ABSTRACT

Ceramic open cell foams with porosities > 90 vol.% and pore sizes < 700 μm may be used as gas distributors, current collectors and load bearing structural parts at the cathode or the anode side of a SOFC. We report about the electrical conductivities, creep resistivities, and high temperature compressive strengths of La$_{0.84}$Sr$_{0.16}$Co$_{0.95}$MnO$_3$ perovskite foams.

INTRODUCTION

A key problem in the successful use of solid oxide fuel cells is the collection of current on the cathode side. Most metallic current collectors developed so far have a coarse regular design. The sizes of the current contacts are typically in the order of millimetres leading to inhomogeneous current densities (1).

A promising alternative is an electrically conducting ceramic foam which acts as air distributor and current collector at the same time. The electric current in this design is collected by many more and much smaller contact points. The foam has to fulfill three important requirements: 1. high electrical conductivity, 2. sufficient mechanical strength and 3. good creep resistance. Fig. 1 (a) illustrates the traditional design of a metallic current collector whereas in Fig. 1 (b) the alternative foam current collector is shown.

Ceramic foams are already widely employed e.g. in metal filtration, gas and diesel engine exhaust filters, high temperature insulation, chemical filtration and separation, catalyst supports, and numerous others.

These foams are treated as porous cellular solids which can be classified as either two or three dimensional. The three-dimensionally foams can further be subdivided in open and closed cell foams. In open cell materials, both the porosity and the solid phase are three dimensionally connected while in closed cell solids, the pores are isolated within the cells due to the presence of solid faces (2-4). For the application as current collector only the open cell foams are feasible for sufficient gas permeability. In this study we present the processing of these ceramic foams and their electrical and mechanical properties.
METHODS

Material

To avoid thermal and chemical mismatches between the cathode and the ceramic foam, the foam was made from the material as the cathode itself: La₀.₈₄Sr₀.₁₆Co₀.₀₂MnO₃ (LSM) (Rhône-Poulenc, France). The powder used for the ceramic suspension had a median particle diameter of 0.5 µm and a specific surface area of 6 m²/g.

Foamed, open cell polymers, which are available in different porosities are used as starting materials (Polyester S30 - S80, Koepp, Germany). The porosities are measured in ppi numbers (pores per linear inch). The pores have a diameter of 200 - 800 µm depending on the ppi number.

Processing of the ceramic foams

Plastic foam samples were dipped into a LSM suspension, which consisted of finely dispersed ceramic LSM-powder, water, dispersant, and binder. Then, the coated polymer was compressed to fill the void space and squeezed by a set of rotating rollers to remove the excess slurry. After this process, the single plastic struts were coated with a layer of green ceramic with a thickness in the range of 30 – 40 µm. The infiltrated foam was dried at room temperature for 24 hrs. Subsequently, the coated foam was slowly heated to 1720 K. During this process, the polymeric skeleton pyrolyses, leaving triangular voids within the struts. In this step, controlled heating is important to prevent collapse of the ceramic framework. Sintering was performed at 1720 K for 2 hours. The result was that the structure of the polymer foam was approximately replicated in the ceramic. The ceramic specimen had a density of 4 – 28 % TD (6.5 g/cm³) due to different strut thickness.

For all experiments, cylindrical shaped specimens (50 mm diameter, 5 mm height) were cut out of the polymeric foams. The sintered ceramic foams had a diameter of 38-39 mm and a height of 3 – 3.5 mm, which corresponds to a sinter shrinkage of about 25%. All of the specimen were cut from the same billet of polymer material to ensure reproducibility.

A flow chart of the manufacturing of these foams is given in Fig. 2.

Electrical conductivity

Van der Pauw’s method was used to measure the electrical conductivity of the sintered LSM foams in the temperature range 300 - 1170 K (5). This measurement technique allows for the use of samples of arbitrary shape and allows for a great amount of freedom in the placement of the contact leads. The set up of this method is sketched in Fig. 3. Four
Platinum wires were contacted to the periphery of the sample and were attached with silver paste.

The conductivity is determined as

$$\sigma = \frac{\pi d}{\ln 2} \frac{(R_{AB,CD} + R_{BC,DA})}{2} f\left(\frac{R_{AB,CD}}{R_{BC,DA}}\right)$$

where \(f\) is a function of the ratio \(R_{AB,CD}/R_{BC,DA}\) and satisfies the relation

$$\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} = \frac{f}{\ln 2} \text{arcosh} \left\{ \frac{\exp\left(\frac{\ln 2}{f}\right)}{2} \right\}.$$  

The resistance values \(R_{AB,CD}\) and \(R_{BC,DA}\) are calculated by

$$R_{AB,CD} = \frac{V_{CD}}{I_{AB}} \quad \text{and} \quad R_{BC,DA} = \frac{V_{DA}}{I_{BC}}.$$  

The electrical conductivity was measured before and after the strength and creep tests.

**Mechanical behavior**

The compressive strengths of sintered LSM foams were measured with an universal testing device using a crosshead speed of 0.5 mm/min (Instron Limited, United Kingdom). The compressive specimens were placed on an alumina felt, and a similar felt isolated the specimen from the test fixture. These compliant faces were used to eliminate the effects of uneven loading due to the surface topography of the material. Cylindrical shaped samples were loaded between these alumina felts and \(\text{Si}_3\text{N}_4\)-plates. The measurements were performed at room temperature and at 1070 K. 45-80 ppi foams were tested having different relative densities.

16 LSM foams with a ppi number of 60 and densities of 0.13% were tested in compression at room temperature and five foams were tested at 1070 K. Creep tests were performed at 1070 K with constant loads of 10 to 50 N. This temperature and these loads were chosen as typical values for the performance of a SOFC. For the creep tests the alumina felts were not used because the felts themselves showed an extreme high creep rate even at low temperatures.
RESULTS

Processing of the ceramic foams

In Fig. 4 and 5, SEM pictures of the polymeric precursor and the resulting ceramic foam are shown. Note the typical triangular form of a single strut of the polymeric foam, which results in an triangular void down the centre for the ceramic LSM foam. The macrostructure of the ceramic foam can be described as a network of single struts. The cells are interconnected such that there is a continuous pore phase throughout and the solid is an interconnected array of struts.

Electrical conductivity

Fig. 6 illustrates the temperature dependence of the electrical conductivity of an almost dense sample and a 60 ppi foam. The ln $\sigma$ vs $1/T$ curve shows a linear behavior over a wide temperature range. The conductivity of a foam with 70 % TD is 450 S/cm at 1170 K. The 60 ppi foam shows a conductivity of 100 S/cm at 1170 K. The activation energies, $E_a$, for the two samples are 0.09 and 0.084 eV, respectively. This is in good agreement with data reported by Katayama where a dense La$_{0.85}$Sr$_{0.15}$MnO$_3$ sample was tested using the four probe method (5). The foam’s electrical conductivity remains in the same region even after 100 h of creep testing at 800 K with a constant load of 10 N.

Mechanical behavior

A typical stress-strain curve for a ceramic foam is depicted in Fig. 7. There is a constant increase in strain with increasing stress up to the point where the foam has its crushing point. This highest load was taken as the compressive strength of this specific foam. Region 1 is the specimen and loading fixture alignment. Region 2 corresponds to the elastic region and can involve strut fracture, either in the contact region or internally. As a crack propagates through the cellular material it does so by fracturing individual struts which can be clearly seen in region 2 where the fracture of single struts are connected with some load drops. At the crushing point (region 3), macroscopic cracks propagate with an associated load drop (region 4). In the LSM materials this corresponds to sections of material breaking away from the sample. Additional deformation of the fractured material occurs in region 5 where the strain is independent of stress as the material progressively crushes. The important fact for the cell performance is that even if a crack propagates through the foam it can still fulfil the load bearing and conductivity task in a solid oxide fuel cell.

The compressive strengths of several foams with different relative densities are shown in Fig. 8. There is an almost linear relationship between the compressive strength
and the relative densities of the foams. This behavior was already described by Gibson and Ashby (2). The Weibull plot of the 16 foams tested at room temperature is given in Fig. 9. The Weibull modulus was 5.4. For alumina foams Weibull moduli of 2-4 are reported (3, 4). The average strength, $\sigma_{\text{m}}$, was 0.89 MPa whereas the five foams tested 1070 K showed an average strength of 0.58 MPa.

The foams did not show creep at 1070 K or 1270 K. After 100 hours measurement time with 50 N load at 1070 K, the foam were still intact and showed no degradation in the electrical measurements.

SUMMARY

Ceramic $\text{La}_{0.84}\text{Sr}_{0.16}\text{Co}_{0.02}\text{MnO}_3$ foams acting as current collectors in SOFC could be produced successfully. Such three-dimensionally structures are a materials with multifunctional characteristics: The ceramic phase provides electrical conductivity and strength whereas the porous phase provides the required transport property. The electrical and mechanical behavior of these foams have been studied. The properties of the LSM foams were found to depend, above all else, on their relative densities They showed good electrical conductivities, their high temperature compression strength was sufficient and they did not show any creep.

ACKNOWLEDGEMENTS

This study was financially supported by the Swiss Federal Department of Transportation, Communication, and Energy. The authors are grateful to M. Gödickemeier, A. Mitterdorfer and C. Kleinlogel for their helpful suggestions and discussions.

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Fig. 1: (a) design of a metallic current collector
Fig. 1 (b) alternative ceramic foam current collector

Fig. 2: Process flow chart for the manufacturing of ceramic foams.

Fig. 3: Schematic diagram of the set-up of the Van-der-Pauw measurements
Fig. 4: (a) Polymeric precursor, 60 ppi, pore size 500-700 μm.

Fig. 4: (b) Triangular shaped single strut

Fig. 5: (a) Resulting ceramic LSM foam with open porosity and 3-dimensional connected ceramic struts.

Fig. 5: (b) Triangular voids within the strut as a result of polymer burnout. Thickness of LSM layer: 10 - 30 μm.
Fig. 5: Temperature dependence of the electrical conductivity, measured with van der Pauw’s method, activation energies are indicated.

Fig. 6: Stress Strain behavior of a foam specimen, numbers are explained in the text.

Fig. 7: Compressive strength of LSM foams with different rel. densities.

Fig. 8: Weibull plot of 16 LSM foams, 60 ppi, density 0.13%.