NEW COST-EFFECTIVE CERAMIC OXIDE PHASES USED AS PROTECTIVE COATINGS FOR CHROMIUM-BASED INTERCONNECTS

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ABSTRACT
Stability of high-temperature solid oxide fuel cells (SOFC’s), fitted with metallic interconnects can only be achieved when protective coatings are deposited on all surfaces prone to chromium oxide formation. Thermally sprayed substituted lanthanum manganites have proven to be effective in restricting the evaporation of chromium during service from these surfaces. The dense coating hinders transport of chromium species, both in the solid and gaseous phase, eliminating any performance degradation that may be caused by condensation of chromia in and on the cathode. Sulzer HEXIS Ltd. has successfully used this method in extended endurance testing of stacks and systems. Unfortunately however, because of the large quantities of material required to coat the interconnects and the high cost of the raw materials that enter the composition of the coating, the estimated cost of this coating is significantly higher than what can be allowed for market entry. A new family of perovskites, rich in alkaline earth elements and containing little or no lanthanum, were evaluated. Compositions such as Sr$_{1-x}$La$_x$MnO$_3$, Ca$_{1-x}$La$_x$MnO$_3$ and Ca$_{1-x}$Y$_x$MnO$_3$ were evaluated for their thermal expansion, high temperature conductivity and phase stability. Thermal spraying trials were carried out on chromium-based alloys and the contact resistance of the coated samples was measured.

INTRODUCTION
The evaporation of chromium from chromia-forming refractory metals is an inevitable phenomenon that will occur in all high temperature SOFC systems using these materials. Chromium-rich vapours emanated from the oxidised interconnect surface are transported to the cathode. Their subsequent condensation in and on the electrode surface results in a steady decay of electrochemical performance with time.

In the HEXIS design, metallic components are in intimate contact with the cell, functioning as integrated heat exchangers as well as current collectors. These components are made from chromia forming alloys and therefore need to be treated to prevent chromium induced performance degradation. By thermal spraying a ceramic coating on the surface of the current collector, the transport of chromium may be hindered. Furthermore, this protective coating must also be:
- chemically compatible and stable with regard to substrate, contact layer and electrodes;
- thermodynamically stable over the applied temperature range;
- resistant to solid state transport of chromium; and finally,
- offer minimal ohmic resistance, for maximum efficiency.

After an extensive study on possible coating solutions to limit the evaporation effects of chromium, thermal spraying of Lao.8Sr0.2MnO₃ powders by HVOF (High Velocity OxyFuel) appeared to be the most appropriate choice (1). It was selected because of:
- its good conductivity and chemical compatibility with the cathode and the Cr-5Fe-1Y₂O₃ alloy, supplied by Plansee Ltd.;
- its availability (LSM in submicron form is used by many SOFC manufacturers as a cathode material); and,
- its matched thermal expansion to the Cr-5Fe-1Y₂O₃ alloy, thus, showing good resistance to spallation during thermal cycling.

By coating the surface of its current collectors with this protective layer, Sulzer HEXIS was able to demonstrate a significant increase in electrochemical stability. Transport of chromium was inhibited and stability was extended to more than ten thousand hours of service. Since then, this coating in combination with the Cr-5Fe-1Y₂O₃ alloy, has

Figure 1. Average stack performance of a 5-cell stack tested with hydrogen. The cells were supplied by ECN and current collectors by Plansee Ltd. The Lao.8Sr0.2MnO₃ standard protective coating was used. The abrupt drops in the curve represent thermal cycles. Operating conditions: gases were hydrogen and air; stack temperature was 920°C; and operating electrical efficiency was 30%. The data shows that the targeted electrochemical degradation of less than 1% per 1000h was achieved.
successfully been used in stack and system testing by HEXIS (2). Figure 1 shows the electrochemical performance of a five-cell stack as a function of time. During the over ten thousand hours of service and several thermal cycles, no significant change in performance was observed.

Unfortunately however, because of the large quantities of material required to coat the interconnects and the high costs of the raw materials that enter the composition of the La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3} coating, the estimated cost of this coating was found to be significantly higher than what can be allowed for market entry. Therefore, despite the advantages offered by the La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3} system, a new family of ceramic oxides needed to be identified where the concentration of strategic elements is significantly reduced.

This paper summarises the effort performed by Sulzer HEXIS to reduce the cost of its thermal spray protective coating. Oxide phases, rich in alkaline earth elements and containing little or no lanthanum, were evaluated as substitutes.

**EXPERIMENTAL**

Small quantities of powder were prepared by solid state calcination of oxides and carbonates. After several iterations of heat treatment and milling, the powders were checked for their phase purity by X-ray diffraction. Pellets were then pressed and sintered to full density. Bars, approximately 3x3x40mm in size, were cut and the conductivity/temperature relationship determined by the 4-point method. Similar samples were used to determine the thermal expansion characteristics of the compositions. Table I lists some of the different compositions tested in this study.

| Sr_{1-x}La_{x}MnO₃ | Ca_{1-x}La_{x}MnO₃ | Ca_{1-x}Y_{x}MnO₃ |
|-------------------|-------------------|------------------|
| Sr_{0.6}La_{0.4}MnO₃ | Cao_{0.6}La_{0.4}MnO₃ | Cao_{0.75}Y_{0.25}MnO₃ |
| Sr_{0.8}La_{0.2}MnO₃ | Cao_{0.8}La_{0.2}MnO₃ | Cao_{0.8}Y_{0.2}MnO₃ |
| Sr_{0.6}La_{0.4}MnO₃ | Cao_{0.6}La_{0.4}MnO₃ | Cao_{0.7}Y_{0.3}MnO₃ |

After performing conductivity and thermal expansion assessments, compositions showing the best combination of characteristics were selected for thermal spray evaluations. Approximately 2kg of fine submicron powder was manufactured by combustion spray pyrolysis (CSP). This was performed by Praxair Speciality Ceramics (USA). The powders were then spray-granulated and depending on the composition, sintered between 1250 and 1450°C. The sintered granules were sieved and the fraction between 20 and 63 µm was used for thermal spraying.

Thermal spraying was primarily performed by HVOF. However, a few attempts were made to evaluate the quality of the coatings obtained by APS and Flame Spraying. The initial trials had as objective to maximise deposition efficiency. After spraying, coated Cr-5Fe-1Y₂O₃ plates were examined by X-ray diffraction, optical and scanning electron microscopy. The conductivities of powders and as-sprayed coatings were also compared.
Finally, the contact conductivity at 920°C was assessed in combination with La$_{0.8}$Sr$_{0.2}$MnO$_3$.

RESULTS

Figures 2 and 3 show, for selected materials, the specific resistance and thermal expansion as a function of temperature, respectively. Electrical conductivity of the Sr$_{1-x}$La$_x$MnO$_3$ and Ca$_{1-x}$La$_x$MnO$_3$ powders tested was higher than that of La$_{0.8}$Sr$_{0.2}$MnO$_3$. It can also be seen that depending on the composition of the Ca$_{1-x}$Y$_x$MnO$_3$ powder, the conductivity will either increase or decrease with temperature. Between $x=0.3$ and $x=0.4$, the transition takes place, and for $x=0.1-0.2$, the conductivity of Ca$_{1-x}$Y$_x$MnO$_3$ resembles closely that of La$_{0.8}$Sr$_{0.2}$MnO$_3$.

Figure 2 Electrical resistivity as a function of temperature

Figure 3 Thermal expansion as a function of temperature
The thermal expansion of Ca$_{1-x}$La$_x$MnO$_3$ and Ca$_{1-x}$Y$_x$MnO$_3$ is compared to that of the Cr-5Fe-1Y$_2$O$_3$ Plansee alloy in figure 3. Ca$_{0.8}$La$_{0.2}$MnO$_3$ showed a phase change at approximately 400°C, accompanied with a significant increase in volume. A similar behaviour was observed for the Sr$_{1-x}$La$_x$MnO$_3$ oxides studied. This increase in volume had deleterious effects on the contact conductivity of the thermally sprayed coatings. Figure 4 shows the contact resistance of thermally sprayed Sr$_{1-x}$La$_x$MnO$_3$ and Ca$_{1-x}$La$_x$MnO$_3$ coatings deposited under different HVOF conditions. All samples showed a steady increase in resistance with time. This increase in resistance was found to be related to spallation of the coating due to phase changes as well as to the unfavorable thermal expansion of the coating.

The Ca$_{1-x}$Y$_x$MnO$_3$ compositions, on the other hand, showed good conductivity and phase stability over the temperature range tested. They had similar thermal expansion characteristics as the Cr-5Fe-1Y$_2$O$_3$ alloy and showed no phase change. Some compositions showed even better behaviour than the standard La$_{0.8}$Sr$_{0.2}$MnO$_3$ coatings. After several thermal spraying iteration trials, the Ca$_{1-x}$Y$_x$MnO$_3$ coatings were successfully deposited with reasonable efficiency. Unfortunately however, conductivity measurements of the as-sprayed samples showed that the electrical conductivity had significantly dropped after thermal spraying. X-ray diffraction analysis showed that a metastable cubic phase was quenched in the structure, increasing the electrical resistance of the coating. This cubic phase could be eliminated by heat treatment at 900°C, restoring conductivity. Figures 5a and 5b show optical micrographs of a Ca$_{0.75}$Y$_{0.25}$MnO$_3$ coating in the as-sprayed and heat treated conditions. The two-phase structure can be clearly seen in figure 5a. Scanning electron microscopy of the same sample showed that under back scattered electron contrast, no chemical segregation occurred, suggesting that during thermal spraying a high temperature allotrope of the Ca$_{0.75}$Y$_{0.25}$MnO$_3$ composition was quenched into the coating.

Figure 4 Contact resistance of thermally sprayed coating deposited with different HVOF parameters

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Figure 5 Optical cross section of a thermally sprayed Ca$_{0.75}$Y$_{0.25}$MnO$_3$ coating by HVOF. (a) In the as-sprayed condition, two phases can be identified. (b) After heat treatment the microstructure reverts to a single phase. Preparation conditions are identical for both samples.

Thermal spray optimisation trials were then carried out, with the objective of reducing the volume fraction of quenched-in cubic phase. Despite the ease with which the cubic phase is transformed to the equilibrium orthorhombic phase, it was demonstrated that by reducing the volume fraction of metastable phase in the sprayed coatings, the chances of spallation during subsequent heat treatment were reduced. These trials showed that by reducing the cooling rate of the coating during thermal spraying, the amount of metastable cubic phase is reduced. This was possible by either increasing the fuel input, or substrate temperature.

These results show that the Ca$_{1-x}$Y$_x$MnO$_3$ powders have great potential as a cost-effective alternative to La$_{0.8}$Sr$_{0.2}$MnO$_3$. They satisfy the thermal expansion and conductivity requirements and show good thermal sprayability. Raw material cost for large quantities of La$_{0.8}$Sr$_{0.2}$MnO$_3$ powder, was estimated to be approximately 10-15$/kg. In comparison, it was estimated that the cost of raw materials for Ca$_{0.75}$Y$_{0.25}$MnO$_3$ was approximately 1$/$kg, demonstrating the advantage of the new compositions. However, it is clear that these coatings must still be tested in HEXIS SOFC environments, first in 5-cell stack tests and then in systems before qualification.

**CONCLUSIONS**

The conductivity and thermal expansion of Sr$_{1-x}$La$_x$MnO$_3$, Ca$_{1-x}$La$_x$MnO$_3$ and Ca$_{1-x}$Y$_x$MnO$_3$ phases were evaluated and suitable compositions were selected as cost effective alternatives to the La$_{0.8}$Sr$_{0.2}$MnO$_3$ thermal spray powder. Cost reductions are expected due to low concentrations of strategic elements. The Sr$_{1-x}$La$_x$MnO$_3$ and Ca$_{1-x}$La$_x$MnO$_3$ compositions tested had high conductivity but were not suited for thermal spraying due to a phase change resulting in spallation of the protective coating during endurance testing. Compositions in the range Ca$_{0.9-0.75}$Y$_{0.1-0.25}$MnO$_3$ show the best combination of thermal expansion compatibility and conductivity. However, for these compositions thermal spray parameters have to be carefully selected to avoid the formation of large quantities of non-conductive metastable cubic phase that may be
quenched in the coating when cooling rates are high. Verification of these new protective coatings in HEXIS 5-cell stack tests and systems will be carried out in the near future.

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