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Review article

Tailoring the O_2 reduction activity on hydrangea-like $La_{0.5}Sr_{0.5}MnO_3$ cathode film fabricated via atmospheric pressure plasma jet process

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ABSTRACT

An atmospheric-pressure plasma jet (APPJ) is applied to prepare porous perovskite materials, particularly of lanthanum strontium manganite $La_{0.5}Sr_{0.5}MnO_3$ (LSM551) oxide powder and film. LSM nano powder around 50.0 nm is obtained, and characterized by X-ray diffraction, scanning electron microscopy, and high-resolution transmission electron microscope. A spherical morphology with hydrangea-like shape is observed as associates to the pure tetragonal phase. LSM film is deposited onto yttria-stabilized zirconia (YSZ) electrolyte-support substrate as cathode layer for the operation in a solid oxide fuel cell at 600–900 °C operating temperatures. A series of symmetrical cells possessing high exchange current density of 30.12 mA/cm^2 at 800 °C. The prepared samples are assessed as an object to discover the diffusion mechanism of oxygen pathways for LSM/YSZ system based on the microstructural (particles size, and porosities) and electrochemical (kinetic and impedance) data. The mechanism of oxygen pathways is directly associated with the triple phase boundary lengthiness, in which the surface and bulk pathways occurring in APPJ-prepared LSM layer on YSZ lead to an increasing in activity of oxygen reduction reaction. Moreover, a fabrication of desirable ternary metal oxide, LSM, with highly porous structure via an advance-innovative APPJ preparation is outlined.

1. Introduction

In recent years, a drive towards low pollutant emission, high energy-conversion efficiency, and power sources with fuel versatility has created a great deal of interests in solid oxide fuel cell (SOFC) [1–4]. The major challenge of SOFC is to reduce the thermal mismatch of each component under the high operation temperatures and can be well-operating in the intermediate or lower temperatures (500–900 °C) [5–8]. The thermal mismatch is not only affecting the polarization of both electrolyte and electrode, but also leading to low stability of the cell [2,9,10]. The approaches on gaining such a high performance of SOFC include: 1) lowering the operation temperature, 2) a fabrication of thin electrolyte, and 3) the development of highly porous cathode [11–13]. Though other cathode materials are given higher catalytic activities rather than lanthanum strontium manganite ($La_{0.5}Sr_{0.5}MnO_3$, LSM551). However, the combination of catalytic activity, thermal and mechanical stability of LSM cathode with yttria-stabilized zirconia (YSZ) as the electrolyte is not only marvelous, but as a renewal interest to exploiting its advantage [1,2,4,10,14–20].

Principally, the performance of intermediate temperature SOFC (IT-SOFC) is limited by the cathode overpotential due to the increasing polarization resistance (Rp) in a low operation temperature. Therefore, in the case of the first proposed method, lowering the operation temperature reflects to the high voltage losses [21–23]. However, the first method can only be implemented by the development of thin electrolyte and porous cathode (the second and the third methods). It is assumed that the three approaching methods cannot be stand-alone.

Various fabrication technologies, such as screen-printing, tape casting, chemical/physical vapor deposition, alcohol solution precursor plasma spraying, spray pyrolysis, etc., have been employed for cathodes manufacturing [20,24–26]. However, these techniques are relatively expensive, time-consuming, and inflexible. For commercializing applications in IT-SOFC systems, atmospheric pressure plasma jet (APPJ) is an innovative-advanced plasma technology, because of its fast oxidation process for nanoparticle preparation, the possibility of deposition in a large surface area, and it does not require any vacuum system. In our previous studies, APPJ process is successfully achieved on producing a multicomponent oxide particle to forming a metal oxide (single metal and bimetal oxides) for SOFC application [27–29]. The current challenge is producing a ternary metal oxide from the deposition of LSM oxide material on electrolyte substrate (without any undesired phases) in a one-step deposition process. During the deposition, microstructural changes are evidently affecting the performance of the cell [30,31]. The highly porous structure of LSM cathode is mandatory for

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affecting the size and the distribution of triple phase boundary (TPB) [2,22,32]. Duong et al. have suggested the importance of TPB's length in determining an SOFC cathode performance, and denoting the boundary adjoining the electrode and electrolyte materials, and open volume through where the gaseous reactants are transmitted (the porosity effect) [33].

TPB is defined as a region where the catalytic activity (oxygen reduction reaction, ORR) occurs [3,4,34]. The output performance of LSM cathode on YSZ electrolyte is measured from the electrochemical data and is strongly influenced by the TPB region [33–37]. Bisquert et al. have described the TPB as a subject of permanent interest [35]. Fleig has also strongly supported by proposing three possible paths for cathodic reaction, which includes of the electrode surface path, the bulk path, and the electrolyte surface path [38]. One or more elementary steps determines the corresponding reaction rate in which the cathodic reaction will simultaneously occur in all three paths. The interference might be occurred because of the parallel reaction pathways and the crossover of these various pathways. For example, the incorporation rate into the cathode (bulk pathway) is dependent on the surface concentration of oxygen adsorption, and thus is influenced by the surface diffusion occurring via the electrode surface pathway mechanism. In this study, an APPJ deposition technique for LSM cathode with a well-defined geometry (highly porous structure) has provided an insight kinetic of ORR by the qualitative and quantitative correlations for cathode microstructure and electrochemical behaviors.

2. Experimental details

2.1. Precursor solution preparation

Commercial lanthanum nitrate hexahydrate ($La(NO_3)_3{\cdot}6H_2O$, Acros Organics), strontium nitrate hexahydrate ($Sr(NO_3)_2{\cdot}6H_2O$, Acros Organics), and manganese nitrate tetrahydrate ($Mn(NO_3)_3{\cdot}4H_2O$, Acros Organics) are prepared as the precursor solution. The salts are dissolving into de-ionized water to form an aqueous solution (0.05 M) with the fixed metal ions ratio (La:Sr:Mn) of 0.5:0.5:0.1, then ascribed as LSM551.

2.2. Powder and films preparation

Atmospheric pressure plasma jet (APPJ) is employed to synthesize the LSM551 powder, and the resulting powder is collected in two methods: 1) powder collection by de-ionized water in a Pyrex beaker, and 2) powder collection by scratching the deposited LSM film on the substrate. In this study, the powder is collected by the second method, and delivered to the dynamic light scattering (DLS, Malvern Instruments v2.0, Fig. S1, ESI) for the mean particle size distribution analysis. The details of powder collection by the first method are highlighted in our previous studies [28,29]. During the preparation of LSM powder, a DC power is supplied at 500 W, and the flow rate of clean dry air (CDA) as working gas is maintained at 30 slm. The atomized precursor solution droplets are generated by piezoelectric oscillator (2.45 MHz frequency) and transferred to the plasma region by oxygen (O_2) carrier gas (flow rate:1.8 slm).

Dense 80 mol% yttria-stabilized zirconia (8YSZ) electrolyte substrates (0.5 mm thick and 1.5 cm diameter) are prepared by die-pressing and then sintered at 1500 °C for 10 h. The circular disks are placed on the x-y moving stage with 80 scanning times for the deposition process. The speed of two-axis stage and spray distance between the head jet and the substrates are maintained at 10 mm/s and 15 mm, respectively. The schematic picture of APPJ system is depicted in our previous work [29].

2.3. Materials characterization

Microstructures of LSM powder are obtained by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6500F). Morphology and selected area electron diffraction (SAED) of powder are characterized by high resolution transmission electron microscopy (HR-TEM, Philip Tecnai G^2F20). The powder collected from the second method is dispersed, and the mean particle size is examined by dynamic light scattering (DLS, Malvern Instruments v2.0). Crystalline structure of LSM cathode films is obtained by X-ray diffractometer (XRD, Bruker D2 Phaser) in Cu Kα radiation of $\lambda = 1.5405$ Å. Total reflection X-ray fluorescence spectroscopy (TXRF, Bruker S2 PICOFOX) is used to examine the chemical composition of the prepared samples. Cross sectional micrograph of LSM cathode films are performed to confirm the microstructures of deposition results. The surface porosity of the deposited films is analyzed by Image-J software.

2.4. Electrochemical characterizations

For the electrochemical characterizations, the prepared cells were placed at an in-house furnace. The measurements were carried out in the standard two-probe DC method on the Electricity Workstation (Jiehan Technology Corporation, ECW-5000/5600) at 600–900 °C. The ORR behavior of APPJ-deposited LSM cathode coating was obtained under the symmetrical cell in a two electrode configuration at an open circuit voltage (OCV) condition under air environment. Electrochemical impedance spectroscopy (EIS) is used to study the electrochemical behavior of the half-cell using the potentiostat (VSP 274, Bio Logic Science Instruments) with the frequencies range from 0.05 to 100 kHz in an open circuit voltage (OCV) condition.

3. Results and discussions

3.1. Microstructural analysis

Fig. 1(a)-(b) showed SEM images of LSM powder synthesized by APPJ at low and high magnifications, respectively. The porous structure of LSM (42.1% porosity) is obviously observed in Fig. 1(a), and the small solid particle aggregates in hollow-spherical of which a hydrangea-like formation is visible, as shown in Fig. 1(b). The size of aggregates is 292.5 nm, while the average size of small solid particle is 50.8 nm (Fig. S1, ESI). In addition, TEM image (Fig. 1(c)) confirmed that the particles are uniformly distributed with an average size of 40.0–50.0 nm. SAED image shown in Fig. 1(d) is suggested as the nanocrystalline ring pattern, or consists of fine crystal fragments. All diffraction rings of LSM powder are well confirmed to the tetragonal phase and indexed as (110), (112), (202), (220) and (310) diffraction planes, respectively. For the calculated lattice constants, $a = 5.470$ Å and $c = 7.695$ Å ($d_{110} = 3.867$ Å, $d_{112} = 2.727$ Å, $d_{202} = 2.229$ Å, $d_{220} = 1.934$ Å, $d_{310} = 1.729$ Å), were close to the theoretical values of $La_{0.5}Sr_{0.5}MnO_3$, $a = 5.442$ Å and $c = 7.766$ Å ($d_{110} = 3.845$ Å, $d_{112} = 2.73$ Å, $d_{202} = 2.23$ Å, $d_{220} = 1.92$ Å, $d_{310} = 1.72$ Å). For the issue of nanoparticle synthesis, the particles size of LSM powder prepared by APPJ is much smaller than those reported by Wang et al. (0.2–2 µm and ∼ 1 µm, via alcohol solution precursor plasma spraying and suspension plasma spraying, respectively), Chen et al. (100 nm, via electrophoretic deposition), Fukui et al. (∼ 100 nm, via spray pyrolysis), Gómez et al. (1–3 µm, via aqueous tape casting) [2,10,39–41].

In the APPJ technology, the intended composition of LSM (in a solution) and composition of the deposited film (as-prepared LSM cathode) are the same, as proven by XRF analysis in Fig. 2(a). In a referring to the XRD examination, the phase of APPJ-prepared LSM powder is obtained without undesired mixing peaks. This finding meets in good agreement with the study of phase transformation. For each state, the composition must be the same when the phase is transforming from the liquid state to the solid state, but the initial (liquid phase) and the final (solid phase) volumes are different.

The XRD pattern of APPJ-prepared LSM powder in Fig. 2(a) shows the well-crystalline tetragonal perovskite phase. The details' examination reveal that the diffraction peaks at $2\theta = 23.093°$, $2\theta = 32.736°$,