JTTEE5 9:348-353

Peer Reviewed

Integrated Fabrication Process for Solid Oxide Fuel Cells in a Triple Torch Plasma Reactor

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(Submitted 31 January 2000)

This paper describes an approach for an integrated manufacturing process for solid oxide fuel cells. The approach is based on successively depositing the different layers of the cell using plasma deposition processes in a controlled-atmosphere chamber. Cells have been manufactured following this approach with minimal changes in process conditions for the different processes. The cells have been evaluated with regard to their materials characteristics and with regard to their electrical performance. The cell performance has been acceptable, with open circuit voltages of about 1 V and power densities between 325 and 460 mW/cm^2. Process modifications to improve the performance further are possible. The described process has the potential for being easily automated.

Keywords plasma spraying, solid oxide fuel cells, thermal plasma CVD porosity, zirconia

1. Introduction

Numerous developments exist having the objective of producing a manufacturing process for solid oxide fuel cells (SOFCs) which would drastically reduce the cost of these devices.[1–4] Depending on their design, SOFCs consist of three or four different layers: a porous cermet anode (typically nickel-zirconia is preferred), a dense electrolyte permeable only to oxygen ions (typically yttria-stabilized zirconia [YSZ] is used), and a porous perovskite cathode (strontium-lanthanum-manganite is frequently used). In the case of stacked planar cells, these cell structures are separated by a fourth layer, the electrically interconnecting bipolar plate that is used to serve as a duct for the fuel and oxygen gases. Ideally, these layers are manufactured in a minimum number of process steps. In a recent international collaborative effort involving several research groups, various plasma-based processes have been compared with respect to their potential for such an integrated manufacturing process.[5]

Although there are numerous processes for manufacturing the porous electrode layers, making the impermeable solid electrolyte layer has been the most expensive process step. The electrolyte layer deposition is the central part of the solid oxide fuel cell fabrication process. A fault in this layer will have the strongest consequence on the performance of the cell, and a deposition process must be extremely reliable. Yttria-stabilized zirconia is usually used as electrolyte because of its good O^{2-} conductivity at high temperatures. The film should have a very low gas permeability at a thickness of less than 100 μm, 30 μm being close to the optimum. It needs to be well bonded to the electrode layers even after frequent temperature cycling.

In this paper, one approach is presented to develop an integrated SOFC manufacturing process. This approach is based on different plasma deposition processes performed successively in the same chamber. In the following section, the deposition reactor used and deposition conditions for the different layers are described, followed by a description of the evaluation of the layers with regard to materials properties, and of the cell with regard to its electrical performance. In the final section, this process is compared to other plasma deposition processes.

2. Description of Apparatus and Approach

The goal of this process development has been to obtain the three layers of a solid oxide fuel cell deposited with minimal requirements for changing process conditions. The substrates have been mounted in a plasma reactor that uses three torches as plasma sources,[6] and the three layers have been deposited successively with essentially changing only the feedstock and the chamber pressure, process steps which could be easily automated. A schematic of the triple torch plasma reactor (TTPR) is shown in Fig. 1. Three dc plasma torches are mounted on the top flange of a controlled-atmosphere chamber, and the position of the three torches can be adjusted independently. The jets of the three torches coalesce to form one enlarged plasma jet. The deposition precursors are injected through a water-cooled probe, the tip of which is located above the point where the three plasma jets merge. Two powder feeders and a liquid injection system are being used for providing the deposition precursors. A porous stainless-steel or Inconel substrate is used, and the substrate is mounted on a water-cooled substrate holder, the position of which can be adjusted during operation. Substrate surface temperatures are monitored using a two-color pyrometer and are controlled by the substrate holder position and the power level of the torches. Three process steps have been followed:

(1) *Deposition of the graded cermet anode layer.* To obtain the Ni-YSZ cermet, NiO and YSZ powders (40 vol.% NiO and 60 vol.% YSZ) are injected simultaneously from two powder feeders. The NiO is reduced during the first fuel cell operation with hydrogen at the operating temperature of 900 °C. Because the successive deposition of layers with strongly differing thermal expansion coefficients has resulted in high stresses between the

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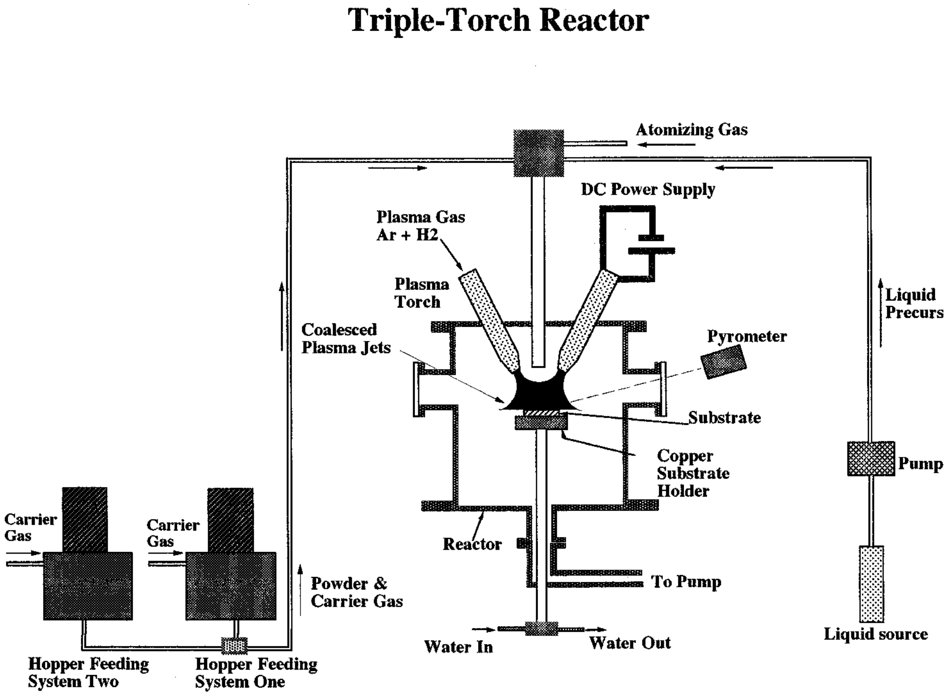

Fig. 1 Schematic of triple torch plasma reactor setup

cermet and the dense electrolyte layers, the cermet film has been graded by reducing the NiO powder flow rate towards the end of the 2 min deposition process. Simultaneously, the chamber pressure has been reduced from 1 atm to about 100 Torr to obtain a gradient in porosity in the film. Total layer thickness is about 300 μm. Typical deposition conditions are presented in Table 1.

(2) *Deposition of the YSZ electrolyte layer.* Fine YSZ powder containing 14.6 wt.% Y_2O_3 and 10 to 40 μm in size, suspended in argon carrier gas, is injected axially through a central probe into the region where the three plasma jets merge. The chamber pressure remains at 100 Torr. The center injection-low pressure plasma spray process (CI-LPS)[7,8] results in a 40 to 70 μm thick, dense layer in 1 to 2 min. The heating and cooling rates of the substrates are carefully controlled to avoid spalling of the YSZ film from the substrate. The deposition parameters have been optimized with respect to density and uniformity of the YSZ film. Typical deposition parameters are shown in Table 2.

(3) *Deposition of perovskite cathode layer using thermal plasma CVD.* Thermal plasma CVD (TPCVD) is a deposition technique that combines the control over the film composition of conventional CVD techniques with the high deposition rate of thermal plasma processes.[9] It is widely used for the deposition of diamond films and of high T_c superconductors. TPCVD has the advantage that a variety of deposition precursors can be used because the precursors are vaporized before deposition. This allows a selection of the most economical precursor and an adjustment of the composition of the precursors to assure the proper stoichiometry of the deposited material. Typically, the reactants are injected into the plasma jet where they are vaporized and transported towards the substrate. The substrate usually requires cooling because it is heated by the plasma jet, and if the boundary layer in front of the substrate is very thin, homogeneous nucleation is avoided and the vapors condense on the substrate surface. For thicker boundary layers, some formation of particulates in the boundary layer will occur, and the deposited film typically exhibits a somewhat higher porosity. The boundary layer thickness is controlled by the torch power and the gas velocity, and by the substrate position.

For the deposition of the perovskite cathode layer, a mixture of the nitrates of Sr, La, and Mn dissolved in distilled water with a concentration of 0.35 mole/L have been used. The liquid is atomized at the exit of the injection probe, and the resulting spray

Table 1 Deposition conditions for the cermet anode layer in the TTPR

Torch power	3 × 12 kW
Plasma gas and flow rate	16 sL/min Ar + 0.35 L/min H_2 for each torch
Chamber pressure	700–100 Torr
Powder feed rate	18 g/min
Carrier gas flow rate	5 sL/min Ar
Stand-off distance	170 mm

Table 2 Typical deposition parameters for CI-LPS process

Power input	3 × 12 kW
Plasma gas and flow rate	16 sL/min Ar + 0.35 sL/min H_2 for each torch
Chamber pressure	100 Torr
Powder feed rate	8 g/min
Carrier gas flow rate	5 sL/min Ar
Stand-off distance	150 mm

Table 3 Process parameters for the TPCVD of the perovskite cathode

Torch power	3 × 12 kW
Plasma gas and flow rate	16 sL/min Ar + 0.35 sL/min H_2
Chamber pressure	250–300 Torr
Liquid precursor flow rates	2.5 mL/min
Atomizing gas flow rate	6 sL/min
Substrate stand-off distance	100–120 mm
Substrate temperature	800–850 °C

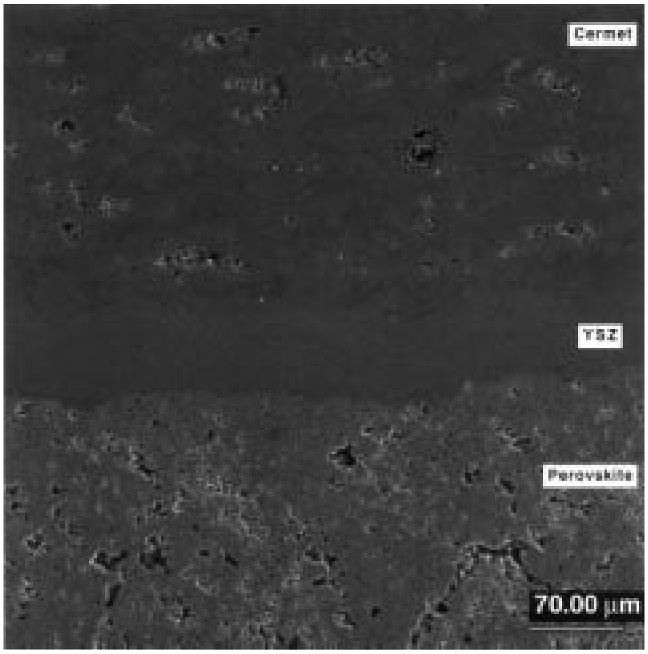

Fig. 2 SEM photo of cross section of SOFC prepared in the triple torch plasma reactor

is entrained into the plasma jets. A 160 to 200 μm thick layer is formed within 30 min on the previously deposited YSZ electrolyte layer. The process conditions are given in Table 3.

3. Coating and Cell Evaluations

The individual layers have been evaluated using standard materials characterization techniques (scanning electron microscopy [SEM], X-ray photo-electron spectroscopy [XPS], and x-ray diffraction), and the entire cell has been evaluated for its electrical performance.

An SEM micrograph of a cross section of a cell with a graded cermet layer is shown in Fig. 2. The change of composition and of porosity in the cermet are clearly visible in this figure. Details of the gradients in composition and porosity are shown in Fig. 3.

The major characterization effort has been devoted to the electrolyte layer. The films have been analyzed for porosity with image analysis of the micrographs of the cross sections, and values for porosity consistently below 1% and as low as 0.3% have been observed. Micrographs of the etched cross-sectional surface (Fig. 4) show that the film is composed of ultrafine lamellae together with fine equiaxed grains less than 1 μm in size.

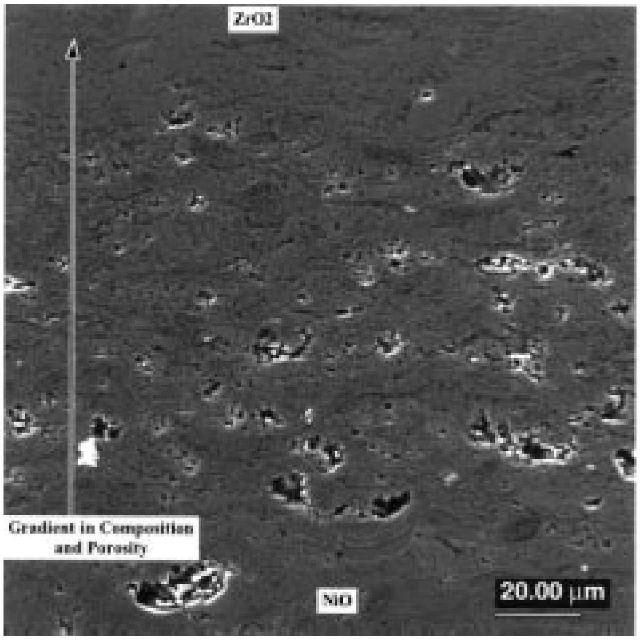

Fig. 3 SEM photo of cross section of graded cermet anode layer deposited in the triple torch plasma reactor.

X-ray diffraction scans with regular angle region of $2\theta = 20$ to 80° in 0.5° steps and high-angle region of $2\theta = 71$ to 77° in 0.01° steps have been used to determine the phase structure of the deposited films. The high-angle scan corresponds to the {400} region. In the case of a tetragonal structure, the peak separation between (004) and (400) occurs in the {400} region, whereas in the case of cubic structure, there is no peak separation. As shown in Fig. 5, only one peak in the {400} region is found; therefore, it can be concluded that the deposited film possesses a cubic structure, which is required for application in the SOFCs.

To compare the film obtained with the CI-LPS in the triple torch reactor with YSZ films obtained with the same powder under atmospheric pressure spraying (APS) conditions, a double layer has been prepared in which a YSZ has been deposited using the CI-LPS process on top of a YSZ film deposited under standard APS conditions. The coated substrate has been fractured by four-point bending. Figure 6 shows an SEM micrograph of a fracture surface of the CI-LPS film on the APS-YSZ layer. As shown in the figure, the APS-YSZ layer exhibits a delamination type fracture with columnar grains visible inside the lamellae and with laminar porosity or microcracks along the lamellae. Therefore, the lamellae in the APS layer are thought to be bonded together by mechanical interlocking. In contrast, the CI-LPS layer shows a translamella type of fracture resulting from interlamellar chemical bonding brought about by a liquid sintering effect and higher velocities of the particles involved in the film preparation. The CI-LPS layer is well adhered to the APS layer. With the aid of a telemicroscope and a video camera, we have been able to observe the surface during deposition. From the image, it appears that droplets remain in the liquid state for a longer time after impinging on the surface compared to regular plasma spraying, and it appears that there is some vapor phase

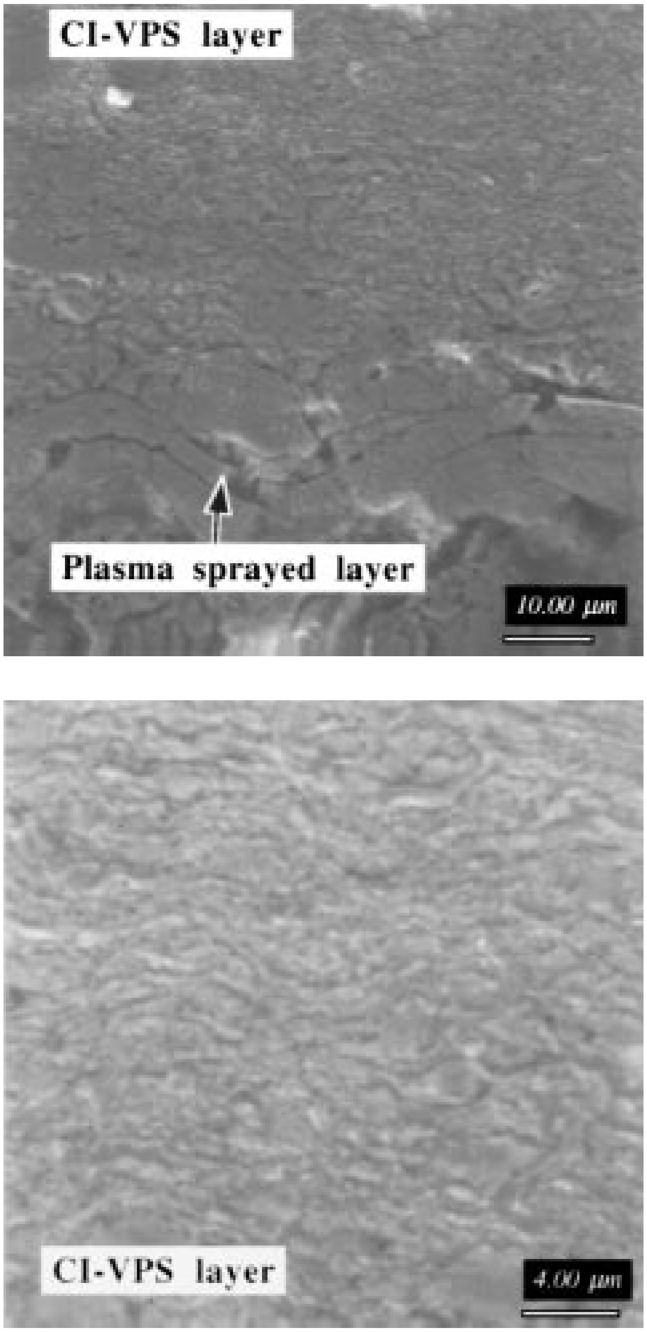

Fig. 4 SEM photos of etched cross sections of YSZ layer deposited by the CI-LPS process on top of an APS-deposited YSZ layer showing the difference in microstructure

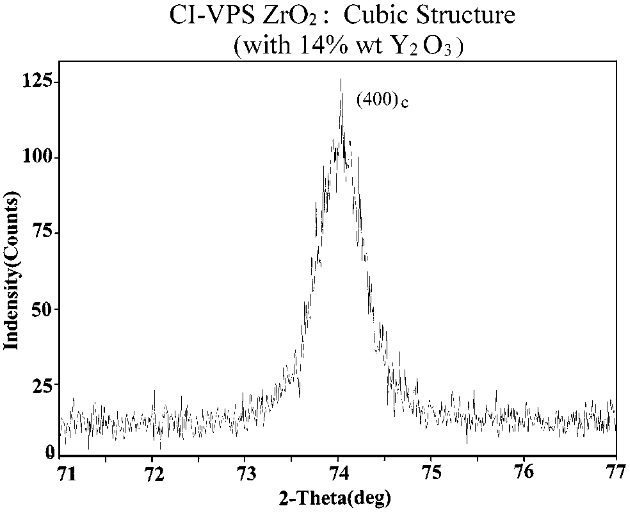

Fig. 5 Large angle x-ray diffraction pattern of the CI-LPS-deposited YSZ layer showing only cubic structure peaks

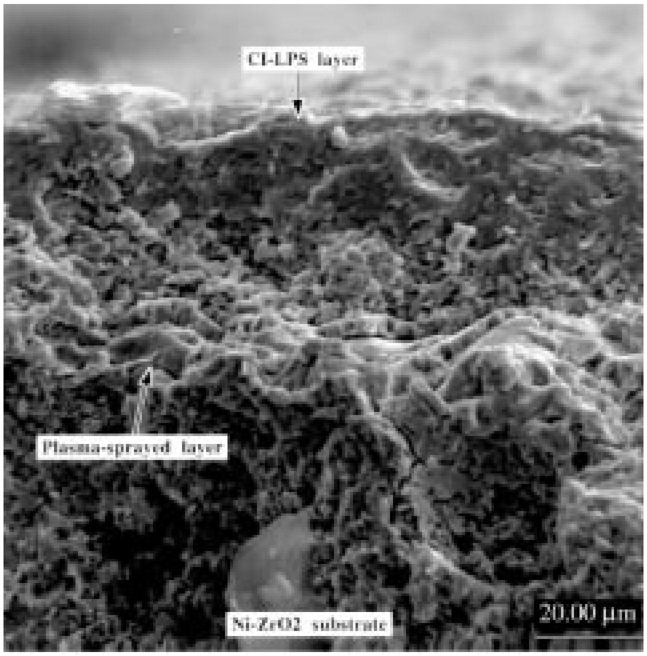

Fig. 6 SEM photo of fracture surface of YSZ layer deposited by the CI-LPS process on top of an APS-deposited YSZ layer showing the different fracture mechanisms

deposition as well. The following combination of conditions is unique to the CI-LPS process: (1) all particles pass through the hot plasma region created by the coalescence of the three plasma jets, and all are in a molten state when they impinge on the substrate; (2) the heat flux from the three plasma jets in combination with the low thermal conductivity of the porous substrate will result in higher substrate temperatures than one usually encounters in spray deposition; and (3) there is additional deposition from the vapor phase because some of the material from the particles is vaporized. These factors allow liquid sintering to occur, resulting in the very dense coating without visible lamellar structures.

A cross section of the deposited perovskite film is shown in Fig. 7. The film clearly exhibits sufficient porosity. The x-ray diffraction pattern shown in Fig. 8 does indicate the perovskite structure of $La_{0.8}Sr_{0.2}MnO_3$. There has been no independent optimization of the perovskite film deposition process with respect to fuel cell performance, because no standard electrolyte/cermet

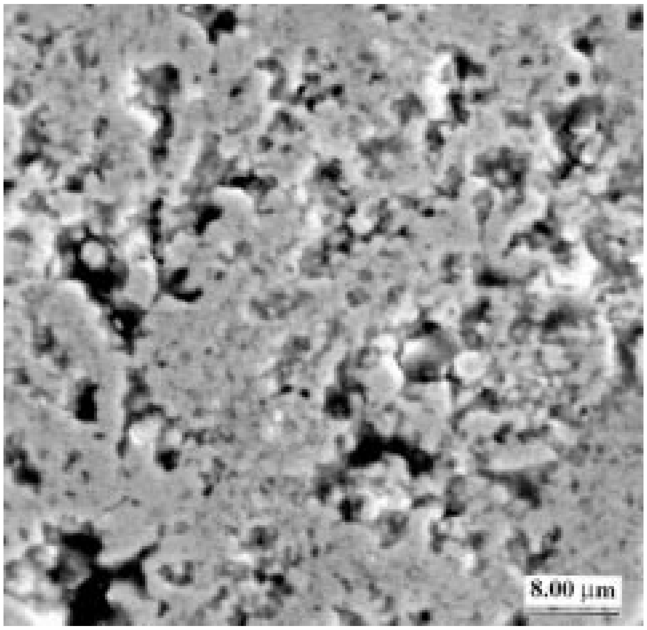

Fig. 7 SEM photo of the cross section of the porous perovskite cathode layer deposited by TPCVD

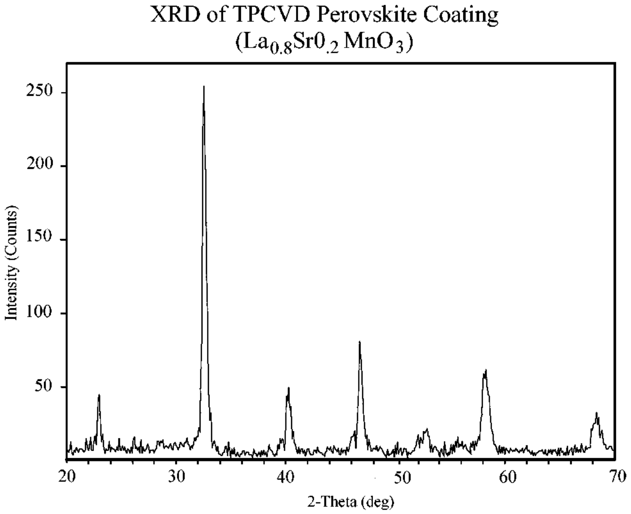

Fig. 8 X-ray diffraction spectrum indicating the $La_{0.8}Sr_{0.2}MnO_3$ perovskite structure of the cathode layer

substrates have been available. Consequently, it is possible that fuel cell performance can be further improved by the optimization of this process.

The electrical performance is shown in Fig. 9. Open-circuit voltages of approximately 1 V (0.98 to 1.08 V) and peak power densities of 325 mW/cm^2 at 900 °C have been obtained. Higher power densities have been obtained in cells in which a thin platinum film served as the cathode layer (480 mW/cm^2). Therefore, it should be possible to increase the power density by increasing the porosity of the perovskite layer, which could be done without major difficulty.

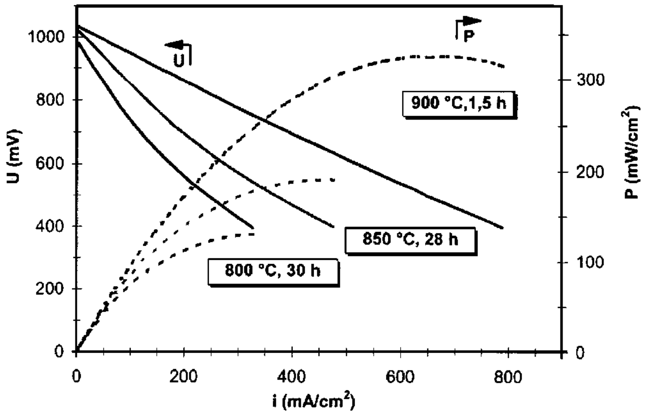

Fig. 9 Voltage-current and power-current behavior of SOFCs prepared in the triple torch plasma reactor, measured at different temperatures

4. Discussion and Conclusions

The CI-LPS process has produced cell structures with acceptable electrical performance, and further process improvements will likely improve the performance. The cells have a diameter of 3 cm and total manufacturing time has been less than 1 h with minimal manual effort required. Fabrication of larger diameter cells is possible if the substrate is moved during the deposition, and movable substrate holders have been developed for our reactor. However, one of the frequently cited economical factors involves processing in a chamber at reduced pressures (100 Torr in our case).

To assess potentially more economical alternatives, experiments have been performed with deposition of the anode and electrolyte layers using atmospheric pressure plasma spraying. For the deposition of the cermet anode layer, the substrate holder has been held at an angle of 30° with respect to the spray direction to obtain the desired porosity in the film. When these anode films are combined with CI-LPS-deposited electrolyte layers, good electrical performance has been obtained (1.08 VOC and 460 mW/cm^2). This result indicates that atmospheric pressure spray processes can be used for the deposition of the cermet layer. However, we have not been able to deposit a thin film of a YSZ electrolyte layer with the necessary low permeability at a thickness of less than 50 μm on a porous substrate using an APS process. We do not see an advantage to depositing the cermet layer using an APS process and then the electrolyte layer using the CI-LPS process. The crucial issue for going to an atmospheric pressure process is, therefore, the development of an APS process for the impermeable, thin YSZ electrolyte layer.

No experiments have been conducted with atmospheric plasma spraying of the porous perovskite layer. Although this process should pose no major problems, it will require the expensive perovskite powder as feed material. It is not clear if the cost of depositing this film in a chamber at a slightly reduced pressure is compensated for by the use of inexpensive nitrate solutions as feed.

We may conclude that the integral plasma process described here can be used for generation of SOFCs with acceptable performance. The minimal labor cost and the relatively low cost of the raw materials are attractive features of this process from an economic point of view.

Acknowledgments

This work has been supported by the New Energy and Industrial Technology Development Organization (Tokyo) and by the Engineering Research Program of the Office of Basic Energy Sciences at the U.S. Department of Energy, Grant No. DE-FG02-85ER13433.

References

1. T. Yoshida, T. Okada, H. Hamatani, and H. Kumaoka: *Plasma Sources Sci. Technol.,* 1992, vol. 1, p 195-201.
2. H. Gruner and H. Tannenberger: *Proc. Thermal Spray Conf. TS90,* Deutscher Verlag für Schweisstechnik, Düsseldorf, Germany, 1990, p 194-96.
3. H. Gruner, and J. Moens: *2nd Eur. Solid Oxide Fuel Cell Forum,* B. Thorstensen, ed., European Fuel Cell Forum, Oberrohrdorf, Switzerland, 1996, p 261-67.
4. R. Henne, G. Schiller, V. Borck, M. Mueller, M. Lang, and R. Ruckdäschel: *Proc. 15th Int. Thermal Spray Conf.,* C. Coddet, ed., ASM International, Materials Park, OH, 1998, p 933-38.
5. T. Yoshida, coordinator: “Development of Integrated Fabrication Process for Solid Oxide Fuel Cells Using Advanced Plasma Technology,” Final Report for NEDO International Research Grant, NEDO, Tokyo, Japan, 1998.
6. Z.P. Lu and E. Pfender: *Proc. 9th Int. Symp. Plasma Chemistry,* R. d’Agostino, ed., University of Bari, Bari, 1989, p 675-80.
7. H.C. Chen, and J. Heberlein: *Proc. 13th Int. Symp. Plasma Chemistry*, C.K. Wu, ed., Peking University Press, Beijing, China, 1997, p 1077-82.
8. H.C. Chen, J. Heberlein, and T. Yoshida: *Proc. 15th Int. Thermal Spray Conf.,* C. Coddet, ed., ASM International, Materials Park, OH, 1998, p 1309-14.
9. J.V.R. Heberlein and E. Pfender: in *Plasma_Properties: Deposition and Etching,* J. Pouch and S.A. Alterovitz, eds., *Materials Science Forum* 140–142, Trans Tech Publications, Aedermannsdorf, Switzerland, 1993, p 477-96.