Reinvestigation of an Electrophoretic Deposition of Thin YSZ Films

การศึกษาซ้ำการเคลือบฟิล์มบาง YSZ ด้วยเทคนิคการตกเคลือบแบบอิเล็กโตรโฟเรติค

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ABSTRACT

Yttria-stabilised zirconia (YSZ) films deposited on a stainless steel sheet and a non conductive NiO-YSZ pellet were fabricated by an electrophoretic deposition (EPD) technique. Various deposition conditions using an electrolytic solution prepared from an iodide in combination with ethanol or acetylacetone were investigated under the applied DC voltage up to 300 V. A scanning electron microscopy (SEM) was used to identify an optimum material processing condition based on the presence of porosities and cracks on the films after they were sintered at 1400 °C. Under the optimized condition, the dense YSZ film without significant through-holes across the film was achieved on the NiO-YSZ substrate in a merely 20 s, yielding a desirable thickness of approximately 5 μm. The optimized electrophoretic deposition is, thus, suitable to produce a dense YSZ electrolytic film on a porous NiO-YSZ anode, which is a half cell of a solid oxide fuel cell, in a short period.

บทคัดย่อ

ฟิล์มอิเล็กโตรไลต์ Yttria-stabilised zirconia (YSZ) ถูกเตรียมขึ้นด้วยเทคนิคการเคลือบแบบอิเล็กโตรโฟเรติคบนวัสดุรองรับที่ทำจากสเตนเลสและเม็ดสาร NiO-YSZ ซึ่งไม่นำไฟฟ้า และได้ทำการศึกษาเงื่อนไขต่างๆในการเคลือบฟิล์ม โดยใช้ไอโอดีนเจือจางในเอทานอลหรืออะซิทิลอะซิโตนเป็นสารละลายอิเล็กโตรไลท์ กระแสไฟฟ้าเป็นไฟกระแสตรงขนาดไม่เกิน 300 โวลต์ เงื่อนไขที่เหมาะสมสำหรับการเคลือบฟิล์มพิจารณาจากภาพถ่ายด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด โดยพิจารณาจากความพรุนและรอยแตกร้าวบนฟิล์มที่ถูกเผาที่อุณหภูมิ 1400 องศาเซลเซียส ภายใต้เงื่อนไขที่ดีสุดนี้ทำให้ได้ฟิล์ม YSZ ที่หนาแน่นบนวัสดุรองรับ NiO-YSZ โดยฟิล์มที่ได้มีจำนวนรูทะลุผ่านน้อยจนถือว่าไม่มีนัยสำคัญ โดยใช้เวลาในการเคลือบเพียง 20 วินาที ซึ่งทำให้ได้ฟิล์มที่มีความหนาประมาณ 5 ไมครอน เทคนิคการเคลือบฟิล์มแบบอิเล็กโตรโฟเรติคในสภาพการปลูกที่ดีที่สุดจึงเหมาะสมสำหรับการผลิตฟิล์ม YSZ บนขั้วแอโนดซึ่งทำจาก NiO-YSZ ที่มีรูพรุนในระยะเวลาอันสั้น และถูกใช้เป็นครึ่งเซลล์ของเซลล์เชื้อเพลิงแข็งได้

Key Words: YSZ, NiO-YSZ, Electrophoretic deposition
คำสำคัญ: YSZ NiO-YSZ การเคลือบแบบอิเล็กโตรโฟเรติค

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Introduction

Solid oxide fuel cell (SOFC) is a solid state electrochemical cell which can generate electricity from heat and gases such as oxygen and hydrogen-sources. Generally, the performance of an SOFC is high when the operating temperature is at around 600-800 °C. However, such a high temperature can lower the longevity of the cell due to the reaction between an electrolyte and electrode materials, and the thermal expansion mismatch between ceramic components resulting in the formation of undesirable insulating phases and the high thermal stress, respectively. One way to reduce the operating temperature is by decreasing the thickness of an SOFC electrolyte down to less than 10 microns in order to allow fast transportation of conductive ion species. However, the good mechanical strength of the thin film electrolyte is to be maintained in order to prevent the explosive mixture of hydrogen and oxygen gases.

Yitttrium stabilized zirconia (YSZ) is regarded as a commercially viable materials to be used as an SOFC electrolyte due to its low cost, good mechanical strength and good stability under reduced atmosphere. Thin YSZ film can be fabricated by several vacuum and non-vacuum based techniques. One of the simple non-vacuum based techniques is an electrophoretic deposition (EPD). The technique is employed to coat particles on a substrate with the application of an electrical power that drives the particles charged with a proper electrolyte onto the opposite-sign electrode where a substrate is typically placed (Rahaman, 2007 and Corni, 2008). This technique is thus compatible with an electrical conductive substrate. However, a porous non-electrical conducting substrate can also be used, providing that a conductive plate is properly attached to its backside, and the substrate has sufficient pores allowing the electrolyte to go through. These make it rather challenging to implement the EPD technique with the non-conductive substrate. Unsurprisingly, there are limited numbers of literatures on the fabrications of YSZ films on a non-conducting NiO-YSZ with the EPD technique using ethanol (Hosomi, 2007) and acetylacetone (ACAC) (Besra, 2006) as solvents. Based on these two papers, this research reinvestigated the fabrications of YSZ films on the NiO-YSZ using EPD when ethanol and ACAC were used as solvents. The appearances of the films deposited on conducting and non-conducting substrates were compared.

Experimental

Materials and Substrates

The sub-micronized YSZ powders and NiO-YSZ powders were purchased from Fuelcellmaterial.com. Ethanol and ACAC were AR grade from QReC. The dispersants were iodine (QReC) and phosphate ester. A smooth conductive stainless steel sheet cut into 15x25 mm^2 was used for tuning the optimized deposition condition of as-deposited films. NiO-YSZ powder mixed was uniaxially die-pressed without the addition of organics into pellets with a diameter of 13 mm and then fired at 1000 °C for 2 h in air. The fired NiO-YSZ pellets had the thickness of 0.6-1 mm and the porosity of about 40 %.

Electrophoretic deposition

YSZ powder and a solvent were mixed together by an ultrasonic agitator. Concentration of suspension was fixed at 10 g/L which was suitable for producing dense films. The two electrodes were placed 5 mm from each other (Fig. 1). Deposition area was set at 15x15 mm^2. A DC power was supplied under the constant voltage mode from 10 to 300 V. NiO-YSZ pellets were fixed in a specially-made teflon holder with stainless steel backing electrode.

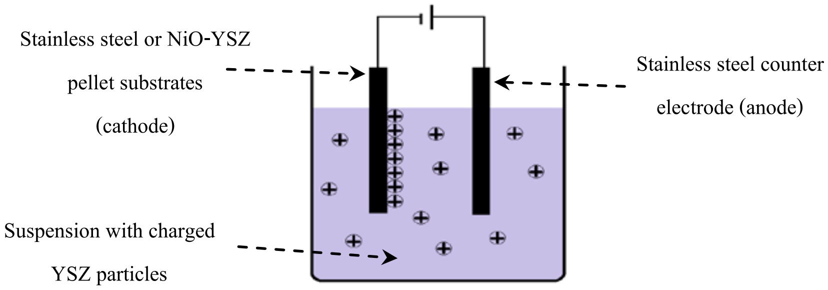

Fig. 1 A schematic diagram of the EPD setup

Deposition weights were recorded. Microstructures of dry films on a stainless steel sheet and a sintered semi-SOFC cell, the YSZ electrolyte/(NiO-YSZ) pellet, were observed by a scanning electron microscopy (SEM).

Results and Discussion

For an electrophoretic deposition under a constant-voltage mode, the deposited weight per unit area can be expressed as:

$$w = \frac{2}{3} C \varepsilon_r \varepsilon_0 \xi \eta^{-1} E L^{-1} t \qquad (1)$$

where C represents the concentration of particles in the suspension, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of solvent, ξ is the zeta potential of particles, η is the viscosity of solvent, E is the applied voltage, L is the distance between electrodes, and t is the deposition time (Chen, 2001). Hence, the deposition weight basically associates with the strength of an electrophoretic field and a deposition time. Directly finding proper deposition conditions based on multiple variables can be troublesome dealing with rough non-conductive NiO-YSZ substrates. The attempt of this research was to use a stainless steel substrate to screen out the conditions leading to the films with unacceptable pores and cracks.

Deposition on stainless steel

Deposition voltage and time validate the quality of the YSZ film on the stainless steel. To achieve a dense and crack-free YSZ film, according to our experiments, the application voltage of 150-200 V is determined to be a good deposition range. The film deposited on a stainless steel at a lower voltage range (under 150 V) has a cracking issue after the film is dried in air, because the adhesion of particle-particle and particle-substrate, depending on strength of the electrical field that drives them, is not sufficient. Whereas, the applied voltage higher than 200 V may also cause cracking and rough surface, since the deposition rate is too high. Regarding the duration time, it was found that a suitable duration time should not be longer than 10-30 s. Moreover, these deposition times were enough to obtain films of less than 10 µm. Another important parameter that dictates the consistency of the film is the distance between cathode and anode, a minimum distance between the two electrodes was kept at least 5 mm, because the dense and homogenous films cannot be fabricated at a shorter distance.

Zhitomirsky and Petric (2000) used phosphate ester as a dispersant to increase deposition rate of YSZ film in ACAC. On the contrary, in our experiment, the deposition rate was reduced, therefore the addition of phosphate ester was not pursued in our case. Instead, the study was focused on the influence of iodide which was sometimes added in the electrolyte to raise the deposition rate due to the increase in the electrolytic conductivity. The relationship between the concentration of iodide and the deposited weight of YSZ under 20 s are shown in Figure 2. The addition of iodides into the ACAC solutions distinctively enhances the amount of deposited YSZ powder. Nevertheless, increasing of iodide contents in ethanol does not show significant change in the film weight. This may be due to the impediment of proton generation on YSZ particulate surfaces when iodide, which may react with ethanol, is added.

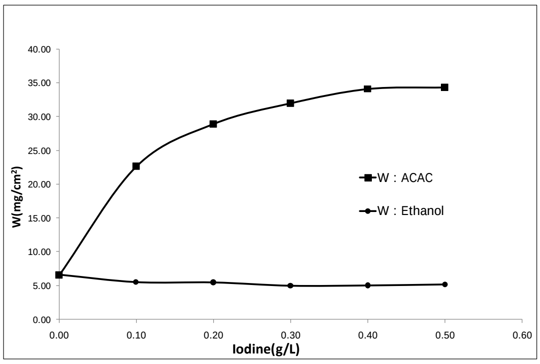

Fig. 2 Effect of iodine concentration on deposition weight (YSZ suspended in ethanol and ACAC)

Interestingly, iodides contribute to the increase in YSZ deposition mass. Adding 0.1 g/L iodide into the ACAC solution promotes a sharp rise in the mass of the deposited film. Further increases of the iodide beyond 0.1 g/L also enhance the deposition rate, but the effect is not as strong as that of the former amount. Saturation of deposited increment with the increasing iodide is revealed when the 0.4 g/L and more is added in the ACAC solution. Both ethanol and ACAC are protonic-donor solvent, but ACAC also act as a bi-dentate ligand providing a better dispersion capability of particulate suspensions. Nevertheless, the deposition rate in ACAC solution is very close to that of ethanol. Note here that Besra (2006) did report that ACAC alone was adequate for the development of a positive surface charge on YSZ particles enabling the deposition of YSZ films on porous NiO-YSZ substrates. However, in our case, it was found that if a sole ACAC or ethanol was used, the film with numerous non-closed pores were formed on a stainless steel and a NiO-YSZ pellet. Further investigations by adding 0.1 g/L iodide into the ethanol or into the ACAC electrolytes was carried out in order to properly increase the deposition rate and to resolve the porosity issues, if possible, since the electrolytic conductivity was increased. The impact of a composite solution between iodide-ethanol and iodide-ACAC on qualities of YSZ films was compared in Fig 3. As expected, the lower deposition rate in the ethanol case yielded a film with a better packing density. The results of films deposited on the insulated NiO-YSZ substrate were shown in Fig 4.

Deposition on NiO-YSZ

10 g/L YSZ in ACAC or ethanol with 0.1 g/L iodine was deposited on NiO-YSZ at 200 V for 20 s. After drying in air for 24 h, the deposited film was co-fired with the substrate at 1400 °C for 3 h in air.

The film morphologies shown in Fig. 4 a, c and Fig. 4 b, d reveal that both films are sintered, but there are some remnants of non-closed pores. Ethanol, which provides an acceptable film on a stainless steel substrate and is better than ACAC, surprisingly yields inferior results when compared to the films deposited with ACAC in the case that the non conductive porous NiO-YSZ is used.

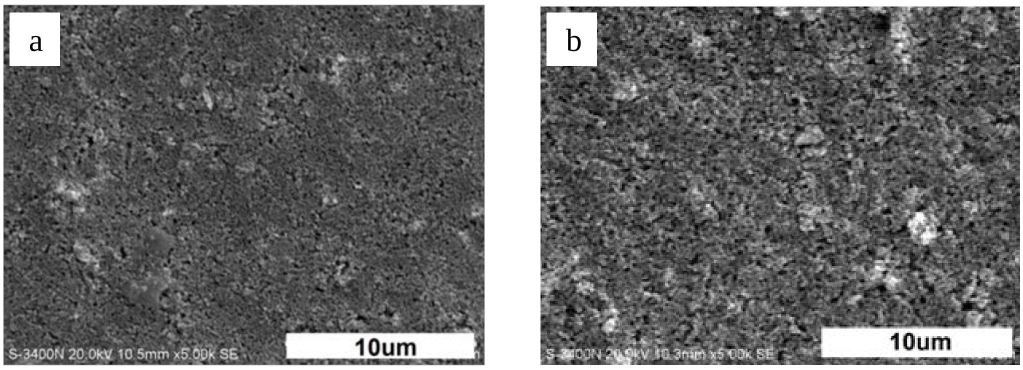

Fig. 3 Microstructures of dried films deposited on stainless steel sheets using 0.1 g/L iodide in ethanol (a) and ACAC (b)

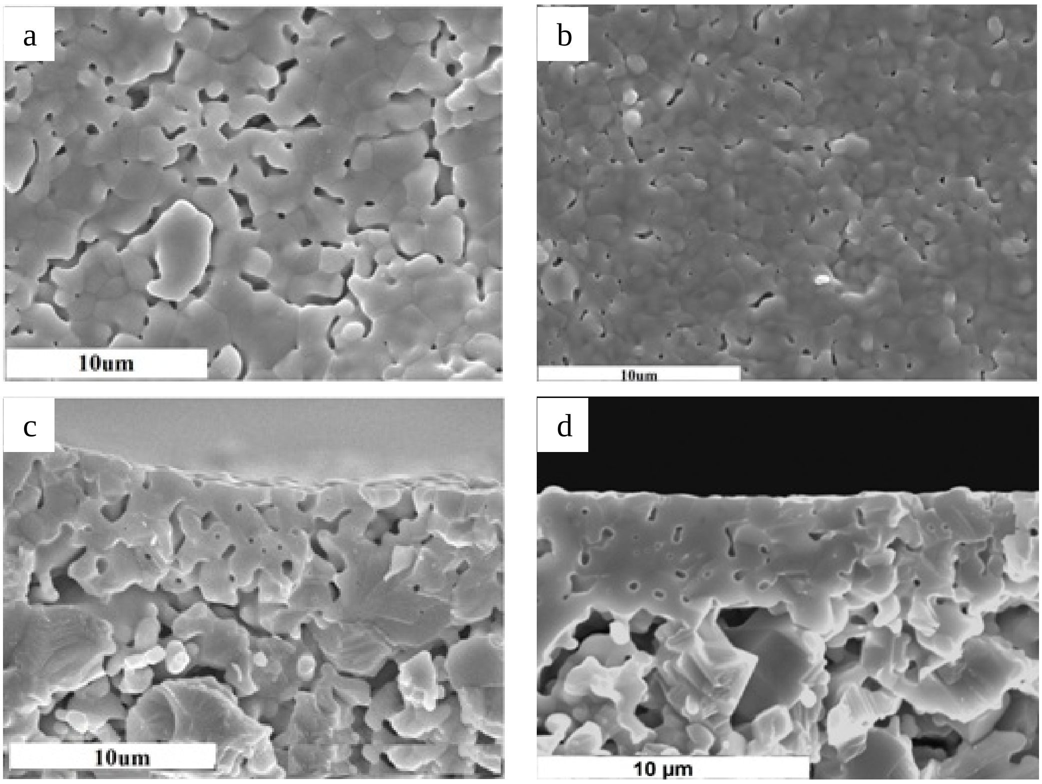

Fig. 4 Microstructures of sintered films YSZ on NiO-YSZ at 1400 °C for 3h: surface (a and b) and cross section (c and d) : a) in ethanol and b) in ACAC suspension

The reason behind this is the change of substrate from a conductive stainless steel to a non conductive NiO-YSZ substrate causing the reduction in the deposition rate of both films. The proper deposition condition found from using ethanol and solvent on a stainless steel substrate does not represent a fine condition for ethanol and NiO-YSZ. On the other hand, the reduced deposition rate turns to be adequate for producing acceptable YSZ film on a NiO-YSZ substrate with the use of ACAC. Iodine-dissolved ACAC was also used by Hosimi (2007) to deposit the YSZ film on porous NiO-YSZ, but it was reported that iodide might increase too many bubbles on the substrate and interfere with the film formation. In our case, the small addition of iodine can deposit rather-dense film on NiO-YSZ. The difference may lie on the fact that a higher volt (400 V) that Hosimi used may facilitate electrolytic decomposition of an electrolyte and may cause gas bubbles to form on a substrate surface. Cross-sectional SEM images hardly reveal through pores on the film in our iodide/ACAC case.

Achieving a thin and dense film on a substrate with rough surface is not a minor task, since the film has to fill up certain substrate depth before completing the full film. At this point, the perfectly dense film without pores on the non-conductive substrate cannot be attuned with the investigated conditions. Further exploration to get a better film quality is being pursued.

Conclusion

A dense YSZ film, deposited electrophoretically on a non-conducting NiO-YSZ substrate, was obtained in only 20 s using ACAC with 0.1 g/L iodide solution. This electrolytic formula produces a dense film without the prevalence of through-holes across the film so it can promisingly be employed to fabricate an SOFC half-cell comprising an YSZ electrolyte and a porous NiO-YSZ anode. Fine tuning on the deposition is under investigation to further improve the film density.

Acknowledgements

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