

# FABRICATION OF CONDUCTING OXIDE COATINGS ON CROFER22APU USED AS METALLIC INTERCONNECTS FOR SOFC

Tak-Hyoung Lim, Seong-Soo Pyo, Seung-Bok Lee, Seok-Joo Park, Rak-Hyun Song,  
and Dong-Ryul Shin

Fuel Cell Research Center, Korea Institute of Energy Research, Daejeon, Yuseong-gu,  
Republic of Korea

## Summary

The conductive ceramic coating was used to improve an electrical performance of substrate steel, as well as to prevent the contamination of the chromium ion in SOFC. The  $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$  (LSM) conductive material was coated on Crofer22APU via a wet spray coating process. The adhesive strength of an interface between coated layer and metal substrate increased with the surface roughness of metallic interconnects. After the oxidation experiments of coated substrate during 8000 hours, the ASR showed a low value of  $23 \text{ m}\Omega \cdot \text{cm}^2$ . These results shown that the coated oxides layer prevents the formation and the growth of scale ( $\text{Cr}_2\text{O}_3$  and  $(\text{Mn}, \text{Cr}, \text{Fe})_3\text{O}_4$  layer) and enhance the long-term stability and electrical performance of metallic interconnect for SOFC.

## Keywords

Conducting Oxide, Metal Interconnect, SOFC

## Introduction

Metallic interconnects offer a number of advantages over ceramic interconnects such as  $\text{LaCrO}_3$ -based oxides in SOFCs, including low material cost, good mechanical properties, high thermal conductivity, high electrical conductivity, and an easy manufacturing process for large areas.[1] Metallic interconnects must satisfy several functional requirements under SOFC operating conditions. Many high-temperature alloys, including a Cr-based alloy, a Ni-based alloy, and a Fe-based alloy have been studied as metallic interconnects. Recently, there have been several studies related to Fe-based alloys as metallic interconnects for low temperature SOFCs such as Crofer22APU. The Fe-based alloy has many advantages, such as similar thermal expansion coefficients to other cell components, good workability, and low manufacturing cost [2]. Since the Fe-based alloy also has the chromia scale with low conductivity, the improvement of electronic conductivity of the oxide scale is required [3]. The improvement of the oxide scale by addition of rare-earth elements or by addition of an effective protection layer having high electric conductivity and oxidation resistance is required. A few researchers reported the effects of protective coating methods [4]. In this study, Commercial Fe-based alloy (Crofer22APU) was selected as a metallic interconnect material. A conductive ceramic material was coated on Crofer22APU via a wet spray coating process. The influence of the oxide scale on the electric conductivity behavior of the coated Crofer22APU was examined and the experimental results were discussed as related to the elemental distribution of the oxide scale and its electric conductivity.

## Experimental

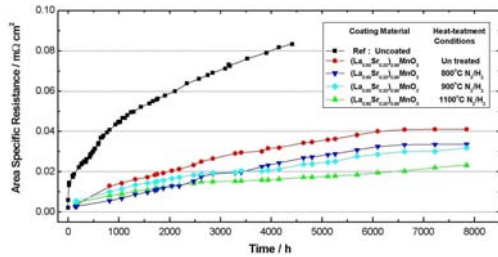
Preparation of slurry for wet spray coating process: The commercial cathode material, LSM was selected. The coating slurry was made by mixing the LSM cathode powder, organic binder, some additives, and solvents. The slurries of various conditions were made in order to know the slurry type for wet spray coating process.

Fabrication of LSM coating on Crofer22APU: The commercial alloy used in this experimental is Crofer22APU. The composition of Crofer22APU is shown in Table 1. Specimens were prepared with thickness of 6.5mm and area of  $15 \times 15 \text{ mm}^2$ , and then surface treated using sandblast equipment. The conductive material LSM was coated on Crofer22APU by a wet spray coating process and heat treated at  $1100^\circ\text{C}$  for 3 hours.

Measurement of area specific resistance and Observation of microstructure: Area specific resistance of the LSM coated Crofer22APU was measured as a function of holding time and temperature in air by using a two-point, four-wire method. Long-term stability of coated Crofer22APU was examined at  $800^\circ\text{C}$  in oxidizing atmosphere for 7848 hours.

## Results and discussion

The area specific resistance of the un-coated, coated specimens were measured by a DC two point & four wire probe method in oxidizing atmosphere at  $800^\circ\text{C}$ . Fig. 1 shows ASR change curves of conductive oxide coated Crofer22APU specimens. Substrates are treated by heat under the different conditions. Uncoated Crofer22APU shows the high ASR value of  $80 \text{ m}\Omega\text{cm}^2$  about 4,000 hour after the experiment started. On the other hand, conductive oxide coated Crofer22APU specimens shows low ASR value of about  $20 \sim 40 \text{ m}\Omega\text{cm}^2$ . ASR values of all samples



increase parabolically as time increases. It is estimated that in case conductive oxide layer such as LSM is coated in the surface of metals, the growth rate of metal oxides created in the metal surface under oxidation atmosphere could be lowered.

Fig.1. Area specific resistance variation curves of conductive oxide coated Crofer22APU specimens as a function of holding time at 800°C in air.

Fig. 2 shows LSM is coated sample, and shows cross section images of SEM and EDS after the experiment completed. Specimen is treated by heat at 1100°C for 3 hours in N<sub>2</sub> with H<sub>2</sub> gas. ASR value of the sample shows 23mΩ cm<sup>2</sup> after about 8,000 hour. It is observed that the scale of about 5~10 μm is grown between LSM layer and metal substrate through SEM image. In EDS mapping images, it is remarkable that (Cr, Mn)<sub>3</sub>O<sub>4</sub> based oxides are divided into two-layer in interface of coating layer and metal substrate just like the previous case (case not treated by heat after coating, case treated by heat at 800°C and

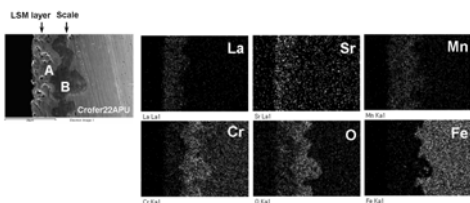


Fig. 2. SEM image and elemental distribution of cross section images of LSM coated Crofer22APU after oxidation for 7848 hours (Specimen was heat treated at 1100°C for 3 hour in N<sub>2</sub> with H<sub>2</sub> gas).

If taking a closer look at mapping images observed in each experiment, there is no clear layer, but it is observed that Mn oxides are plentiful in the place close to the surface. In terms of oxidation behavior of Fe-Cr alloys including Mn in general, it is known that spinel layer of (Mn, Cr)<sub>3</sub>O<sub>4</sub> in the top of Cr<sub>2</sub>O<sub>3</sub> is formed (Chen et al., 2005). These compositions of oxides can be explained by the diffusion rate of Mn<sup>2+</sup> ion in Cr<sub>2</sub>O<sub>3</sub> is hugely faster than Cr<sup>3+</sup> ion. That is, MnCr<sub>3</sub>O<sub>4</sub> spinel is normally formed on the top of Cr<sub>2</sub>O<sub>3</sub> oxides which are the main, because Mn can be diffused by the scale already formed in alloy. Fig. 3(a) and (b) shows EDS analysis results of region A and B shown in Fig. 2. Coating layer functions sufficiently as Cr evaporation barrier. Fig. 3(a) analyzes the coating layer, and Fig. 3(b) analyzes scale grown in interlayer. Considering Cr shows the low distribution in region A, it is observed that the movement of Cr formed in region B is effectively delayed. Conductive oxide coated substrates such as LSM show the lower ASR values than uncoated

samples, and are good in long-term performance. ASR values of samples are different based on whether to be treated by heat. About 8,000 hour after the experiment, about 20~40mΩcm<sup>2</sup> of ASR is shown, which means that protective coating of metallic interconnect is very important.

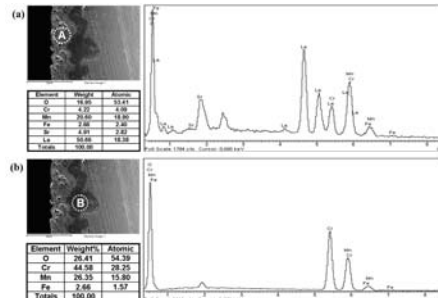


Fig. 3. SEM/EDS analysis of region A and B shown in Fig. 2.

## Conclusions

The conductive materials such as LSM was coated on Crofer22APU by wet spray coating process for metallic interconnect of SOFC. The contact strength of coating layer/substrate (Crofer22APU) interface was increased by using sandblast treatment. During about 8000 hours of testing, the best performance was achieved using LSM perovskite conductive layer that substantially improved the surface stability of the metallic interconnects, and prevented chromium outward migration. The value of the ASR was 23mΩ cm<sup>2</sup>. From the SEM and EDS measurements, we could confirm surely that coated oxides layer play an important role in retarding effectively the formation and the growth of scale (Cr<sub>2</sub>O<sub>3</sub> and (MnCr)<sub>3</sub>O<sub>4</sub> layer). Such a result provides an enhancement of long-term stability, at high temperature under oxidizing atmosphere, for metallic interconnects in SOFC.

## References

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