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Electrochemical properties related to the thickness control of the solid oxide fuel cell component layer using decalcomania paper

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Abstract−We fabricated anode-supported solid oxide fuel cells using decalcomania paper. To investigate the changes in thickness of the component layer and electrical properties in a unit cell, the number of layers of cathodes and the electrolyte decalcomania paper is changed. As a result, the thickness of the electrolyte and cathode layer regularly increases with an increase in the number of decalcomania papers attached. In addition, when only one electrolyte decalcomania paper is attached to an anode support, a tight and dense 8 μm electrolyte layer is obtained. A unit cell with a cathode thickness of 120 μm to which decalcomania paper is attached nine times is shown to have an open circuit voltage (OCV) of 1.08 V and a maximum power density (MPD) of 902 mW cm^{-2} at 800 °C.

Keywords: Solid Oxide Fuel Cells, Decalcomania Method, Cathode Thickness, Cell Performance, Electrolyte Thickness

INTRODUCTION

As a future energy source, solid oxide fuel cells (SOFCs) are highly efficient and can be used directly without fuel reformers for various fuels and pollution-free operations [1]. However, high-temperature operation over a long time will incur many problems such as limited material selection, high material cost, and fast performance degradation of cell components [2]. The advantages of a reduced temperature operation for SOFCs include wider material selection, better long-term stability, and potentially reduced fuel cell costs. Thus, the current trend for electrolyte and electrode development is to reduce the working temperature to the intermediate range (600-800 °C) [3].

In the case of the electrolyte, lowering the operating temperature significantly increases electrolyte resistivity and decreases ionic conductivity [4]. One solution for these problems is to use alternative electrolyte materials with higher ionic conductivity than Y_2O_3-stabilized ZrO_2 (YSZ), which is mainly used at high temperatures [5,6], including doped ceria and doped $LaGaO_{3-\delta}$; the other is to use a thin YSZ electrolyte [7-10]. In addition, in the case of the electrode, for intermediate-temperature SOFCs with a thin-film electrolyte, cathode performance is a very large portion of cell total performance. Thus, to control the thickness of the electrode and the length of the triple phase boundary (TPB), cathode electrodes have been studied not only in terms of chemical composition, but also in relation to the structural properties of the electrodes, such as porosity and thickness [11-15].

In these studies, the electrolyte and electrode layers are manufactured using wet coating methods such as tape casting [16], vacuum slip casting [17], screen printing [18,19], and dip coating [20]. If preparing electrolytes for this process, the electrolyte layer thickness must be more than 10 μm [21]. However, the electrolyte layer thickness formed by conventional methods as mentioned above is not thin enough to maintain ionic conductivity of electrolyte in the intermediate operating temperature range of SOFC [22].

To overcome these limitations, we used the decalcomania method for easy control of layer thickness. This method involves the transfer of designs from specially prepared paper to a wood or glass or metal surface. This method is expected to have some advantages because it is easy to prepare materials of the desired shape and size such as tube, planar and flat tube type; previously made electrolyte layer on the decalcomania paper can be attached simply on the various shapes such as a curved surface, edge and corner part. Thickness of the electrolyte, also, can be controlled easily by the number of attaching times.

In this study, the decalcomania method was developed to fabricate component layers of varying thickness through changes in the number of coatings. Then, cell performance was investigated at various thicknesses.

EXPERIMENTAL

1. Fabrication of Decalcomania Papers

To prepare suitable component layer with decalcomania paper, we selected commercial sources of ceramic materials. The electrolyte powder was prepared YSZ (TZ8Y, Tosoh Co., Japan). The YSZ median particle size (D50) was manufactured to be 3 μm by calcination at 1,200 °C for 2 h, and was controlled by attrition mill for 10 h. The cathode powder was prepared with $La_{0.7}Sr_{0.3}0MnO_3$ (LSM, d50=0.3-0.6 μm, Fuel Cell Materials, USA), and then activated carbon (charcoal activated, particle size <60 μm, MERCK, Germany) was added at 15 wt% as a pore former. Electrolyte paste was manufactured with a rate of raw materials to the benzene series binder of 1 to 0.7, while the cathode paste had a rate of raw materials to the benzene series binder of 1 to 0.5. Each component paste was printed on specialized decalcomania paper (Tullis Russell Coaters Korea)

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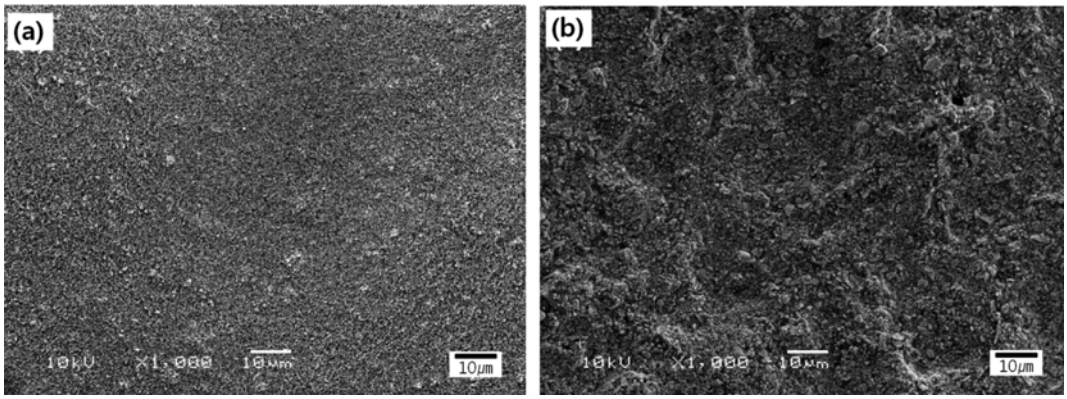

Fig. 1. SEM images of surface of decalcomania paper of component layer (a) electrolyte (b) cathode.

using a screen printing machine (DSP-380VS, Republic of Korea) and then dried in a dryer at 40 °C for 24h.

2. Design and Fabrication of Anode-supported Unit Cells

To study changes in layer thickness and electrical properties, unit cells were prepared by varying the number of attachments of decalcomania paper with the electrolyte and cathode. First, to measure the changes in thickness according to the number of layers of electrolyte decalcomania paper, three unit cells were fabricated, for which one layer of electrolyte decalcomania paper was applied to the anode support of the unit cell, and two and three layers were applied to the anode supports of the other unit cells.

The powder was mixed in a proportion of 52 wt% NiO, 35 wt% 8YSZ, and 13 wt% activated carbon to make the anode support. The mixing powders were compacted under uniaxial pressure to form a disc. The green anode discs were ~25 mm in diameter and ~1 mm in thickness. The green anode discs were pre-sintered at 1,200 °C for 2 h in air to provide adequate strength for anode support. Electrolyte decalcomania papers were taken off of the specialized decalcomania paper, and then attached 1, 2, and 3 times onto pre-sintered anode supports. They were then heated slowly at 1 °C min^{-1} to 400 °C for binder burn out, followed by heating at 3 °C min^{-1} to 1,400 °C and the maximum heat was maintained 10 h. After detaching the cathode layer on the laminated electrolyte from the decalcomania paper and attaching them with three layers, binder burn out was achieved by raising the temperature to 600 °C at 1 °C min^{-1}. Next, the temperature was raised to 1,200 °C at 100 °C h^{-1}, and the temperature was maintained for 2 h, so that unit cells with an electrode area of Φ 10 mm were fabricated. To measure the changes in thickness according to the number of cathode layers, it was necessary to measure the thickness when the cathode layers were laminated on the dense electrolyte, so that the electrolyte support was used. After seven kinds of cathode layers were added, which ranged from the first to the seventh layer, on the electrolyte support, it was treated by heating according to the same schedule as sintering schedule of cathode. After the change in thickness of the electrolyte and cathode was identified, three unit cells were fabricated, for which one layer of electrolyte decalcomania paper and then 5, 7, and 9 layers of cathode decalcomania paper were attached to the anode support of the unit cell, so that the property of output according to the changes in thickness of the cathode was identified.

3. Physical and Electrochemical Characterization

The surface of the decalcomania paper and the changing of layer thickness and cathode microstructure in the unit cells created by the decalcomania method were examined by a field emission scanning electron microscope (FE-SEM, Hitachi, S-800, Japan). A cell test measured the current-voltage characteristics at 750 °C and 800 °C while supplying 3% humidified 97% H_2 500 sccm and O_2 1,000 sccm to the anode and cathode, respectively. The cell test equipment used was the SOFC Button Cell Test Station (Nara Cell Tech, Republic of Korea).

RESULTS AND DISCUSSION

Cell performance is greatly influenced by the microstructure of electrodes [23]. Accordingly, we selected a decalcomania method that enabled uniform distribution of particles at the electrode, so that the screen printing of components on specialized decalcomania paper could be carried out.

When the particles were evenly distributed in decalcomania paper, a uniform microstructure could be obtained after sintering. Fig. 1 shows a decalcomania paper where the particle distribution was checked. In case of electrolyte decalcomania paper to form the electrolyte layer that it has to be thin and dense, the particles were distributed evenly, the surface was very homogeneous, whereas the surface of cathode decalcomania paper was very inhomogeneous. This

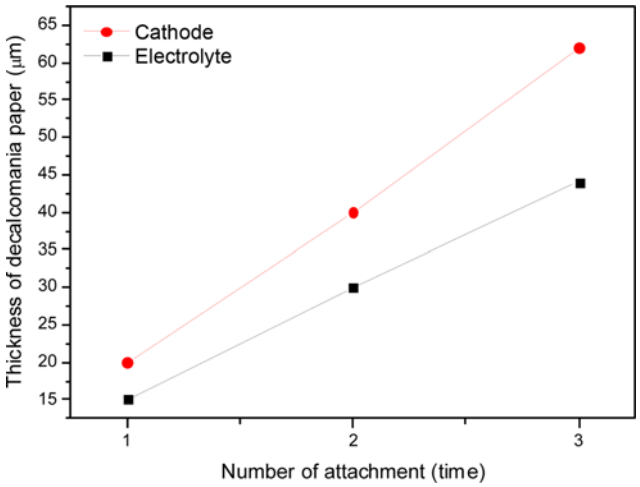

Fig. 2. Thickness change according to the number of attached decalcomania papers after drying.

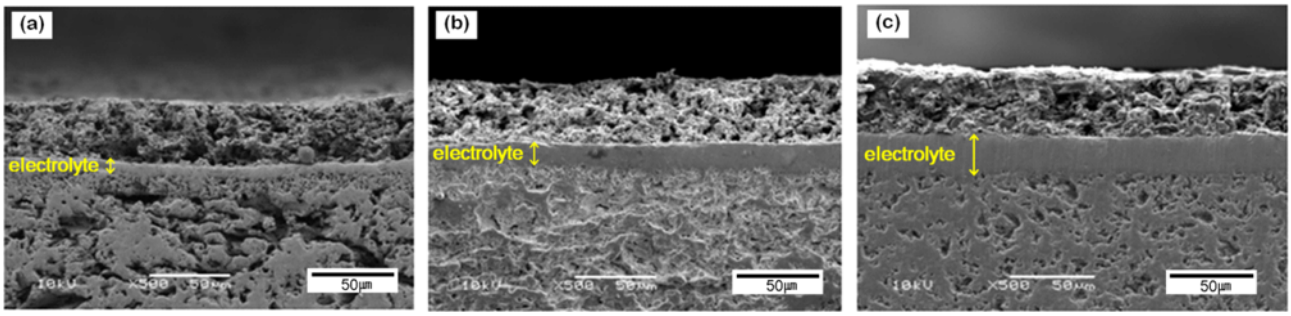

Fig. 3. SEM images of anode-supported unit cells according to the number of attachments of the electrolyte layer (a) once, (b) two times, (c) three times.

result seems to be influencing the control of the particle size, as electrolyte was controlled the particle size by crushing after calcination of commercial powders, whereas cathode included activated carbon particles as large and nonuniform. Therefore, control the particle size is needed in order for homogeneous pore formation for the cathode.

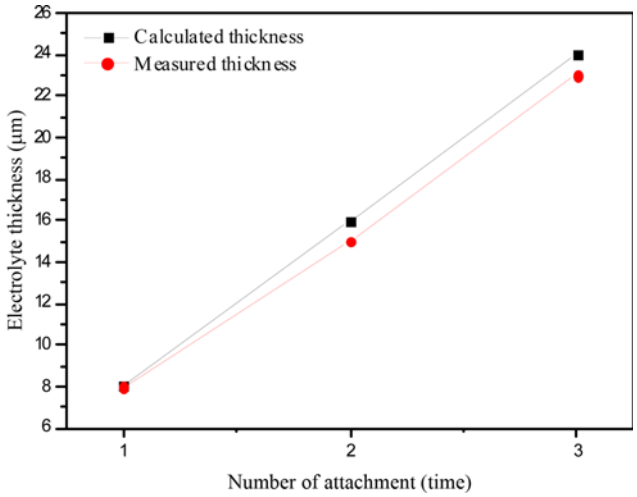

Fig. 4. The calculated and measured thickness after sintering according to number of layers of electrolyte decalcomania paper.

Fig. 2 shows the thickness change after drying decalcomania papers according to the number of attachments. When the attachment number was increased due to 1, 2, and 3 layers of dried electrolyte decalcomania paper, the paper thickness was increased regularly to 15 μm, 30 μm, and 44 μm, respectively. When the attachment number was increased due to 1, 2, and 3 layers of dried cathode decalcomania paper, the paper thickness increased regularly to 20 μm, 40 μm, and 62 μm, respectively. Through this process, the increase in thickness of decalcomania paper was in proportion to the number of attachments, so that it was possible to estimate the thickness of the required component layer by adjusting the number of attachments.

Fig. 3 shows the SEM images of a cross-section of the cells when

Table 1. Calculated and measured thickness after sintering according to number of layers of electrolyte decalcomania paper

Thickness (μm) \ Number of layers	1	2	3
Calculation	8	16	24
Measurement	8	15	23
Difference	0	+1	+1

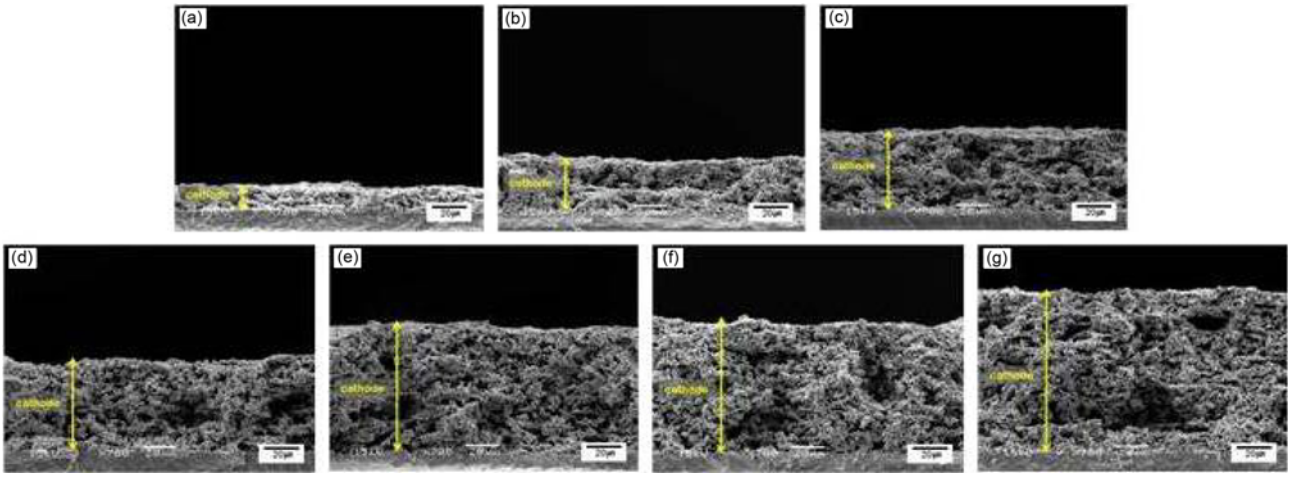

Fig. 5. SEM images of anode-supported unit cells according to the number of layers of the cathode layer (a) once, (b) two times, (c) three times, (d) four times, (e) five times, (f) six times, (g) seven times.

unit cells were sintered after the attachment number of the electrolyte decalcomania paper was changed from once to three times. The results are confirmed in the cross-section of cell, when the attachment number was increased at 1, 2, and 3 times with dried electrolyte decalcomania paper of 15 μm thickness; the sintered electrolyte layer thickness was regularly increased at 8 μm, 15 μm, and 23 μm, respectively (Fig. 2).

Fig. 4 and Table 1 show the aspects of calculated and measured values by measuring the thickness of laminated electrolyte on the actual unit cells, when the increasing thickness according to the number of attachment was established as calculated values on the basis of thickness of electrolyte of cells, which was sintered after attachment of one layer of electrolyte decalcomania paper. There was up to a 1 μm difference between the calculated and measured thickness, so the calculated and measured thicknesses were similar.

Fig. 5 shows the SEM images of a cross-section of the unit cells when the coating number of the electrolyte decalcomania paper was changed from one to seven times. When the attachment number was increased from one to seven times with dried cathode decalcomania paper of 20 μm thickness, the sintered cathode layer thickness increased regularly at 13.3 μm, 27.9 μm, 41.3 μm, 52 μm, 68 μm, 78.6 μm, and 93.1 μm, respectively. On the basis of the thickness of the cathode of sintered cells after one attachment of cathode decalcomania paper, as the calculated value, we took the thickness—which had increased according to the number of attachment of decalcomania paper after sintering—and then calculated and measured the values by measuring the thickness of laminated cathode on actual unit cells. These results are presented in Fig. 6 and Table 2. There was up to a 1.5 μm difference between the calculated and measured thicknesses, so that the calculated and measured thicknesses

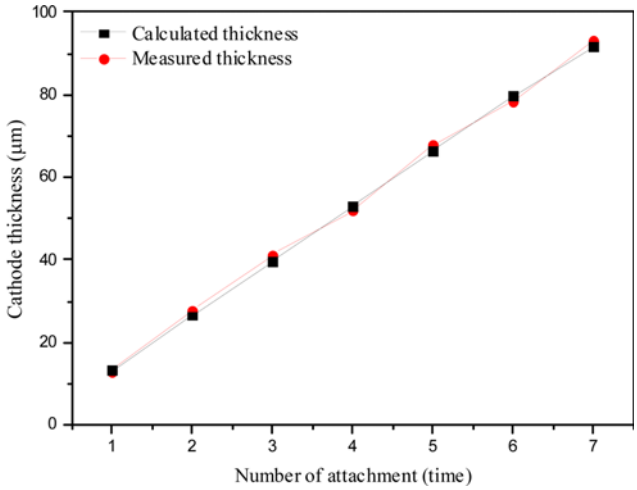

Fig. 6. The calculated and measured thickness after sintering according to number of layers of electrolyte decalcomania paper.

Table 2. Calculated and measured thickness after sintering according to number of layers of cathode decalcomania paper

Thickness (μm) \ Number of layers	1	2	3	4	5	6	7
Calculation	13.3	26.6	39.9	53.2	66.5	79.8	91.8
Measurement	13.3	27.9	41.3	52	68	78.6	93.1
Difference	0	−1.3	−1.4	+1.2	−1.5	+1.2	−1.3

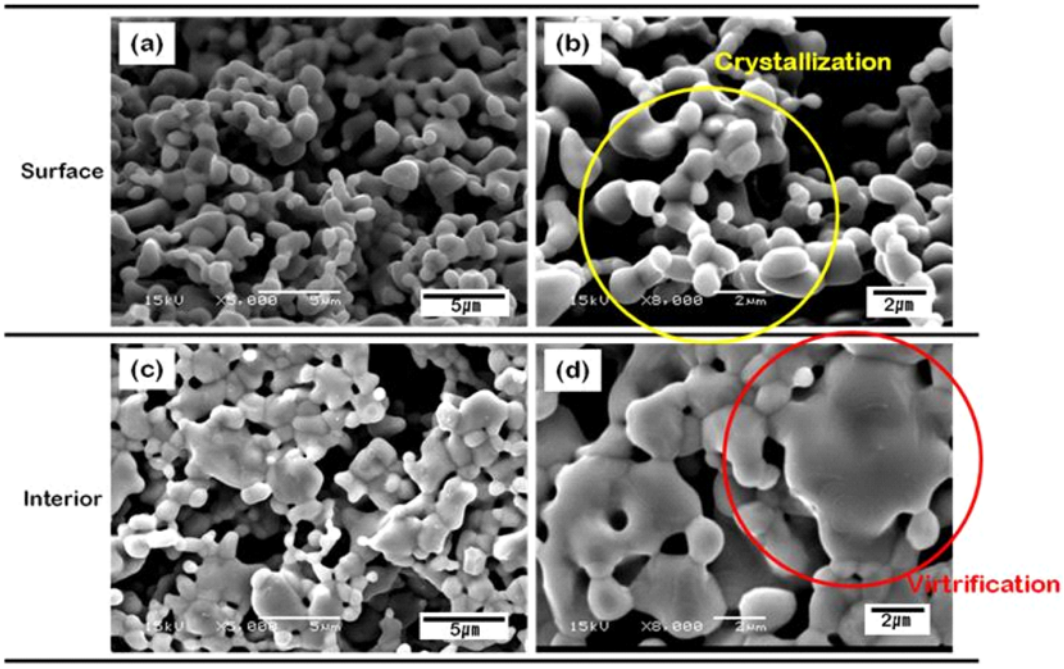

Fig. 7. SEM images of microstructure of the interior ((a) and (b)) and surface ((c) and (d)) of the cathode layer.

were similar.

Fig. 7 shows microstructures of particles of LSM according to their position within the cathode. Figs. 7(a) and (b) represent the interior, and (c) and (d) the surface of the cathode layer. In the case of the interior of the cathode layer, crystallized particles were formed, as the grains could be identified. In contrast, in the case of the surface of the cathode layer, this provided additional verification, because the surface temperature was relatively higher due to the direct heating during sintering. Thus, the increasing thickness of the electrode according to the number of attachments of decalcomania paper could not be calculated with complete accuracy, but it was shown to be similar through experimental results. Consequently, we concluded that the decalcomania method, which enables easy adjustment of the thickness of the component layer, is the optimal method for the design and fabrication of SOFC.

A thin layer of electrolyte increases ionic conductivity. The experiments by Haanappel et al. [24] showed that a cathode thickness of at least 45-50 μm was required for optimal cell performance. Thus, electrolyte decalcomania paper was attached once to form the thinnest electrolyte layer, and then cell performance was measured according to cathode thickness by changing the number of attachments of cathode decalcomania to 5, 7, and 9 layers. As a result, the thickness of the electrolyte layer was 8 μm and the thicknesses of the cathode layer were 68 μm, 93 μm, and 120 μm, respectively. Fig. 8 gives the cell performance according to the thickness of the cathode at 750 °C and 800 °C. When the cathode thicknesses were 68 μm, 93 μm, and 120 μm, the open circuit voltages (OCVs) were 1.05 V, 1.07 V, and 1.05 V, and the maximum power densities (MPDs) were obtained 283 mW cm^{-2}, 508 mW cm^{-2}, and 763 mW cm^{-2}, respectively, at 750 °C. At 800 °C, the OCVs were 1.09 V, 1.05 V, and 1.08 V, and the MPD were obtained 377 mW cm^{-2}, 735 mW cm^{-2}, and 902 mW cm^{-2}, respectively. When OCV was checked of cell, a thin and dense electrolyte layer formation was found with just once attaching of electrolyte paper. Also, cell performance increased according to the increase in cathode thickness. The reason for the cell performance improvement seems to be the increased active reaction sites due to the thickness increase of the cathode electrode. Therefore, in this study, 120 μm thickness of the cathode layer was found to generate the most effective cell performance.

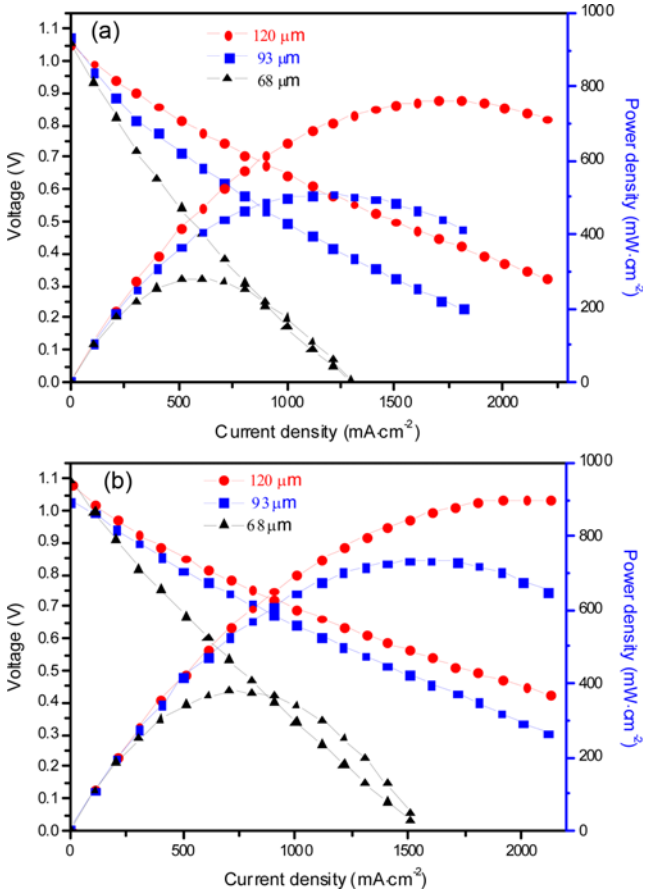

Fig. 8. Current-voltage characteristics for unit cells according to different cathode layer thicknesses, at (a) 750 °C and (b) 800 °C.

CONCLUSIONS

The component layer of SOFC electrode was prepared by decalcomania method. The thickness of the each layer was linearly changed by the number of attachments of decalcomania paper. After attaching one, two, and three layers of 1 μm thick electrolyte decalcomania paper to each of three unit cells, the thicknesses of the sintered layers on the unit cells increased to 8 μm, 15 μm, and 23 μm, respectively. After attaching and sintering 20 μm thick cathode decalcomania paper, ranging from one to seven layers, the thickness of electrode had proportionally increased to 13.3 μm, 27.9 μm, 41.3 μm, 52 μm, 68 μm, 78.6 μm, and 93.1 μm, respectively. Therefore, the desired thickness could be easily obtained by the decalcomania method. The evaluation of cell performance revealed the MPD of 377 mWcm^{-2}, 735 mWcm^{-2}, and 902 mWcm^{-2}, respectively, at 800 °C. The SOFC prepared in this study showed equivalent or better performance than SOFC prepared by conventional method, which supports the promise of the decalcomania method as a competitive and cost-effect way of preparing SOFC cell.

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