Fabrication of YSZ electrolyte using electrostatic spray deposition (ESD):I – a comprehensive parametric study

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Abstract

Electrostatic spray deposition (ESD) was applied to fabricate a thin-layer (~3 μm thickness) yttria-stabilized zirconia (YSZ) electrolyte on a solid oxide fuel cell (SOFC) anode substrate consisting of nickel-YSZ cermet. Reducing the thickness of a state-of-the-art electrolyte, and thereby reducing the cell internal IR drop, is a promising strategy to make the intermediate temperature SOFC (ITSOFC) operating at 600–800 °C possible. About 8 mol% YSZ colloidal solution in ethanol was sprayed onto the substrate anode surface at 250–300 °C by ESD. After sintering the deposited layer at 1250–1400 °C for 1–6 h, the cathode layer, consisting of lanthanum strontium manganate (LSM), was sprayed or brush coated onto the electrolyte layer. Performance tests on the cell were carried out at 800 °C to evaluate the electrolyte layer formed by ESD. With a 97% H_2/3% H_2O mixture and air as fuel and oxidant gas, respectively, open circuit voltage (OCV) was found to be close to the theoretical value.

1. Introduction

In this paper, a novel technique for depositing SOFC components as thin layers, suitable for an intermediate temperature (IT)-SOFC is introduced. This technique is demonstrated by successful deposition of the electrolyte onto the anode substrate with state-of-the art (high-temperature SOFC) materials.

A major disadvantage in the design of a practical IT-SOFC for operation at 600–800 °C, is that state-of-the-art SOFC materials and structures are less suitable at these lower temperature than at the 900–1000 °C operating temperature of the conventional SOFC. Traditionally, YSZ has been used as the electrolyte because of its chemical stability and strength properties. But even at 1000 °C the specific ionic conductivity is relatively low (0.1 Ω^{-1} cm^{-1}), so the thickness of the layer must be kept small. At the high operating temperature of the conventional SOFC, the grain-boundary morphology connected with segregation, sintering, etc., can change and this threatens the long-term and cycling stability of the SOFC. Therefore, currently much effort is under way to define and manufacture ceramic materials suitable for an IT-SOFC, whose stability is expected to be better than that of a conventional SOFC.

Parallel with this, a search for an improved structure of the SOFC cell is under way. Many researchers believe that, using such an improved structure in a planar configuration, the IT-SOFC may be realized with state-of-the-art materials. The key requirement for an improved cell structure is to minimize overall voltage loss. This has led to exploration of alternative designs different from the electrolyte-supported cell configuration typical of the tubular SOFC.

Both the novel-materials and the novel-structure approach to the IT-SOFC require a new look at the method of producing the desired novel structure (which, moreover, may incorporate novel component materials). The need to explore new methods of fabricating the multi-layer structure follows directly from the requirements, which IT-SOFC operation implies for the cell structure as well as materials. This is particularly easy to see for planar cell stacks.

2. Thin-film electrolyte IT-SOFC

A key requirement for the IT-SOFC, whether or not using state-of-the-art electrolyte such as YSZ, is the reduction of ohmic losses. These occur across mixed ionic–electronic conducting electrodes as well as ionic conducting electrolyte, but the main contribution is from the electrolyte, hence reduction of its thickness is most effective. When the electrolyte is a very thin film

(5–15 μm), its resistance at intermediate temperature is comparable to, or less than that of a state-of-the-art electrolyte layer of 30–40 μm at 900–1000 °C.

In order to maintain IT-SOFC power densities well above those of the high-temperature SOFC, the thickness of the YSZ electrolyte must be reduced to a few micrometers [2]. In practice, the lower limit of thickness of such a "ceramic membrane" is dictated in part by the limitations of the production process such as electrochemical vapor deposition (EVD), tape casting and other processes. As the thickness is reduced, the microstructure of the film becomes more important as a key to realizing the desired reduction of ohmic resistance. If SOFCs can be produced with a thin-film electrolyte having a grain size of 100 nm or less, then the overall electrolyte resistance will be reduced to an acceptable level [3].

In this work, a novel technique for fabrication of SOFC, electrostatic spray deposition (ESD), is described. Using this technique with a colloidal solution of YSZ, a NiO–YSZ anode-supported planar thin-film SOFC has been manufactured, with a final electrolyte thickness after sintering of 4–10 μm. To put the ESD technique in perspective, in the following section various techniques of electrolyte deposition are briefly reviewed with respect to speed of deposition, mechanical strength, and uniformity of the product layer. A more extensive discusion can be found elsewhere [4].

3. Techniques of electrolyte deposition

Roughly, these can be divided into three categories depending on how the material to be deposited is supplied (as powder or precursor) and on the medium in which it is moving toward the substrate: (1) electrolyte particles are suspended in a liquid and the resulting slurry applied to the substrate, (2) electrolyte particles or their solid precursors are convected through the gas-phase or a plasma toward the substrate and (3) solid or liquid precursors are evaporated and travel through the gas phase or plasma, often while reacting with the medium or among themselves, to form a deposit on the substrate.

Category (1) includes the traditional ceramic techniques such as slurry coating, tape casting, and screen printing. Category (2) includes various sprays and sputtering processes, such as spray pyrolysis, plasma spraying, laser spraying, radio frequency sputtering (RFS) and magnetron sputtering. Category (3) includes EVD, chemical vapor deposition (CVD), chemical aerosol deposition technology (CADT), laser evaporation, electron-beam (EB) evaporation, and plasma-enhanced CVD. An example of the latter is plasma-enhanced metal organic CVD (PE-MOCVD).

In the traditional ceramic and plasma processes (Category 1 and 2 respectively), the deposition process itself is one-step and relatively simple, but the burden and expense of multi-step processing is shifted largely toward powder preparation and processing under rigorous quality control.

Category 3 processes are based on the rational strategy of a one-step process without introducing prefabricated particles. The *in-situ* formation of particle-precursors (nuclei) or particles takes place in a gaseous medium or plasma, and this process can, in principle, be designed and controlled like in a chemical reactor. Likewise, particle agglomeration onto the substrate can be controlled by suitable regime of convection, diffusion, and migration in an electric field (if applicable). But there are disadvantages to most of the Category 3 processes: the very complicated nature of the gas-to-solid process kinetics makes design optimization and control difficult. In cases where the gas-phase transport and reaction processes are relatively straightforward (as in EVD), the growth rate may be slow because it is controlled by solid-state diffusion in the deposit film.

Therefore, there is an incentive to develop a process that combines some of the attractive features of the chemical-reactor like processes (Category 3) with those of the particle-based deposition processes. The ESD process described in the next section has several features of such a combination as discussed in further sections.

4. Electrostatic spray deposition

ESD makes use of solutions or very fine (near-colloidal) suspensions of one or more precursor materials of the material to be deposited (in this case, YSZ). Atomization, in this case electrostatic atomization, is used to disperse the solution(s) or suspension(s) into a gaseous atmosphere. The drops undergo a rapid, but controlled, evaporation process. The resulting precursor particles react within the controlled mini-reactor formed by the evaporating droplet.

The ESD process resembles other deposition processes in which the precursor is dispersed in the form of drops. A liquid can be dispersed by several methods, namely blast atomization (by means of a stream of gas at high velocity), ultrasonic atomization (by ultrasonic irradiation), or electrostatic atomization (by applying a high DC voltage).

ESD makes use of electrostatic charging to disperse the liquid. The advantage of electrostatic dispersion is that the unipolar (usually positive) charge helps to achieve very small drop size. The charge also prevents coalescence of drops, hence agglomeration of particles, during flight. Moreover, the electric field allows a high degree of control over the direction of flight and the distribution of the rate of deposition over the substrate. Indirectly, the electrostatic technique, because it is able to produce extremely fine, almost uniformly sized drops, also allows a good control over the extent of the precursor reaction and the morphology (crystal structure and grain size) of the product

particle formed. Moreover, if very small drops, and thus particles, are generated, elevated temperatures are not necessary to achieve the heterogeneous reaction and interdiffusion necessary for satisfactory uniformity of the product particles and the deposit layer. High gas temperatures in the reactor (typical for spray pyrolysis) can then be avoided, and even post-deposition annealing may be unnecessary. Thus, the ESD process seems particularly suited to electrolyte deposition at relatively low temperature, as desirable for the IT-SOFC.

Thin (few tens of μm thickness) uniform layers of oxides starting from liquid solutions of precursors can be deposited by ESD at relatively low temperature and has been demonstrated recently in research focusing on lithium battery electrode materials [5].

It should be possible to deposit porous layers of SOFC electrode materials (doped lanthanum manganate, and mixed nickel oxide–YSZ) similarly by ESD. Deposition of zirconia electrolyte by an electrostatic spray process has recently been demonstrated. However, the deposit density achievable by ESD and the in-cell compatibility of ESD-deposited electrolyte with other layers are still open to question.

Diethelm [6] reported deposition of YSZ thin films onto porous anode substrates by electrostatic spray pyrolysis. (ESD appears to differ from electrostatic spray pyrolysis only by a deliberate emphasis on creating the conditions for a deposit of well-defined properties.). The YSZ thin films of 1 μm thickness deposited by this technique would be suitable as electrolyte for SOFCs.

Schoonman [7] mentions two methods of spray pyrolysis, namely ESD and flame assisted ultrasonic spray pyrolysis (FAUSP). A study of the spray type and surface morphology along with the dependence of the deposition temperature on the layer morphology in the case of deposition of cathode material $LiCoO_2$ was presented. A further review of thin-film fabrication techniques, especially for stabilized zirconia, including spray pyrolysis, has been presented in a study by Will et al. [8]. Nguyen and Djurado [9] have reported using the ESD technique to prepare tetragonal zirconia films. A detailed study of the various ESD parameters involved in deposition of YSZ has been presented in further sections of this work.

5. Objectives and strategy

ESD was applied in this work to confirm its suitability for thin-layer YSZ deposition and, specifically to understand the conditions necessary to produce near 100% density.

ESD is a versatile technique that can be adapted to both solutions and suspension or emulsions, and to various organic and mixed aqueous/organic solvents or electrolyte solutions. With regard to YSZ deposition, there are two main approaches, with each method having its own merits: (1) spray deposition from solution(s) of precursors and (2) using colloidal (or near-colloidal) suspensions of YSZ or of yttria and zirconia separately.

In this work, a colloidal suspension of YSZ was employed. A few advantages of ESD using a colloidal solution are: (1) no chemical reaction occurs during the dispersion and deposition process, hence optimization of operating conditions is simpler and the chemical composition of the deposit is *a priori* uniform; (2) low-temperature operation is adequate since breakdown or reaction of precursors, requiring high gas or substrate temperature, is not involved; (3) maximum flexibility of operating conditions, which facilitates the optimization of the process from the dispersion, evaporation, and deposition viewpoint.

With respect to cell assembly, the approach chosen was to match the thermal expansion coefficients of the anode and electrolyte materials as closely as possible. This focuses the in-cell testing of the assembled cell on the effectiveness with which the anode pores are covered by the thin electrolyte layer. Therefore, Ni/YSZ composite material was used for the anode. The choice of this composite material also allows flexibility of porosity and pore size, which is needed to ensure a large enough effective surface area for electrochemical oxidation. The anode-supported cell design was used (which requires a minimum thickness of 100–200 μm), and therefore the anode was prepared by hot-pressing a NiO/YSZ powder mixture, and the reduced anode served as substrate for YSZ deposition.

6. Experimental

6.1. Electrolyte

About 8 mol% yttria-stabilized zirconia (YSZ) from a commercial source (Tosoh Corporation, Japan) was ball-milled in a glass bottle for 18 h with zirconia balls of 3 mm diameter. The milled YSZ was then dispersed in ethanol and filtered (< 0.8 μm). The concentration of YSZ in ethanol was about 0.1 w.t.%.

6.2. Electrostatic spray deposition of YSZ

6.2.1. ESD set-up
Figure 1 shows a schematic of the ESD apparatus. The ESD set up consists of a nozzle with pump or syringe as means of liquid supply, a hot plate, and a high voltage power supply. The distance between nozzle and hot plate is adjustable, and the nozzle and hotplate can be mounted inside a controlled-atmosphere box. The nozzle in these experiments pointed upward, and the substrate (in this case, a pre-sintered anode), fixed onto the hotplate, pointed downward. A high DC voltage was applied between the nozzle (positive polarity) and the YSZ colloidal suspension was supplied to the nozzle with a syringe pump.
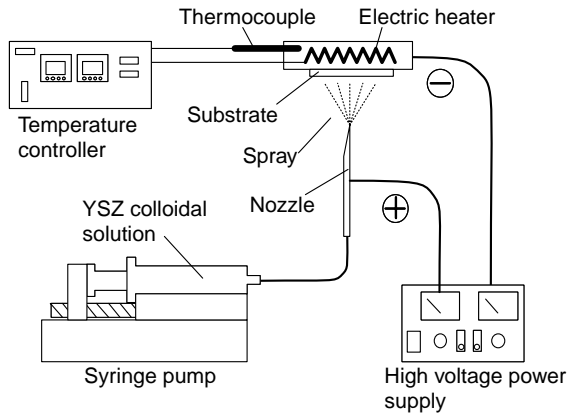
Fig. 1. Schematic of ESD apparatus.

6.2.2. Operating parameters

Typical for ESD is the large number of independently variable operating parameters:

(1) Precursor concentration in the feed solution or suspension (fixed in this study; concentration of YSZ in the suspension medium ~0.1 w%), (2) Particle size of feed solution (in case of suspension) (fixed in this study; YSZ particle size: less than 0.8 μm), (3) Solution or suspension medium (fixed in this study; suspension medium: ethanol), (4) Feed flow rate, (5) Nozzle tip shape, (6) Distance between nozzle and substrate, (7) Applied voltage, (8) Substrate material (fixed in this study; material: pre-sintered NiO–YSZ cermet anode pellet), (9) Substrate temperature and (10) Ambient gas composition, temperature, and pressure (fixed in this study; ambient gas: air at room temperature, and atmospheric pressure). The remaining five parameters namely feed flow rate (l), nozzle tip shape, nozzle–substrate distance (h), applied voltage (V), and substrate temperature (T) were varied. In addition the effect of suspension concentration specifically on dispersion (spray shape) was studied. The effects of the variable operating parameters on liquid dispersion and deposit character were studied qualitatively. In addition to the anode substrate, a slide glass was used to observe deposits.

6.2.3. Spray patterns and liquid dispersion

The electrostatic spray was not stable during the first 10 min of operation. Therefore, observations of spray patterns were made after 30 min of operation, and recorded as laser sheet images.

Using a needle with perpendicular-cut orifice, four types of spray were observed as shown in Figure 2.

Type I: The feed liquid forms a cone with its base at the orifice of the needle, and a thin cylindrical column extending from the apex of the cone. The column breaks up into droplets. The spray angle is narrow.

Type II: The feed liquid forms a cone as in Type I but the liquid column extending from the cone is absent. The tip of the cone breaks up into droplets.

Type III: The feed liquid breaks up into spray almost immediately as it emerges from the orifice. One to five break-up points can be observed.

Type IV: Similar to Type III but the spray angle is very wide and the spray has a hollow core.

Table 1 summarizes how the variable operating parameters affect spray type. From Type I to Type IV, the spray angle increases (dramatically so in the transition to Type IV). This causes a decrease in lateral uniformity of the spray and, in turn, a decrease in uniformity of the deposit (see also next section).

The shape of the needle tip strongly affects the type of spray (Table 2), as well as the stability of the various spray types, i.e., the range of an operating parameter over which the spray remains of a certain type. For example, a sharp wedge-shaped needle tip keeps the Type I spray stable over a wide range of the variable operating parameters. Another example is that a fine flat-cut needle keeps the Type III spray stable over a wide range of the variable operating parameters. These observations are in agreement with studies of electrostatic atomization [10]

Besides the transition due to controlled variation of operating conditions, a gradual change from Type I to Type IV may be observed over time. This change may be slow or rapid, depending on operating conditions, and
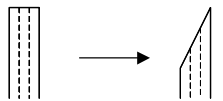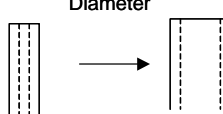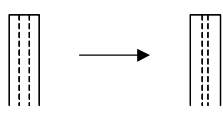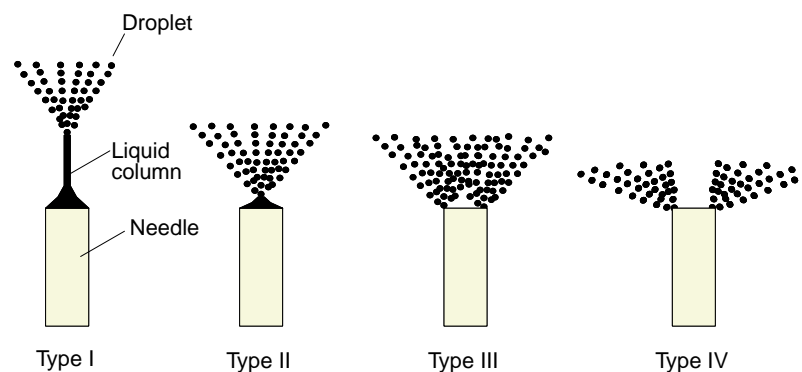

Fig. 2. Schematic of types of dispersion (spray) observed.

Table 1. Effect of various operating parameters on spray type

Parameter	Change in spray type	Remark
$c \nearrow$	Type I to Type IV	–
$h \nearrow$	Type IV to Type I	–
$V \nearrow$	Type I to Type IV	–
$I \nearrow$	Type IV to Type I	–
$T \nearrow$	Type I to Type IV	weak effect

Table 2. Effect of the space of the needle tip on spray type

Parameter	Change in spray type
Wedge angle	Type IV to Type I
Diameter	Type I to Type IV
Rim thickness	Type IV to Type I

Fig. 3. Schematic of collar used to control spray angle.

ESD, V=5.1 kV, h=20mm, l=5 ml hr^{-1}, c=0.5w%, T=150°C, t=50 min.

Fig. 4. Effect of collar on deposit area.

affected especially by the needle tip (perhaps due to interior surface changes and possibly due to small changes in needle-tip to substrate distance as the deposit thickens).

For maximum stability, a type III spray (using a fine flat-cut needle) was applied in the deposition studies. The flow rate was varied over a wide range, but best stability was obtained at 5–10 ml h^{-1}. Under optimal stability conditions, the maximum growth rate was about 10 μm h^{-1}.

6.2.4. *Effect of spray angle on deposit uniformity*

Uniformity of deposit thickness is a very important requirement for successful use of ESD in SOFC fabrication. This uniformity depends to a large extent on the lateral uniformity of the dispersion. In turn, this depends on spray angle, but also on needle tip–substrate distance (h), which was varied between 20 and 40 mm.

Considering the non-uniform electric field between needle tip and substrate, it would seem that increase in h would result in better uniformity. However, the increase in h leads to an increase in deposition area. This increases the time necessary to reach a certain deposit thickness. To suppress the increase in deposition area, the spray angle was decreased by channeling the electrostatic field immediately near the needle tip. Figure 3 shows the collar used to narrow the spray angle. The material of the collar was aluminum or silicon rubber.
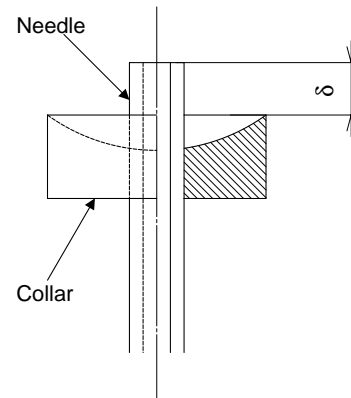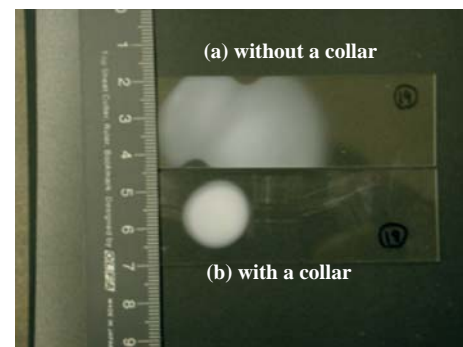
No difference in the effect was observed between those two materials. The exact location of the collar on the needle tip is an important factor in achieving a narrow and uniform, yet stable, dispersion. Figure 4 shows how a correct placement decreases the deposition area.

Non-uniform heating of the electrolyte can lead to delamination of cell components and other threats to the useful lifetime of cells. Therefore, the electrolyte thickness must be uniform. Figure 5 shows the cross-section of a 10-μm YSZ deposit on glass (glass thickness 100 μm). The YSZ film thickness is uniform and there is no defect. The thickness profile of a deposit on glass such as that of Figure 5 can be measured quantitatively by digitally recording the light intensity transmitted across the layer with uniform backlighting.

Figure 6 shows the measurement set-up, and Figure 7 the result. The effect of the collar can be seen clearly. With increase of deposition time (t), the thickness profile around the center of deposition area becomes flat. The initial non-uniformity seems to be due the unsteadiness of the spray distribution in the beginning of the operation.

6.3. *Sintering of YSZ layers deposited by ESD*

To assure complete densification the YSZ layers deposited on anode substrate were sintered at 1250–1400 °C
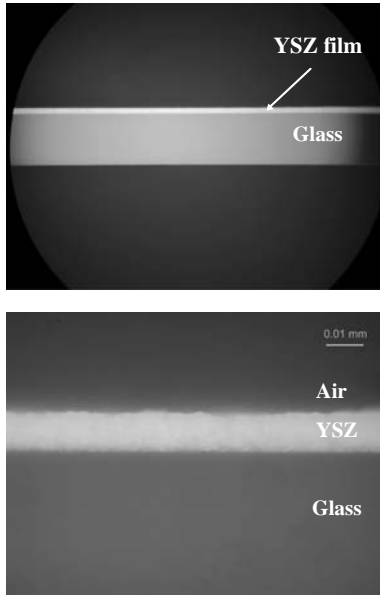
ESD with a collar, V=8.5 kV, h=20mm, l=4 ml hr^{-1}, c=1 w%, T=125°C, t=60 min.

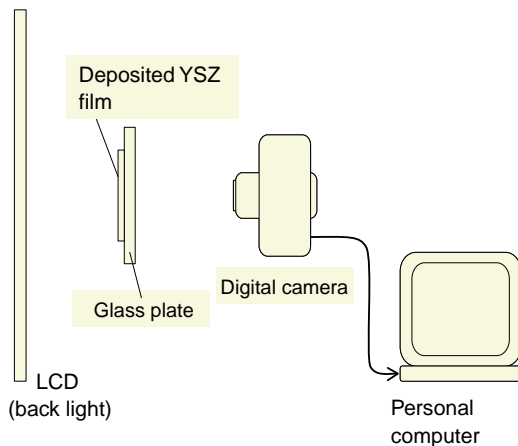*Fig*. *5*. Cross-section of 10 μm YSZ layer on glass slide of 100 μm thickness.

Fig. *6*. Measurement method of YSZ thickness profiles.

for 1 to 2 h. YSZ particles start to sinter around 900 °C. If sintering is carried out at such a low temperature, the required duration is very long. Therefore, sintering at several temperatures above 900 °C was explored. The sintered YSZ layer was transparent and its surface slightly wrinkled. Such wrinkles appear to be formed during the cooling process.

Adhering to a well-defined temperature program during sintering is essential. The temperature program can be validated only by post-sintering in-cell checks of gas-tightness. Micro-cracks in the sintered YSZ layer can seldom be observed with an optical microscope. Some defects caused by sintering ESD-generated YSZ layers on anode substrate can be observed. The main types to guard against are as follows:
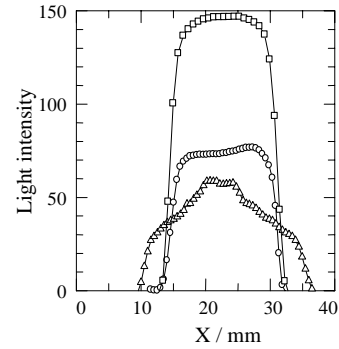
−△−:ESD, V=5.1 kV, h=10, l=5ml hr^{-1}, c=0.5 w%, T=100°C, t=5 min

−○−:ESD with a collar, V=8.5 kV, h=20, l=5ml hr^{-1}, c=0.5 w%, T=100°C, t=5 min

−□−:ESD with a collar, V=8.5 kV, h=20, l=4ml hr^{-1}, c=1 w%, T=125°C, t=60 min

Fig. *7*. Thickness profiles of YSZ layers.

– Warping of the bilayer (or cell) when the shrinking force of the YSZ layer is too much for the mechanical strength of the anode.
– Growth of NiO crystals across the YSZ layer. This occurs when YSZ and NiO in the anode pellet have not been mixed sufficiently.
– Spot-peeling of the YSZ layer. This occurs if the layer thickness is not uniform.
– Large cracks occurring when the temperature program of the sintering process is inappropriate.

6.4. *Cell assembly*

After sintering of the YSZ layer deposited on the anode substrate, test-cells were completed as follows: cathode material was coated on the YSZ layer by brush-coating or precipitation. The three-layer cell assembly was next sintered (1200 °C, 1 h), following a pre-determined sintering program.

The porous LSM layer could have been produced equally well by ESD, following a procedure similar to that used in depositing $LiCoO_2$ or $LiMn_2O_4$ layers. Work on this topic is now in progress.

After sintering of the three-layer assembly, platinum-mesh current collectors were attached to both of the anode and cathode with platinum ink, and the assembly heated to ensure good bonding. Current and potential leads were similarly attached and bonded. The cells, of 20.5-mm diameter and about 1-mm thickness, were attached across the top of a 19.5-mm inner diameter (ID), 25.4-mm outer diameter (OD), 50-cm long zirconia pipe and sealed in place with several layers of ceramic cement.

7. Cell performance test

Test cells were slowly brought to a temperature of 800 °C, and operated at 800 °C. Figure 8 shows the open circuit voltage (OCV) over the temperature range 600–800 °C. The values are very close to theoretical, with an OCV of 1.06 V attained at 800 °C. This showed
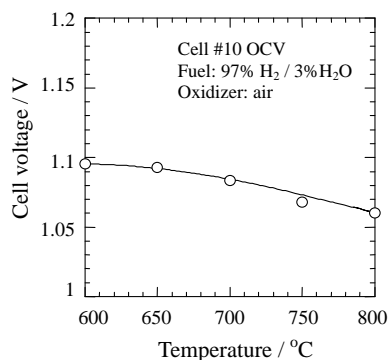
Fig. 8. OCV of a typical cell as function of temperature.

that the gas tightness of the cell assembly was satisfactory, and there were no electrical leaks by inadvertent contact of electric leads.

Results and discussion

A detailed parametric study of ESD was conducted for the case of YSZ deposition on a Ni/YSZ cermet. The important effects of nozzle shape and collar on the spray type and deposition are demonstrated in this work. Typical spray parameters are summarized in Table 3.

Table 3. Typical spray deposition parameters

Deposition temperature	250–300 °C
Voltage	8–10 kV
Flow rate	10 cc h^{-1}
Nozzle distance from substrate	25 mm
Nozzle shape	Flat

The OCV of the cell was found to be approximately 1.06 V, which is very close to the theoretical value. This demonstrates that the deposition parameters and subsequent sintering program were sufficient to achieve a near 100% dense electrolyte layer. In recent work [11] a similar deposition study using spray pyrolysis for deposition of a layer of YSZ and ceria yttria solid solution (CYO) via the precursor route onto NiO–YSZ anode substrates has been presented. The highest OCV at 770 °C was 0.880 V, and deposition temperatures, along with composition of precursor solution were presented as the most important parameter affecting surface morphology and gas tightness of the thin film. In other work [12], thin YSZ electrolyte (20 μm) and thin LSM cathodes (5 μm) were deposited using the spray deposition technique with the utilization of an air brush, and an anode substrate temperature of 100 °C. An OCV of 0.9 V at 850 °C was achieved in their work. Thus, the operating parameters of the ESD employed in the present work are assumed to be suitable to achieve an

almost totally dense thin electrolyte film for utilization in the fabrication of IT-SOFCs with minimal post-deposition heat treatment.

9. Conclusion

ESD of thin-layer YSZ electrolyte for an IT-SOFC has shown several attractive features. It appears to be very suitable for maintaining uniformity of thickness in thin-layer production, since even at the relatively low flow rates of ESD droplet size of the spray can be reduced and the cone angle of the spray can be controlled to optimize deposit uniformity. Deposition in multiple layers to build up thickness is unnecessary. Although the demonstration reported here was with a 10 μm-thick layer, thinner layers can easily be produced. Micro crack-free electrolyte layers are produced with good adhesion to the anode substrate and to a later deposited cathode layer, as proven by in-cell open-circuit and longevity testing.

Acknowledgements

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