Electrophoretic Deposited LSCF-SDCC-Ag Cathode Coating on Ferritic Stainless Steel Interconnect for SOFC

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Abstract. The application of electrophoretic deposition (EPD) technique in development of composite cathode as a coating layer on ferritic stainless steel (FSS) interconnect for solid oxide fuel cell (SOFC) has acquired a great interest. The aim of this study is to determine the capability of EPD technique in producing composite cathode coating. The lanthanum strontium cobalt ferrite (LSCF)-samarium doped ceria carbonate (SDCC) composite cathode powder with silver (Ag) addition was fabricated adopting the EPD technique. LSCF-SDCC-Ag suspension was prepared by using organic-aqueous solvent for the deposition. The coated FSS substrate was first heat treated at 600°C for 90 minutes in air. The deposition was carried out at different applied voltages (5, 7 and 10 volt) and deposition durations (5-20 minutes). The increment of applied voltage and deposition duration was found to contribute to the increment of LSCF-SDCC-Ag deposited weight. The highest deposited weight and thickness of coating was 2.47 mg/cm² and 62.73 μm respectively attained by deposition of 10 volt for 20 minutes. According to the obtained results, deposition at 10 volt within 5 to 20 minutes has shown a better deposition. It is thus clear that EPD is indeed a feasible technique applicable for the development of composite cathode for SOFC interconnects and yielded better coating thicknesses of LSCF-SDCC-Ag on FSS interconnect for SOFC.

1. Introduction

Solid Oxide Fuel Cell (SOFC) is a highly effective fuel cell which oxidizing fuel from chemical energy into electrical energy [1]. Generally, a single SOFC comprises three components which are anode, cathode and electrolyte. Interconnects are the component to vividly separate each single fuel cell and prevent them from electrically contact and delivering electricity from single fuel cell to external circuit [2]. SOFC traditionally operates in high temperature (approximately 1000°C) while ceramic (for example, LaCrO₃) is the common interconnect material [3]. Various efforts have been attempted recently to lower down operating temperatures of solid oxide fuel cell which is ranged between 400°C to 800°C. This has enabled metallic interconnect to be applied instead of ceramic as it is low cost, good manufacturability, excellent electrical conductivity, matched thermal expansion coefficient (TEC) and better compatibility with adjacent components [4]. Ferritic stainless steel is considerably applied as interconnect. This is due to its TEC is very compatible with less than 10 % different from most anode, cathode and electrolyte materials at around 10-13°C⁻¹ [5, 6]. There are variety of ferritic stainless steel suitable to be applied as interconnect such as ferritic stainless steels and have been reported of having considerable chromium poisoning issue [7]. Long term working in
elevated temperature would diffuse out chromium from interconnect to the air and formed chromia scale depositing on cathode. Consequently, it declines catalytic activity of electrodes and hence deteriorates whole cells conductivity and performance.

In order to impede this undesirable phenomenon, the surface of stainless steel has to be modified by depositing protective coating. Compounds such as LaSrMn (LSM), LaSrCoFe (LSCF) and LaSrCo (LSC) have been deposited on interconnects [8-10]. From new generation mixed ionic and electronic conductor (MIEC) cathode materials, LSCF exhibits excellent conductivity and low polarization resistance [11-13]. LSCF has been successfully deposited on stainless steel with desired coating quality, deposited thickness and area specific resistance (ASR) [14, 15]. However, LSCF is reported of having significant high number of TEC (~16 °C-1) which is not beneficial to stainless steel interconnect [16]. LSCF composite has been developed by incorporating electrolyte powder such as samarium doped ceria carbonate (SDCC) and metallic catalytic such as silver (Ag) into LSCF cathode. The TEC of the composite LSCF-SDCC-Ag is reported to be 13 °C-1 which is very matched with TEC of ferritic stainless steel in less than 10 % different [17].

In this study, LSCF-SDCC-Ag was coated on SUS 430 ferritic stainless steel by electrophoretic deposition method (EPD). EPD is a method of coating a conductive substrate with particles suspended in a fluid dispersion under the influence of an electric field applied between the work part and the counter electrode[18].

2. Materials and Method

2.1 Sample preparation

SDCC was mixed using a low speed wet ball-milling method containing 80wt% of SDC nanopowders (Sigma Aldrich, Malaysia) and 20wt% of binary carbonates (67 mol % Li₂CO₃: 33 mol % Na₂CO₃) (Sigma Aldrich, Malaysia). SDCC was dried and later calcined at 680°C for 2 hours. Then, 50 wt% SDCC powder was mixed with 50 wt% perovskite LSCF6428 (Kceracell, Taiwan) by high speed wet ball-milling method. The LSCF-SDCC powder was dried and calcined at 750°C for 2 hours. Low speed dry milling method was carried out to mix 5 wt% of Ag (Sigma Aldrich, Malaysia) with LSCF-SDCC.

2.2 EPD set up

A glass beaker was used as electrolytic cell. SUS430 ferritic stainless steel was selected as substrate and counter electrode with the area of deposition of 1 cm². The distance between two parallel electrodes was fixed at 10 mm. 10g/l LSCF-SDCC-Ag suspension was prepared for EPD process by using aqueous-organic suspension with ratio of 1:1 ethanol and deionised water. Polyethylene glycol (PEG) as dispersing agent was added to suspension by 1wt % from the dry weight of the powder. Suspension with pH 8 has been identified by zeta potential analysis (Malvern, UK) to be the most suitable suspension for EPD process. The deposition was carried out at room temperature with different applied voltages (5, 7 and 10) and deposition durations (5-20 minutes). The deposited coatings were dried at room temperature and then heat treated at 600°C in air atmosphere.

2.3 Characterisation

X-ray diffraction (XRD, Bruker D8 Advance, Germany) and Field Emission Scanning Microscopy (FESEM) (JEOL JSM 7600F, Japan) were used to identify the crystalline phase structure, morphology of LSCF-SDCC-Ag composite powder. After EPD process, the LSCF-SDCC-Ag coatings were analysed for its weight deposition and coating thickness. Meanwhile, the coating surface morphology was observed via FESEM (Hitachi, SU1510, Japan).
3. Result and Discussion

3.1 Phase Identification of composite powder

Figure 1 presents the XRD diffraction patterns of the raw cathode composite powders namely LSCF, SDC and Ag and LSCF-SDC-Ag after going through milling and calcination process. It could be seen clearly that the addition of 5wt % Ag in LSCF-SDC composite cathode had not caused any changes of LSCF-SDC (LSCF JCPDS No. 01-089-1268 and SDC JCPDS No. 01-075-0158) lattice structure. After calcination, carbonate was observed to be in amorphous state and thus no distinct phase was detected in the XRD pattern. The crystal phase of Ag was in face-centered cubic with JCPDS pattern No. 00-004-0783. No distinct secondary phase was appeared and it can be concluded that high speed milling method and calcination process at 750°C did not affect the composite cathode structure and calcined composite has distinct crystalline perovskite intensity.

![XRD patterns of composite cathode LSCF-SDC-Ag before and after milling.](image)

3.2 Morphology of composite powder

FESEM micrographs of the uncalcined LSCF-SDCC, uncalcined LSCF, calcined SDCC, calcined LSCF-SDCC and LSCF-SDCC-Ag powders are as shown in Figure 2. Presence of agglomeration and irregular shaped particles were presence in uncalcined powders as shown in figure 2(a) 2(c). Calcination process removes secondary residue remaining in the ash and convert it to well-defined crystalline perovskites LSCF and SDCC phases as shown in figure 2(b) and 2(d). During calcination process, the agglomerated particles would strengthened, leading to formation of strong bond between the particles agglomerates and increment in particle size [19]. The growth of particles and changes in shapes can also be clearly seen.

3.3 Weight and thickness of LSCF-SDCC-Ag coating

Figure 3(a) illustrates the highest weight deposition of LSCF-SDCC-Ag (3.70 mg/cm²) obtained at applied voltage 10 volt with deposition duration of 20 minutes. While, the highest deposition thickness, 62.73 μm was also obtained by deposition at 10 volt for 20 minutes (Figure 3 (b)). It could
be observed from Figure 4 that the deposited film was very homogeneous, uniform and dense. There were no pores appeared on the film. This may be owing to the fine LSCF-SDCC-Ag powder used and that the particles were well suspended with no agglomeration issues.

3.4 LSCF-SDCC-Ag Coating Morphology

Micrograph of the LSCF-SDCC-Ag coating deposited at 5 volt (Figure 5 (a), (b), (c) and (d) clearly produce non-uniform deposition. This phenomena may occur due to the electrolysis of water and poor particle distribution [20]. Uniform coatings were obtained at higher deposition duration and higher applied voltage. The micrographs of LSCF-SDCC coating at 10 volt indicated lesser crack with denser microstructure, which may be contributed to the increment of deposition duration. Higher deposition can increase the homogeneity and uniform surface structure which contributed to less crack deposition. Hence, a more packed and dense coating layer may be produced.

Figure 2. Morphology of (a) uncalcined LSCF, (b) uncalcined SDCC (c) uncalcined LSCF-SDCC, (d) calcined LSCF-SDCC and (e) LSCF-SDCC-Ag powders.

Figure 3. (a) Deposition weight and (b) Deposition thickness as a function of deposition time for LSCF-SDCC-Ag coating on SUS430
Figure 4. Micrograph of coating deposited at applied voltage 10 volt for 20 minutes.

Figure 5. Micrographs of heat-treated LSCF-SDCC-Ag coating deposited at 5 volt, 7 volt, and 10 volt with deposition time (a) 5 min, (b) 10 min, (c) 15 min, and (d) 20 min.

4. Conclusion

Ag exhibits good thermal compatibility with the composite LSCF-SDCC-Ag. Crystalline phase and morphology of composite powder indicated good compatibility after milling process and calcination. LSCF-SDCC-Ag was successfully deposited on the surface of SUS430 ferritic stainless steel with better deposition weight and coating thickness attained at deposition of 10 volt for 20 minutes. Thus the study confirmed the possibility of obtaining LSCF-SDCC-Ag coatings by EPD from mixed aqueous-organic suspensions.

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References

1. Mahato, N., et al., 2015 Progress in Materials Science, 2015. 72: p. 141-337.
2. Fergus, J., et al., Solid oxide fuel cells: materials properties and performance. 2016: CRC press.
3. Chen, G., et al., Mn 1.4 Co 1.4 Cu 0.2 O 4 spinel protective coating on ferritic stainless steels for solid oxide fuel cell interconnect applications. Journal of Power Sources, 2015. 278: p. 230-234.
4. Brouzgou, A., A. Demin, and P. Tsiakaras, Interconnects for Solid Oxide Fuel Cells, in Advances in Medium and High Temperature Solid Oxide Fuel Cell Technology. 2017, Springer. p. 119-153.
5. Mehran, M.T., et al., Nano-CeO 2 and-LaCrO 3 dispersed ferritic stainless steels as potential interconnect materials for solid oxide fuel cells. Journal of Alloys and Compounds, 2017. 709: p. 453-463.
6. Bian, L.-z., et al., Oxidation resistance, thermal expansion and area specific resistance of Fe-Cr alloy interconnector for solid oxide fuel cell. Journal of Iron and Steel Research, International, 2017. 24(1): p. 77-83.
7. Talic, B., et al., Effect of coating density on oxidation resistance and Cr vaporization from solid oxide fuel cell interconnects. Journal of Power Sources, 2017. 354: p. 57-67.
8. Hwang, H. and G.M. Choi, The effects of LSM coating on 444 stainless steel as SOFC interconnect. Journal of electroceramics, 2009. 22(1-3): p. 67-72.
9. Przybylski, K., et al., Oxidation properties of the Crofer 22 APU steel coated with La0.6Sr0.4Co0.2Fe0.8O3 for IT-SOFC interconnect applications. Journal of Thermal Analysis and Calorimetry, 2014. 116(2): p. 825-834.
10. da Silva, A.L.A., G.G. Castro, and M.M. Souza, Synthesis of Sr-doped LaCrO3 powders by combustion method. Journal of thermal analysis and calorimetry, 2012. 109(1): p. 33-38.
11. Mani, R., et al., A Study on La0.6Sr0.4Co0.2Fe0.8O3 (LSCF) Cathode Material Prepared by Gel Combustion Method for IT-SOFCs: Spectroscopic, Electrochemical and Microstructural Analysis. Research in Chemistry, 2015. 8(6): p. 389-393.
12. Agun, L., et al. Durability and stability of LSCF composite cathode for intermediate-low temperature of solid oxide fuel cell (IT-LT SOFC): Short Review. in Advanced Materials Research. 2014. Trans Tech Publ.
13. Cheng, Y., et al., An Investigation of LSF-YSZ Conductive Scaffolds for Infiltrated SOFC Cathodes. Journal of The Electrochemical Society, 2017. 164(6): p. F525-F529.
14. Tsai, M.-J., C.-L. Chu, and S. Lee, La0.6Sr0.4Co0.2Fe0.8O3 protective coatings for solid oxide fuel cell interconnect deposited by screen printing. Journal of Alloys and Compounds, 2010. 489(2): p. 576-581.
15. Lee, S., et al., High temperature oxidation behavior of interconnect coated with LSCF and LSM for solid oxide fuel cell by screen printing. Applied Surface Science, 2010. 256(6): p. 1817-1824.
16. Shen, F. and K. Lu, Perovskite-type La0.6Sr0.4Co0.2Fe0.8O3, Ba0.5Sr0.5Co0.2Fe0.8O3, and Sm0.5Sr0.5Co0.2Fe0.8O3 cathode materials and their chromium poisoning for solid oxide fuel cells. Electrochimica Acta, 2016. 211: p. 445-452.
17. Agun, L., et al., Influence of Ag on the chemical and thermal compatibility of LSCF-SDCC for LT-SOFC. 2014.
18. Besra, L. and M. Liu, A review on fundamentals and applications of electrophoretic deposition (EPD). Progress in Materials Science, 2007. 52(1): p. 1-61.
19. Hanifi, A.R., et al., Effects of calcination and milling on surface properties, rheological behaviour and microstructure of 8mol% yttria-stabilised zirconia (8 YSZ). Powder technology, 2012. 231: p. 35-43.
20. Rahman, H.A., et al. Electrophoretic Deposition of La0.6Sr0.4Co0.2Fe0.8O3-δ Cathode Film on Stainless Steel Substrates. in Advanced Materials Research. 2010. Trans Tech Publ.