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Application of a coating mixture for solid oxide fuel cell interconnects

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ABSTRACT

Due to high operating temperature (800–1000 °C) of SOFC's, limited number of alloys can be employed for the purpose of current collection. The electrical conductivity of these alloys usually decreases during the operation of SOFC because of highly corrosive cathode (air side) environment. Cr evaporation from such alloys is also an important problem of performance degradation. A spinel $Mn_{1.5}Co_{1.5}O_4$ and perovskite $La_{0.60}Sr_{0.40}FeO_3$ mixture is coated on Crofer alloy for corrosion and chromium protection in the cathode side of a SOFC. In study firstly, the performance of the fuel cell with the Crofer 22 APU as interconnect material was measured up to 100 h without any coating. Secondly, using a screen printing method, bare Crofer 22 APU was coated with $Mn_{1.5}Co_{1.5}O_4$ and finally $Mn_{1.5}Co_{1.5}O_4$ + $La_{0.60}Sr_{0.40}FeO_3$ ceramic powder slurries were employed as the coating material. Then, the performances of a SOFC short stack with interconnects coated by two methods were compared with uncoated interconnect. Results show that uncoated interconnect experienced a significant performance lost from 4.5 W to 3.8 W. On the other hand the cells with screen printing coated with a mixture $Mn_{1.5}Co_{1.5}O_4$ and $La_{0.60}Sr_{0.40}FeO_3$ exhibited decreases only from 5.78 W to 5.42 W in the short-term performance tests.

Introduction

Recently, due to their minimum pollution, increased reliability and high efficiency; interest on solid oxide fuel cells (SOFCs) is increased. Furthermore, solid oxide fuel cells with high energy conversion efficiency and low emission are expected to replace internal combustion engines in a near future [1]. One of the most important components of SOFC is interconnect that provides distribution of fuel and oxidant, while acting as the current collecting in SOFC stack [2]. Because of easy machinability, high electrical conductivity, high chemical resistance and strength at high temperatures, metallic interconnects are usually employed in SOFCs [3]. Because of high operating temperature of SOFC, only special metal alloys can be used as interconnect materials. Many metal alloys are tested as interconnect, furthermore for this purpose many new metal alloy are also developed. Among the tested materials, the best candidate is determined as chromium-based

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alloys [4]. One of such alloys is Crofer 22 APU (ThyssenKrupp VDM GmbH Germany), which mainly contains C, Cr, Fe [5]. The Crofer 22 APU also contains elements such as Rare Earths, Mn, Al and Ti for micro alloying. The micro alloying is usually prepared to produce a thin surface oxide scale with specific characteristics: high mechanical strength, excellent adhesion to metallic substrate; low oxide growth rate (interconnect durability must be around 40,000 h); high chemical resistance (to avoid Cr depletion and electrode poisoning) and low area specific resistance (ASR < 10^{-1} Ω cm^2) [6]. However, long term performance of commercial and even special ferritic stainless steels remains insufficient in SOFC operating conditions and therefore additional surface treatments and/or coatings are usually required [7]. Furthermore, during SOFC operation, the stack performance suffers because of surface corrosion, increased electrical resistance and the formation undesired layers because of interactions of ferritic stainless steel interconnects with deteriorating materials.

Several studies have conducted to increase corrosion resistance and decrease Cr evaporation of ferritic stainless steels. These works includes slurry coating of certain materials or alloys using anodic electro-deposition and cathodic electro-deposition methods [8]. Many other coating techniques such as metal organic chemical vapor deposition (MOCVD) and large areas filtered arc deposition (LAFAD) as well as sol–gel method, chemical and physical vapor deposition (CVD and PVD) techniques, plasma thermal spraying and different surface modifications methods are employed [6]. The most widely used coating materials for high temperature SOFC are $(Mn,Co)_3O_4$ ($Mn_{1.5}Co_{1.5}O_4$) and LSF ($La_{0.8}Sr_{0.2}FeO_3$). $(Mn,Co)_3O_4$ spinel with a nominal composition of $Mn_{1.5}Co_{1.5}O_4$ demonstrates satisfactory electrical conductivity, thermal and structural stability, as well as good thermal expansion match to ferritic stainless steel interconnects [9,10].

A protective $(Mn,Co)_3O_4$ spinel layer forms during the operation of SOFC on special alloys such as Crofer 22 APU. Although this layer provides a protection for corrosion and outward diffusion of Cr cations, it is usually not enough maintaining the low area-specific resistance in long term operation of SOFC. Therefore, the metallic interconnects usually coated with extra spinel $(Mn,Co)_3O_4$ layers to improve corrosion resistance and Cr evaporation thus improve long-term performance of the SOFC [11]. LSF is also employed for protection materials for metallic interconnect. Although thermal conductivity of LSF higher than that of $(Mn,Co)_3O_4$, LSF is shown to not effective in blocking diffusion of chromium into cathode layer. Therefore, main purpose of this study is to benefit advantages of LSF and $(Mn,Co)_3O_4$ spinel materials and to enhance conductivity of coating layer while effectively blocking the chromium diffusion. The LSF and $(Mn,Co)_3O_4$ mixture is screen coated on the Crofer 22 APU interconnect and short-term performance of coating is measured in a short SOFC stack.

Material and methods

In this study, Crofer 22 APU was chosen as the interconnect materials, since it is largely employed in the literature [12]. The chemical composition of Crofer 22 APU is listed in Table 1.

Several 6 cm × 6 cm Crofer 22 APU with 1 cm thickness samples were laser cut from the bulk material and a parallel flow field was machined on each sample as shown on Fig. 1. The metallic interconnect surface to be coated was cleaned as follows: the surface of each Crofer 22 APU sample was grounded employing SiC grinding paper using successively finer abrasive papers (320, 600, 1200), followed by polishing with 2 μm diamond paste. Prior to coating the Crofer 22 APU, any residue from polishing was removed by ultrasonically washing in acetone with pure water with a 10 min purge. Then it was ultrasonically cleaned in ethanol and it was washed with pure water for 2 min again. Thus, cleaning process was completed. Finally all substrates were dried.

Spinel $Mn_{1.5}Co_{1.5}O_4$ and perovskite $La_{0.60}Sr_{0.40}FeO_3$ slurries were prepared from commercial powders. (Nextech Materials, Columbus, OH, USA). Samples were prepared for screen printing with relevant paste materials that were a mixture of the powders, polymer resin, and additives dispersed in an organic solvent mixed by a three roller mill (EXACT 35). The binder, dispersant, and solvent for all the protective and conductive pastes were ethyl cellulose (Sigma–Aldrich), fish oil (Sigma–Aldrich)and α-terpineol (Sigma–Aldrich), respectively. Each paste was successfully applied to the metallic interconnect (Crofer 22 APU) surface.

Five different interconnects for cathode side (air side) were prepared for short term (100 h) SOFC testing. The first case involves a bare interconnect without any coating just surface cleaning described earlier was applied. The first case was prepared as base case for comparison. In the second case, $Mn_{1.5}Co_{1.5}O_4$ was coated by the screen printing method, and then it was oxidized at the 1000 °C in air. The third samples was again produced by coating $Mn_{1.5}Co_{1.5}O_4$ paste with the screen printing method, and then the samples oxidized for 2 h at the 1000 °C in oxygen atmosphere (2 L/min). $Mn_{1.5}Co_{1.5}O_4$ spinel coating was also employed on the fourth group of samples. The dried interconnect is typically heat treated in a hydrogen furnaces (pure H_2 atmosphere) at 850 °C for 4 h, and then oxidized in air at 760–800 °C. The last samples were produced with paste prepared by mixing $Mn_{1.5}Co_{1.5}O_4$ and $La_{0.60}Sr_{0.40}FeO_3$.

The paste then coated by screen printing method to interconnect surface, and then were oxidized at air atmosphere for 2 h at 1000 °C. Three samples were prepared for each samples. The anode side (hydrogen side) of interconnects were identical to case 1 for experiments.

To obtain satisfactory coating density at low sintering temperatures, initially it is necessary heat treat the coating in

Table 1 – Composition of Crofer 22 APU [13].

	Cr	Fe	C	Mn	Si	Cu	Al	S	P	Ti	La
Min	20.0			0.30						0.03	0.04
Max	24.0	Bal.	0.03	0.80	0.50	0.5	0.50	0.02	0.05	0.20	0.20