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A facile method for the deposition of Gd_2O_3-doped ceria films by atmospheric pressure plasma jet

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ABSTRACT

Atmospheric pressure plasma jet was applied to grow 10 mol% gadolinia-doped ceria (10GDC) films on polycrystalline 8 mol% yttria-stabilized zirconia (8YSZ) via precursor solutions of nitrate salts. The morphology of as-deposited gadolinia-doped ceria (GDC) film represented interconnected particles with irregular shapes covered on the 8YSZ substrates. The mixing Ce^{4+}/Ce^{3+} valence state and oxygen deficiency (O/Ce + Gd: 1.75) in as-deposited films were proven by X-ray photoelectron spectroscopy quantification study. As increasing the sintering temperature over 1300 °C, the interdiffusion between 10GDC film and 8YSZ substrate occurred due to the formation of (GDC + YSZ) solution analyzed by X-ray diffraction and Raman analyses, which resulted in the degradation of the total conductivity of electrolytes. For the application of solid oxide fuel cell, 10GDC film sintered at 1300 °C for 2 h with a comparable conductivity could be feasibly applied as the diffusion barrier between 8YSZ electrolyte and cathode materials for the prevention of interdiffusion.

1. Introduction

Solid oxide fuel cells (SOFCs) [1–5] are well-known to have a great potential to be major power sources in the future, because of their low pollutant emission and high energy-conversion efficiency using a variety of fuels, high electrolyte stability, and long stack life. Yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte materials for SOFC application, and it must maintain high operating temperatures (800 to 1000 °C) to have a sufficiently high ionic conductivity (~0.01 S/cm). However, at such high operating temperatures, YSZ as solid oxide electrolytes can lead to complex material problems, such as the thermal expansion coefficient mismatch between ceramic components, coking problems on the electrodes, interfacial interdiffusion, and the possibility of cell sealing [3].

Ceria-based solid solutions have been acknowledged to be the most promising electrolytes for intermediate temperatures (500 to 700 °C) SOFCs (IT-SOFCs) since their ionic conductivity is higher than that of YSZ in the intermediate temperature range [6]. At present, most Sr and Co-containing cathode materials are chemically incompatible with YSZ electrolyte. For example, the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) cathode reacted readily with YSZ at high temperature, and the formation of high resistance phases as insulating layer deteriorated the cell performance [7,8]. Therefore, the Sr and Co-containing cathodes cannot be applied directly on the YSZ electrolyte. In order to use the strontium and cobaltite perovskite type oxides as cathode material for IT-SOFCs, gadolinia-doped ceria (GDC) film has been proposed as a protective layer on the YSZ electrolyte for the prevention of interdiffusion [9–11].

In the literature, several GDC film preparation methods have been reported, such as: chemical vapor deposition [12,13], E-beam [14], and sputtering [15–19]. However, much attention has been paid to utilize the plasma at atmospheric-pressure due to possible advantages of eliminating an expensive vacuum system, on-line processing capabilities, high efficiency, and the scalability to a larger area. Recently, atmospheric-pressure plasma techniques have drawn a wide variety of potential industrial applications, such as surface treatment [20], thin film deposition [21], and nanoparticle fabrication [22]. In this study, a facile method combining the atomization process of spray pyrolysis and plasma enhanced chemical vapor deposition is called atmospheric-pressure plasmas jet (APPJ) for preparing 10 mol% gadolinia-doped ceria (10GDC) films on 8 mol% yttria-stabilized zirconia (8YSZ) substrate. The crystalline structure, morphology, chemical composition and electrical performance of the samples were analyzed using X-ray diffractometer (XRD), field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and DC conductivity, respectively.

2. Experimental

The APPJ system is mainly composed of a plasma jet head, a DC power supply, an ultrasonic generator, a gas delivery system and an x–y two axis moving stage. Commercial gadolinium nitrate hexahydrate ($Gd(NO_3)_3 \cdot 6H_2O$, Across Oranics) and cerous nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, Across Oranics) were used as the precursors without further purification and de-ionized water was used as the solvent. The precursor solution was prepared by dissolving $Gd(NO_3)_3 \cdot 6H_2O$ and

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$Ce(NO_3)_3 \cdot 6H_2O$ into de-ionized water to form an aqueous solution with a concentration of 0.05 M and a ratio of metal ions (Gd/Ce) of 1/9. During the deposition of GDC film, the DC power supplied to the plasma discharge was kept at 300 W, and the flow rate of clean dry air as working gas was maintained at 40 slm, respectively. Next, the solution was ultrasonically atomized at 2.45 MHz into mist and then conveyed by Ar carrier gas to the plasma region with a flow rate of 1 slm. After the deposition, all the samples were subjected to a heat-treatment at 1200 °C–1500 °C for 5 h in atmosphere condition.

During the deposition, the scanning mode is used for all the sample preparations for characterization. Circular disks of 8YSZ as bulk samples were uniaxially die-pressed and then presintered at 1500 °C for 5 h. The dimensions of the bulk samples are 2.0 mm in thickness and 1.5 cm in diameter. The value of the relative density for 8YSZ disks was 99.5%. 8YSZ substrates are located on the x–y stage moving back and deposited for repeating 20 scan times. The moving velocity of two axis stage was set at 10 mm/s along the x and y axes. The crystallite structure of GDC films were verified by the XRD (D2 Phaser, Bruker, USA), employing a Ni filtered Cu-Kα radiation ($\lambda = 1.5405$ Å) and a scanning rate of 0.02 deg·s^{-1} in the 2θ range from 20° to 80°. The surface morphology of samples was examined by FE-SEM (JSM-6500F, JOEL, USA). Chemical compositions of the prepared particles measured by XPS (Theta Probe spectrometer, Thermo Scientific, USA) are performed. Peak positions were then calibrated with respect to the C 1s peak at 284.5 eV from the adventitious hydrocarbon contamination. The peak fitting of data was performed by the Avantage software system, using a Shirley type background subtraction and Gaussian/Lorentzian peak shapes. Structural characterization was carried out by Raman spectroscopy (EnSpectr R532, EnSpectr, USA) using the 532 nm exciting radiation of a 25 mW He–Ne laser. Two-probe DC conductivities of the specimens were measured at temperatures ranging from 500 °C to 700 °C. Platinum electrodes of 0.1 cm diameter were secured to either sides of the sample pellet using Heraeus CL11-5100 Pt adhesive paste and held at 900 °C for 1 h.

3. Results and discussion

The microstructures of 8YSZ substrate and as-deposited GDC film analyzed by SEM were shown in Fig. 1. 8YSZ substrate showed a completely dense without any apparent pores inside (Fig. 1a) and its relative density is 99.5%. During the deposition by APPJ, the as-deposited GDC film represented interconnected particles of irregular shapes covered on 8YSZ substrate (Fig. 1b). From the cross-sectional image of the fracture surfaces, the layer thickness is around 2 μm (Fig. 1c). At higher magnification of cross-sectional SEM image, the microstructure of the film showed incorporated particles with good adherence to the 8YSZ substrates (Fig. 1d).

The chemical binding and composition of as-deposited GDC films on 8YSZ substrates were measured by XPS. In Fig. 2, the binding energies of the Ce 3d, Gd 4d and O 1s photoelectrons for the as-deposited GDC films were consistent with the data in XPS handbook [23]. Ce 3d core levels (Fig. 2a) of as-deposited films determined from XPS can be classified into two sets of spin orbital doublets, namely as (v, u), (v″, u″), and (v‴, u‴) of the characteristic peaks for the tetravalent states of Ce^{4+} binding states at 883.6 and 901.7 eV, 888.5 and 906.8 eV, and 898.7 and 916.9 eV, and (v_0, u_0) and (v′, u′) of the characteristic peaks for the trivalent states of Ce^{3+} binding states at 881.0 and 899.3 eV and 885.8 and 904.0 eV [24–26]. The binding energies of Gd $4d_{3/2}$ and $4d_{5/2}$ in Fig. 2b located at 146.1 eV and 141.5 eV are the characteristic peaks of gadolinium oxide [25]. Two main contributions of peaks in the O 1s core levels (Fig. 2c) are observed at 529.6 eV and 532.1 eV, which are ascribed to the lattice oxygen and adsorbed surface hydroxyl species [24–26].

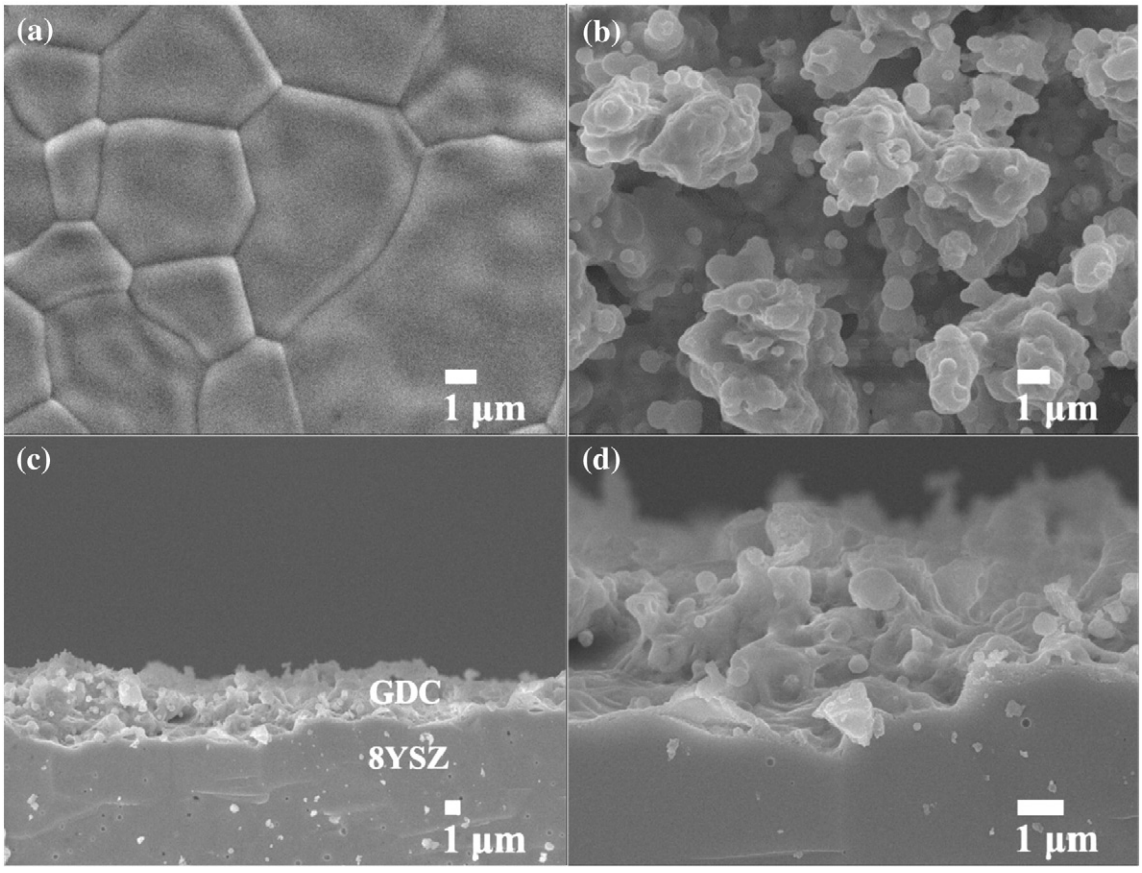

Fig. 1. SEM image of (a) 8YSZ substrate and (b) as-deposited GDC film, and cross-sectional image of as-deposited GDC film at (c) lower magnification (×3000) and (d) higher magnification (×10000).