrO_3$ layers as a protective layer on chromium-containing steels, usually applied as a dense interconnector material for solid oxide fuel cells or porous supports for metal-supported solid oxide fuel cells. The reactive coating method is based on dip coating in aqueous lanthanum acetate/propionate mixtures and subsequent firing. $LaCrO_3$ is formed by a reaction between lanthanum from the coating solution and chromium from the steel. The obtained layers are thin and adhere well to the sample surface. X-ray diffraction reveals the pattern of the $LaCrO_3$ phases. Thermogravimetric measurements show the improved oxidation resistance of $LaCrO_3$-coated steel. Because of the easy-to-apply nature of this method and the wide range of tailoring possibilities, the reactive coating route is a viable alternative to established nitrate- or alcoholate-based wet chemical coating technologies.

Keywords: $LaCrO_3$, reactive coating, oxidation resistance, chemical solution deposition

1. Introduction

In recent years, Solid oxide fuel cells (SOFCs) based on porous metal supports (metal-supported SOFC, MSC) have been demonstrated as a promising fuel cell technology for mobile power generation because of their improved thermal management in the case of rapid thermal cycling. Furthermore, MSCs are attractive because of their cost, mechanical stability, and ease of joining. [1]. Important progress was made in MSC development in close cooperation between Plansee SE (Austria) and Forschungszentrum Jülich GmbH (Germany) [2-5]. High-chromium ferritic steels are used as MSC supports and interconnect materials because of their good corrosion resistance and adapted thermal expansion coefficient. However, some challenges remain. For interconnects, chromium evaporation is a major detriment to the lifetime of a SOFC because of the poisoning of the traditional cathode materials [6-8]. For MSC supports, the interdiffusion of Fe and Cr into the anode and oxidation in humid atmospheres cause crucial long-term stability issues [9, 10]. Therefore, different coating techniques were investigated to protect the interconnects [11, 12] and supports [13, 14]. In particular, perovskitic $LaCrO_3$ is a promising material, as it offers excellent chemical stability in oxidizing and reducing atmospheres, an adapted thermal expansion coefficient, a good electrical conductivity of $\sigma_{800°C\ air} = 0.96$ S/cm, a significant tolerance for lattice substitution (doping), and low Cr-bulk-diffusion rates [15-17]. In this study, a wet chemical process was developed, which is based on the reactive sol-gel coating of pre-oxidized ferritic steel by a lanthanum-acetate-based solution. A $LaCrO_3$ layer with excellent adherence was formed in-situ during subsequent thermal treatment. As a first proof-of-concept, dense and porous metal components were coated, which showed significantly improved oxidation resistances.

2. Experimental

Dense and porous intermediate temperature metal (ITM) sheets (Fe-26Cr, Mo, Ti, and Y_2O_3) were provided for use as substrates by Plansee SE (Reutte Austria). They were cut to a size of 1×3 cm^2 and pre-oxidized at 900 °C in Ar atmosphere. Under these conditions, a Cr_2O_3 layer approximately 100 nm thick formed. To prepare the coating solution, 0.012 Mol of lanthanum acetate hexahydrate (Sigma Aldrich) were dissolved in 40 ml propionic acid (Sigma Aldrich) and 10 ml deionized water. Additionally, in the case of the La-Cr coating solution, 0.003 Mol of chromium acetate hexahydrate (Sigma Aldrich) was dissolved. The solution was placed in an open beaker and heated to 125 °C under constant stirring in order to evaporate the water and acetic acid. After 5 hours the liquid became highly viscous. A 5 - 10 ml volume of propionic acid was added to adjust the viscosity and the solution was allowed to cool. To improve the wettability and adjust the final viscosity of the liquid, 5 µl/ml Lutensol ON50 (BASF, Ludwigshafen, Germany) and 100 mg/ml Pluronic123 (Sigma Aldrich) were added to the solution. After the ITM sheets were dip-coated with a removal speed of 1 mm/s, the samples were allowed to dry in ambient air. Finally, the samples were thermally treated at 950 °C in air for 5 hours to achieve a dense and stable reactive coating.

X-ray diffraction (XRD) patterns of the coatings were recorded using a Bruker D4 Endeavor instrument with Cu-Kα radiation. The scanning electron microscope (SEM) pictures were taken using Zeiss Ultra55. The effect of the coating was evaluated by thermogravimetric measurements under an Ar-2.9 % H_2/4 % H_2O atmosphere in a NETZSCH STA 449 F3 Jupiter using Al_2O_3 crucibles. Buoyancy was then corrected through a reference measurement with the empty crucible.

3. Results and discussion

3.1. Lanthanum chromite coating on compact support

The reactive coating method (Figure 1a) focuses upon the simultaneous calcination of the organic lanthanum precursor and a reaction with chromium from the metal sheet in order to form a stable lanthanum chromite layer. This creates a dense coating with excellent adherence. We found that thin layers of the pure lanthanum-propionate-based precursor readily react with Cr_2O_3 from the support during the sintering. However, the coating layer consists of mixtures of La_2CrO_6 and La_2O_3, as confirmed by XRD (see Figure 1b). These phases are not electrically conductive, which is not favorable for the proposed applications [18].

To overcome this drawback, 20 mol% of a chromium-acetate-including coating solution was applied to the ITM support to adjust the coating layer composition (Figure 1c). The coating based on the La/Cr acetate solution showed reduced layer thickness, thicker remaining chromium oxide scales, and more pores at the layer interface compared to those showed by the coating of the pure La acetate solution. However, even in this case, the coating layer was formed continuously on the ITM support, and XRD analysis of the coating layer shows a pure $LaCrO_3$ phase formation with an Fe-Cr alloy phase support (see

Figure 1d). XRD patterns reveal the paired reaction between the coating layer and Cr_2O_3 scale on the ITM during the sintering. The La-Cr ratio in solution was 4:1, thus the coating layer requires an additional Cr source from the native Cr_2O_3 layer to form the $LaCrO_3$ phase without leaving a residual La_2O_3 phase. The result shows a successful coating with the intended phase formation by control of coating solution composition.

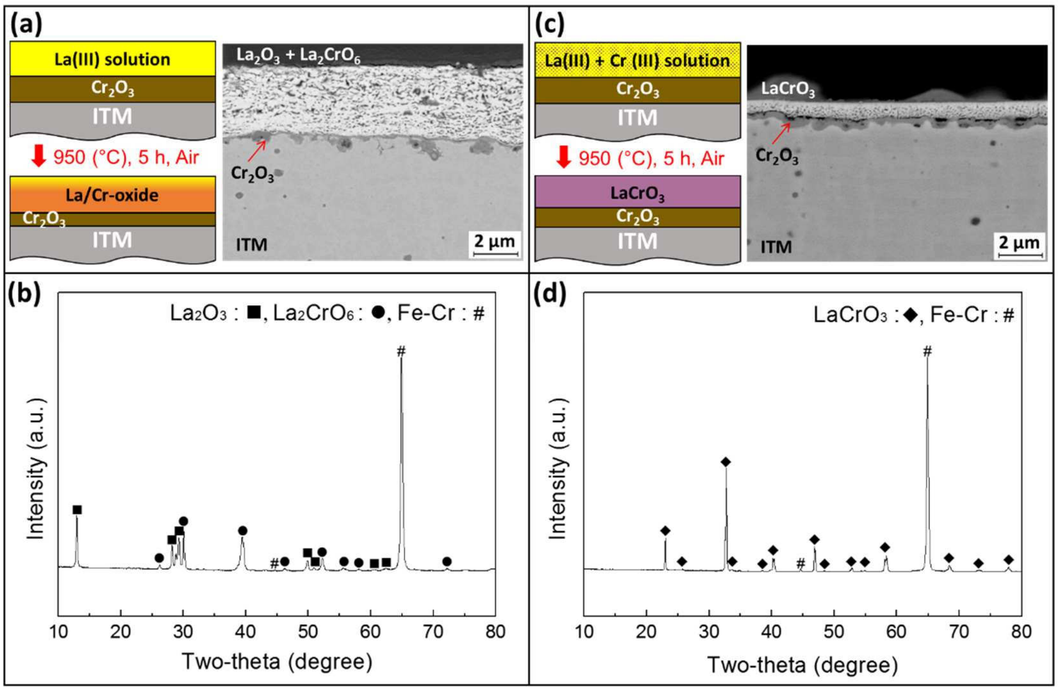

Figure 1. Schematic diagram with SEM micrograph (a) and an XRD phase analysis (b) result after La acetate coating; a schematic diagram with SEM micrograph (c) and an XRD phase analysis (d) result after La-Cr acetate coating

3.2. Coating of porous ITM supports

While the coating of dense ITM supports leads to reproducible and homogenous layers, there is still a need to transfer the results to porous supports. For example, the $LaCrO_3$ coating on the inner surface of a porous ITM support showed much higher deviations regarding layer thickness and homogeneity of the coverage, potentially caused by the effect of gravity during the drying of the coating solution. As shown in Figure 2, the coating layer underneath the struts (point a) is thicker than the upper layer (point b) by the flow of the coating solution immediately after dip-coating. However, the $LaCrO_3$ coating layer covers most of the Cr_2O_3 scale and is sub-micron in scale, in spite of the layer thickness. Adjusting the solution composition, the number of the coating steps, and the sintering process may improve the coating layer quality.

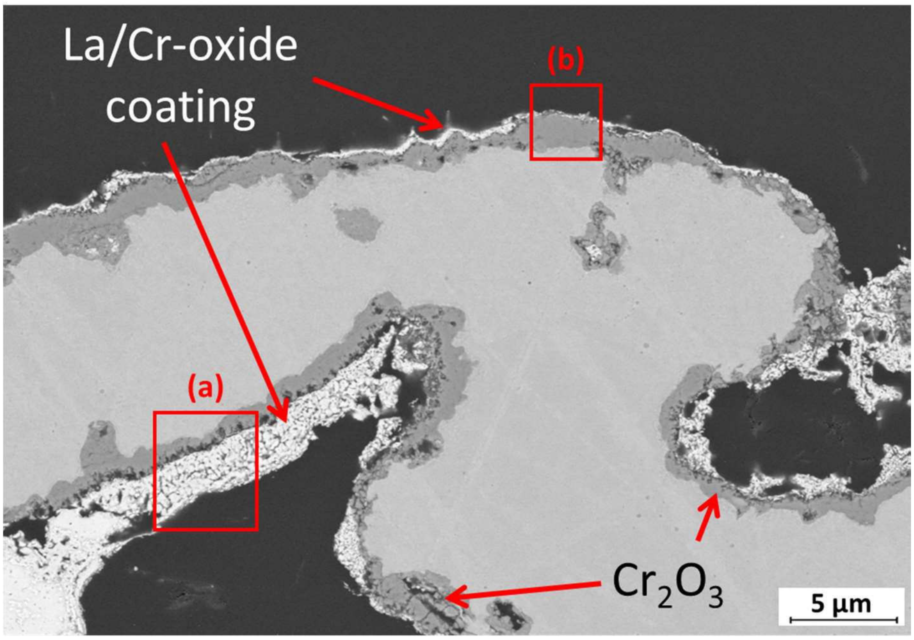

Figure 2. SEM image of porous ITM support after La acetate coating with the indication of area a) thick and area b) thin $LaCrO_3$-coating.

3.3 Thermogravimetric test result

Figure 3 shows the thermogravimetric analysis of a porous ITM support with and without the $LaCrO_3$ coating process. Although the $LaCrO_3$ coating layer was not homogeneous on the porous support, the sample with the $LaCrO_3$ coating shows significantly improved oxidation resistance. With the bare ITM support, a 2.6 % increase in mass was observed over 2880 min (2 days), but the support with $LaCrO_3$ coating showed only a 0.2 % change over the same period. The result indicates that the $LaCrO_3$ layer is highly effective at blocking oxidation even with a sub-micron scale thickness.

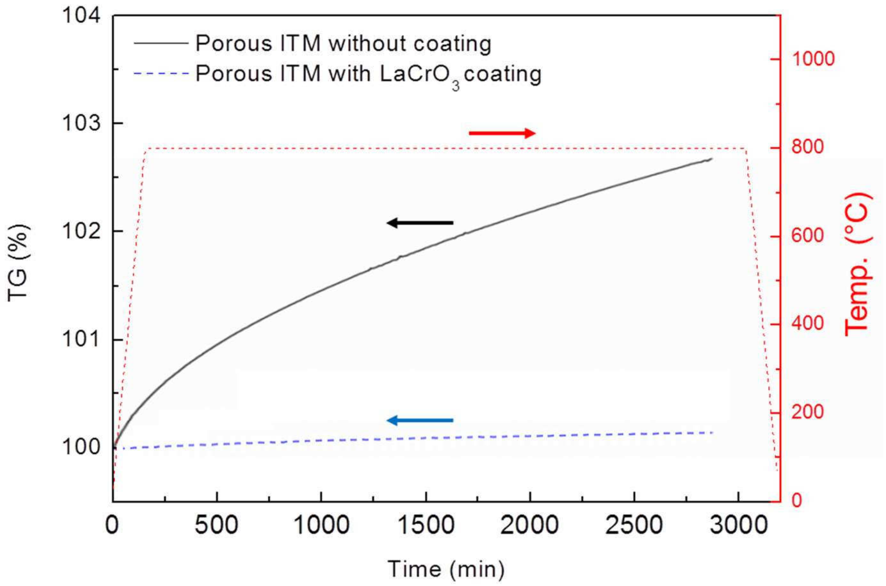

Figure 3. Thermogravimetric analysis result of porous ITM support with and without La acetate coating (Ar-2.9 % H_2/4 % H_2O)

4. Conclusions

In this study, we presented a cheap, easily applied, scalable, and flexible solution-based reactive sol-gel coating method that provides a dense and homogeneous layer of perovskitic $LaCrO_3$ on chromium-containing ferritic steels for SOFC applications. The coating process itself does not require clean room conditions or sophisticated pre-treatment of either the precursors or support. $LaCrO_3$ layers with good adherence were obtained, which have promising applications as protective coatings for the interconnects or metal supports of SOFCs. At this early stage of development, the coating layer thickness was not homogenous; however, most of the surface was covered by the $LaCrO_3$ layer. For a first proof-of-concept, the increased oxidation resistance of porous ferritic steel substrates was demonstrated. Currently, further optimization of the reactive coating process toward improved homogeneity is in progress.

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