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Composite Ceramic Fuel Cell Fabricated by Vacuum Plasma Spraying

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Abstract

Porous composite cathodes for ceramic fuel cells containing $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ *(LSM) and yttria stabilised zirconia (YSZ) were prepared by vacuum plasma spraying (VPS) on prefabricated planar cermet supported zirconia substrates. Three different types of LSM–YSZ-mixtures with volume-ratio of 50/50 or 70/30% and thickness of 20–50 microns have been compared with conventional LSM-cathodes made by VPS. The electrochemical behaviour was tested between 700 and 900°C using impedance spectroscopy. The composite cathode electrochemical performance is discussed. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: VPS, interfaces, perovskites, ZrO_2, fuel cells.

1 Introduction

Advanced cathodes for Solid Oxide Fuel Cells (SOFC) must show good electronic conductivity, a degree of ionic conductivity, thermal and chemical stability, and chemical compatibility with the substrate. Strontium doped lanthanum manganite (LSM) satisfactorily meets these requirements for cell operating temperatures above 900°C.[1] Tsai and Barnett[2] have found that the use of a LSM–YSZ composite improves the performance at lower temperatures, 600–800°C. A question of major attention is how structural features like porosity, particle size and electrode thickness influence the cathode performance. According to Shibuya and Nagamoto[3] the optimal thickness is about 20 μm. Larger grained powders gave better performance.

VPS represents a promising fabrication process[4,5] for SOFC. It allows the deposition of porosity-controlled and compositionally graded structures while suppressing the undesired formation of layers of high resistance like lanthanum zirconates at the electrolyte–cathode interface.

2 Processing

Composite cathodes have been deposited using a 50 kW DC VPS equipment. The substrate was a YSZ electrolyte material, itself supported on a nickel–zirconia cermet,[4] of diameter 60 mm. The processing of composite cathodes was carried out in three different ways. Using a standard VPS equipment, the easiest approach for composite deposits consisted of feeding the two powders, LSM and YSZ, separately to opposite entries on the argon plasma torch. The resulting multi-layered coating [Fig. 1(a)] was not expected to provide the needed two-phase interconnectivity. Attempts to obtain more isotropic composites were undertaken by dry blending of LSM and YSZ in a tumble mixer [pre-mixed powder, Fig. 1(b)] or by fine wet grinding to grain sizes below one micron followed by slurry-drying by atomisation [micromixed granules, Fig. 1(c)]. The micro-mixed granules obtained were applied by the VPS-deposition without previous sintering [Fig. 1(c)].

Usually, the porosity of the cathode affects its performance. The appearance of two cathodes is illustrated in Fig. 2. It is clearly revealed that the micro-mixed composite differs from that mixed during plasma spraying by its considerably lower pore size and higher specific surface.

XRD-patterns of the deposited cathodes show the absence of the undesired lanthanum zirconates. The few milliseconds at elevated temperature during the VPS processing is probably insufficient for the topotactic reaction. This, combined with the

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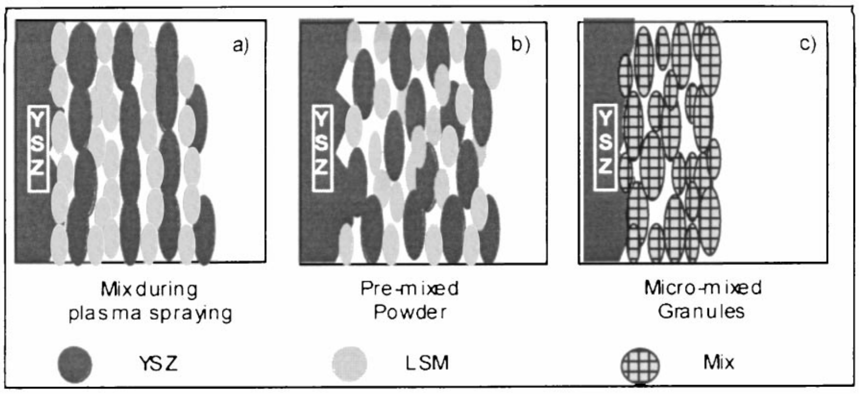
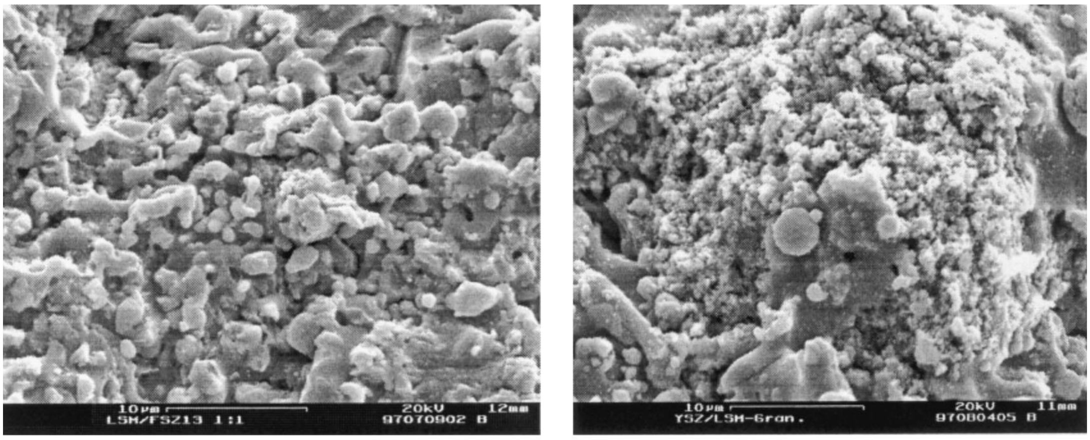


Fig. 1. Different composite cathodes due to various processing routes.



(a) (b)

Fig. 2. (a) SEM top-view: cathode deposited by powder mixing of LSM and YSZ with volume ratio 50/50 during plasma spraying [model Fig. 1(a)]. (b) SEM top-view: cathode deposited from micromixed granules LSM and YSZ with volume ratio 50/50 [model Fig. 1(c)].

economics of short processing time for VPS cathodes and whole cells, present major advantages of the spraying method(s).

3 Electrochemical Behaviour

Impedance spectroscopy allows the determination of the electrochemical polarisation resistance specifically related to interfaces, as distinct from the ohmic losses due to the material resistivities. Because of their asymmetrical design, the standard Medicoat® cell configuration used did not permit to place a functional reference electrode, that would allow to distinguish between the cathode and the anode overpotentials. Very recent measurements on modified cells suggest that the polarisation resistance of the best reported sample (cf. Fig. 3, 25 μm thick cathode) might still be overestimated due to an anode overpotential. Therefore, the real electrochemical performance of that cathode might be still better than reported.

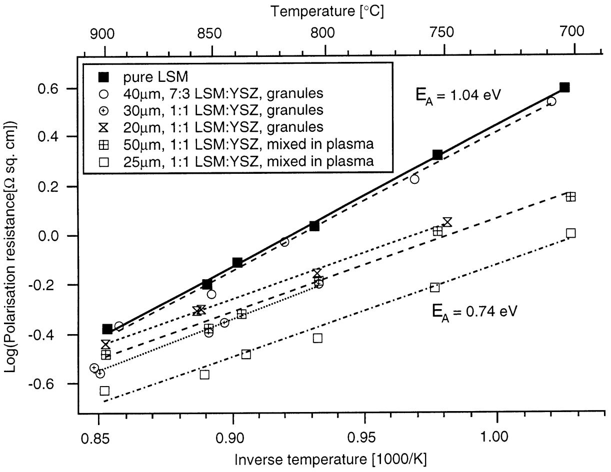


Fig. 3. Standard LSM (solid line) and composite LSM–YSZ cathode polarisation resistances.

Figure 3 is an Arrhenius type plot of the polarisation resistance of the VPS electrodes with the cell potential fixed at 0·7 V (only the plasma mixed and granule samples are shown). The 70% LSM–30% YSZ composite cathodes showed little difference from the standard cathode. However cathodes of the 50% LSM–50% YSZ composite showed a considerably lower polarisation resistance, especially at low temperature. The pre-mixed samples [Fig. 1(b)] showed higher (typ. +50%) polarisation resistance than the standard cathode and even degradation after operation for one day at 900°C. This degradation can be attributed to the contacting material used for those samples, a perovskite (LSCO) slurry, deposited on the LSM–YSZ cathode, which may react with zirconia to form insulating phases.

The activation energy is related to the electrochemical mechanism of the cathodic charge transfer. The observed value for the standard cathode (1·04 eV) is very close to that for densified LSM cathodes previously reported, when a diffusion component in the impedance spectrum is put aside.[6] The relatively high current values observed for dense LSM cannot be sustained by a reaction at the TPB (Three Phase Boundary) alone. According to that behaviour and to the very weak $P(O_2)$ dependance then observed, oxygen adsorption/dissociation has been proposed as the most probable limiting step. The same mechanism is effective for high LSM-content composite cathodes, where the interconnectivity of ion transport through the zirconia phase is not established.[6]

The lower activation energy (0·74 eV), indicates that another mechanism limits the cathodes containing higher zirconia concentrations. Due to the porous zirconia phase, the formal limitation factor appears to be overcome. An activation energy of about 0·8 to 0·9 eV is obtained when the zirconia resistivity is the limiting process.[6] This mechanism should not be confused with the ohmic resistivity losses in the electrolyte, but has the same origin.

The cathodes of the least polarisation resistance present a higher porosity due the YSZ powder used, which is composed of unsintered agglomerates. The very high porosity was still present following the VPS deposition.

4 Conclusion

The VPS technology can be used to produce efficient composite cathodes, providing the zirconia concentration is high enough to allow the grains to interconnect for volumetric ion transport. The next important factor might be the overall porosity of the composite cathode. Cathode thickness does not appear to be of real significance within the tested range (20–50 μm). Alternative powder preparations (prior to spraying) did not show any specific advantage over direct plasma mixing at this stage of the study.

Acknowledgements

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