Application of APS to SOFCs

1. Introduction

Solid oxide fuel cell (SOFC) can convert the chemical energy of a fuel directly into electricity. It is a highly efficient, environmental friendly power generation system. However, the reduction of manufacturing cost is the biggest challenge for industrial commercialization of SOFCs. Atmospheric plasma spraying (APS) is regarded as one of the most promising methods for the manufacturing of SOFCs because of its fast deposition rate. It is also more cost-effective when compared with other film formation processes such as electrochemical vapor deposition [1], vacuum plasma spraying [2], sol-gel methods [3], and dip-coating [4]. Therefore, APS has been employed to fabricate components of SOFCs including anode and cathode.

Atmospheric plasma sprayed ceramic deposits are characterized by lamellar structure. A fraction of porosity from several percent up to 20% can be formed in a thermally sprayed ceramic coating [5]. Pores in the coating will influence many properties such as mechanical and physical properties. These pores are interconnected through vertical microcracks in individual splats in the coating, As a result, APS YSZ coating produced in a conventional route is generally not suitable for use as electrolyte in SOFCs due to high gas permeability. To employ APS YSZ as an electrolyte of SOFCs, post-densification to the as-sprayed ceramic layer has been attempted [6-8].

2. Principle of SOFC

Figure 1 shows an SOFC scheme. It contains a solid oxide electrolyte made from a ceramic such as yttria-stabilized zirconia (YSZ) which acts as a conductor of oxide ions. This ceramic material allows oxygen atoms to be reduced on its porous cathode surface, thus being converted into oxide ions, which are then transported through the electrolyte to a porous anode zone where the oxide ions can react with hydrogen, giving up electrons to an external circuit. Only five components are needed to put such a cell together: electrolyte, anode, cathode and two interconnect wires.

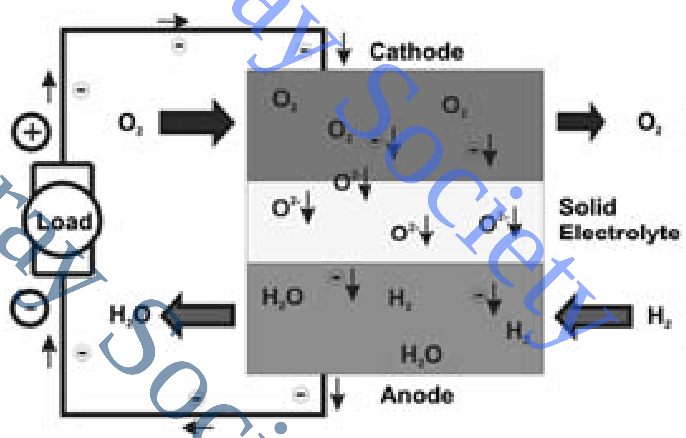

Fig. 1.Schematic of solid oxide fuel cell (SOFC)

3. Application of APS in fabrication of SOFC components

3.1 Fabrication of Electrolyte

Electrolyte for SOFCs requires the highest demand on quality and production. They should be very thin in the range of some μm up to few tens of μm to keep the internal resistance for conducting the oxygen-ion low, but still being dense enough for avoiding the permeation of reacting gases which would not only reduce the performance, but also in the case of H_2-transfer lead to H_2O formation at the cathode side causing increased degradation effects by destroying the cathode with time.

However, the high gas permeability will limit energy efficiency of SOFC due to the leakage of the reacting gases through electrolyte deposited by APS. Therefore, many attempts were made to densify APS coating by post-spray treatment including post sintering treatment [9, 10] and infiltration densification [11]. Li et al. [12, 13] reported that APS YSZ can be sufficiently densified by impregnating yttrium and zirconium nitrate solution into the coating following by heat-treatment at 400 °C for 30 min. The densified YSZ exhibited a gas permeability satisfactory for operation of high temperature SOFCs. The tubular SOFC cell assembled by APS YSZ presented a high output power density. Fig. 2 (a) (b) show the cross sectional structure and the performance of SOFC single cell, respectively.

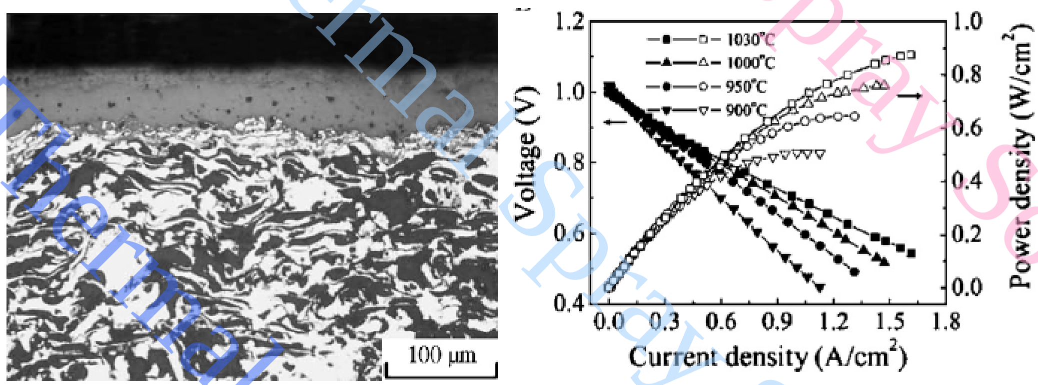

Fig. 2 Cross sectional structure (a) and the performance (b) of SOFC single cell fabricated by thermal spraying

3.2 Fabrication of Anode

Porous Ni/YSZ cermets are the most frequently applied anode materials, at present, prepared conventionally by wet powder and sintering methods.

To obtain an anode by an APS process with a homogeneous mixture of the phases Ni and YSZ and pores, different powder feedstock can be considered. Instead of using Ni powder as starting material, it is also possible to use NiO powder. D. Hathiramani et al. [14] used agglomerated NiO/YSZ powder and injecting NiO and YSZ powders separately into the plasma jet to prepare anodes, as shown in Fig. 3. During the reduction process in the starting phase of the SOFC the anode will gain additional porosity due to the volume change from NiO to Ni.

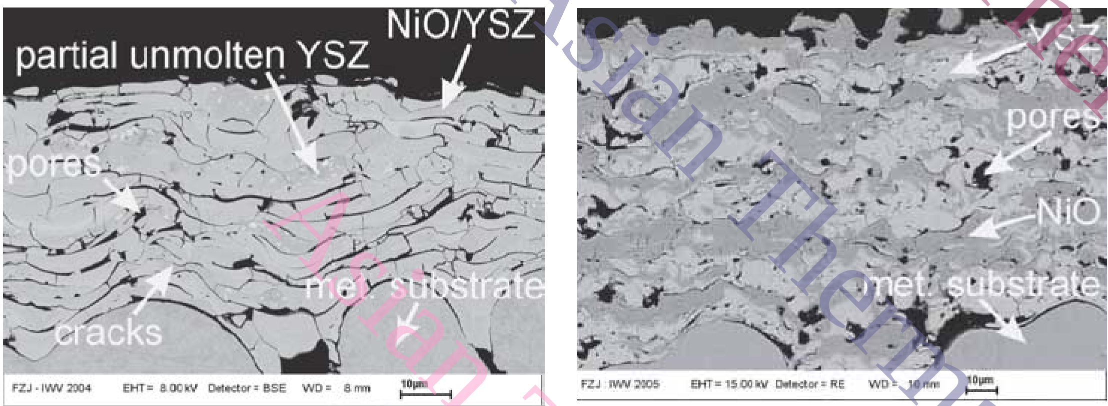

Fig. 3 Cross section of an APS anode coating obtained by using Agglomerated NiO/YSZ powder (left)and injecting NiO and YSZ powders separately into the plasma jet (right)

Another alternative way to make porous anodes is the use of Ni-coated graphite powder (Ni(C) together with YSZ with the idea to get the porosity by burning-away the carbon content during and after the deposition process. Weckmann et al. [15] employed APS to prepare YSZ/Ni-graphite anode, as shown in Fig. 4. The anodes were sprayed with a thickness of 20-50 μm and showed a sufficient porosity and permeability. It was found that by combination with fine YSZ/Ni(C)-powder mixtures anode layers with very homogeneous distributed material and a fine open porosity can be fabricated. Permeability and surface roughness can be adjusted by spraying parameters in a wide range.

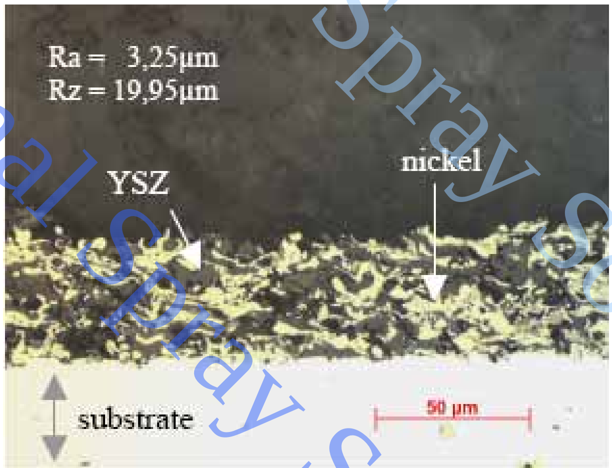

Fig. 4 Micrograph of polished cross-section of coating

3.3 Fabrication of Cathode

At present, several processes have been employed to fabricate SOFC cathodes, which mainly include slurry coating, screen printing, sol-gel method, tape casting, and chemical/physical vapor deposition. However, those processes are often relatively expensive or time-consuming. Compared to these processes, plasma spraying possesses the advantages of consecutive integrated cell fabrication, high efficiency, good cost effectiveness and microstructure tailoring capability. All those features make plasma spraying as one promising candidate. Therefore, plasma spraying has been employed to deposit cathode layers in SOFCs by many investigators.

Nie et al. [16] reported that the performance of plasma sprayed LSM cathodes for SOFCs can be improved after heat treatment in air at 1000◦C. Fig. 5 shows the cross section microstructure of the deposited LSM cathode /YSZ electrolyte. It can be seen that the deposited LSM layers adhered well to the electrolytes.

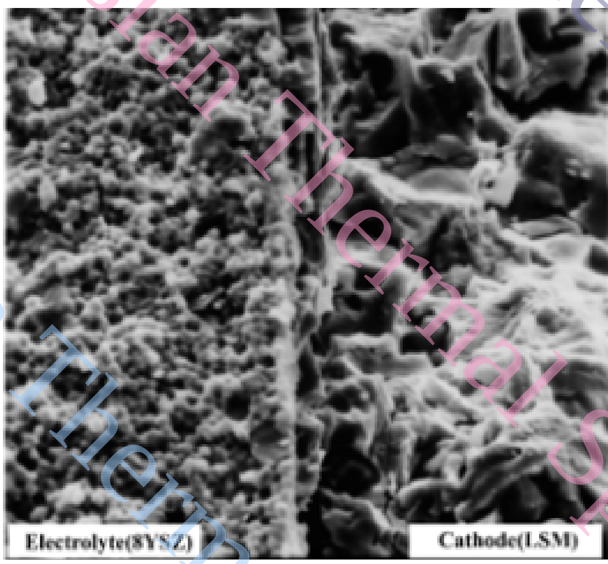

Fig. 5 A cross-section of LSM/8YSZ interface

Muller et al. [17] employed PS processing fabricatied columnar cathode, as shown in Fig. 6. Open porosity of the needle-shaped electrodes offers efficient vertical as well as horizontal gas migration paths and short electrical current paths.

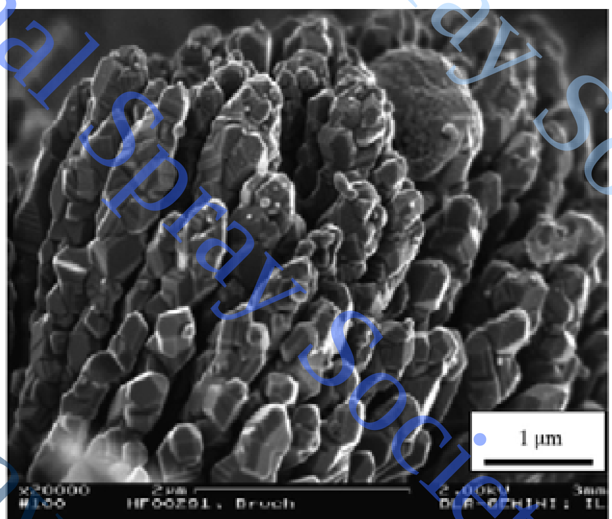

Fig. 6 SEM image of a plasma sprayed LSM coating on a substrate

4. Integrated SOFC Production

The SOFC structures can be divided into two basic types, tubular and planar, and both types have been developed for stationary power generation, on-site power generation, and mobile power sources.

4.1 Tubular-Type Solid Oxide Fuel Cells [18]

Plasma spraying has been applied to the production of tubular-type SOFCs. Fig. 7 shows pictures of such cells of Mitsubishi Heavy Industries. Multiple circular-striped cells are formed on the surface of a support tube of about 20 mm diameter. Fig. 8 shows the structure of the trans-axial section of a cell. On the support tube, multiple ring-shaped cell structures are deposited, each comprising the fuel electrode, the electrolyte, and the air electrode. The electrodes of adjacent cells are connected by means of an interconnecting coating. Since the interconnector material is a cermet of a Ni alloy and Al_2O_3, the Al_2O_3 protective coating for resistance to oxidation is formed on the interconnector coating. The electrolyte coating, which requires especially high density, is deposited by low pressure plasma spraying. The fuel electrode coating made of cermet, the interconnector coating, and the ceramic protective coating are all deposited by atmospheric plasma spraying. Under standard conditions of 200 mA/cm^2, A SOFC stack consisting of 22 cells in a series has an electricity generation capability on the order of 40 W.

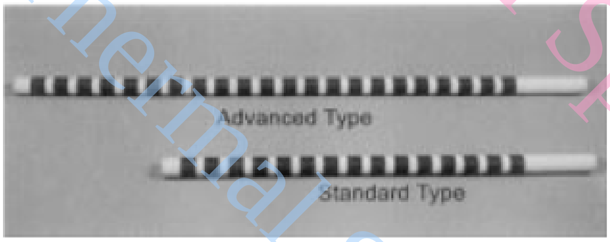

Fig. 7 Tubular type cell of Mitsubishi Heavy Industries

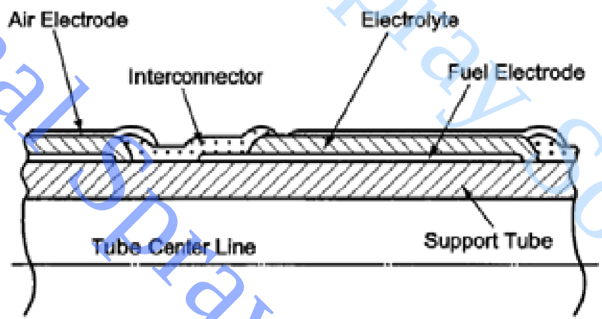

Fig. 8 Structure of the trans-axial section of a tubular cell

4.2 Planar-Type solid oxide fuel cell

Takenoiri et al. [29] present the fabrication procedure of the planar type cell by Plasma spraying. In the fabrication of cells, Ni felts were used as porous substrates, anodes and electrolytes were formed on the Ni-felt substrates using FS and APS, respectively. Figure 5 shows the appearance of the 600 cm^2 Ni felt substrate supported cell.

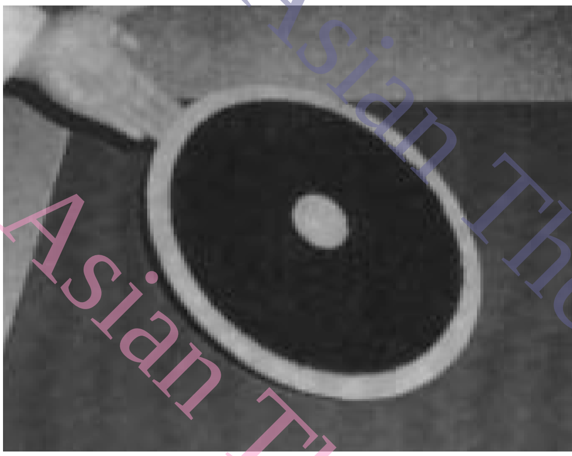

Fig. 9 Planar type cell

X.Q. Ma et al. [20] reported a planar type single SOFC has been fabricated by APS, as shown in Fig. 10. The cell consists of an LSM cathode/LSGM electrolyte/Ni-YSZ anode, which is fabricated for operation in a medium temperature range from 500 to 800°C. The single cells were fabricated by consecutive plasma spray processing, which have been optimized and tailored to each layer to achieve highly porous cathode and anode layers as well as high-density electrolyte layers. The as-sprayed LSGM electrolyte mostly contained amorphous phase; however, a high degree of crystallized LSGM could be achieved by heat treatment at a temperature above 700°C. The OCV data indicate that the plasma sprayed electrolyte layer has satisfactory gas tightness. The power density was measured as 80 to 150 mW/cm^2 at the tested temperatures. These results demonstrate that plasma spray processing is cost-effective and highly promising for the integrated fabrication of SOFCs.

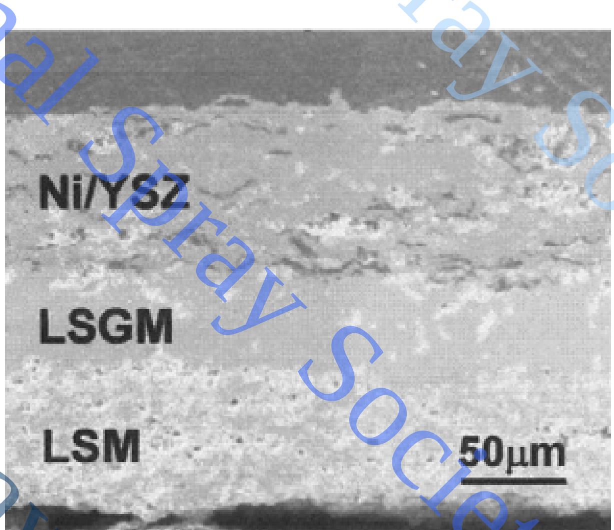

Fig. 10 Cross sectional structure of single cell

5. Summary and Challenges

Despite APS is regarded as one of the most promising methods for manufacturing the components employed in SOFCs including porous ceramic cathode, anode and dense ceramic electrolyte layer because of its fast deposition rate and cost-effective characteristic, significant challenges still remain in the development of plasma spraying with respect to the SOFC wet ceramic production techniques. To employ APS coating as electrolyte in SOFCs, post-densification is necessary to the as-sprayed ceramic layer due to high gas permeability. The process also must be controlled to ensure that the phases deposited have the desired crystalline structure, avoiding delamination, amorphous structures, and to avoid introducing impurities in the raw materials during powder preparation.

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