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Letter

Fabrication of nanoporous metal electrode by two-step replication technique

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Abstract

Nanoporous Ni metal membrane was fabricated by using nano-technique (two-step replication) from porous anodic alumina (PAA) template. In the first step replication, poly(methyl methacrylate) (PMMA) with various concentrations and molecular weights was filled into PAA mother template to obtain PMMA negative-type cylindrical structure. The results indicate that the increasing concentration and molecular weight of PMMA is required to fabricate satisfactory PMMA negative-type cylindrical structure due to the higher intermolecular interaction of molecular chains. The higher intermolecular interaction provided better strength to maintain the desired PMMA negative-type cylindrical structure. In the second step replication, Ni was electrochemically deposited into the PMMA cylindrical structure. After removing PMMA by acetone, nanoporous Ni metal membrane was obtained. The morphology of nanoporous Ni membrane was similar to that of PAA mother template. A film of yittria-stabilized zirconia (YSZ) electrolyte can be finally deposited on the Ni metal membrane by EPD process. This metal membrane might be used as an electrode in the applications of solid electrochemical devices.

Keywords: PAA; PMMA; Two-step replication; Electrochemical deposition; Nanoporous structure

1. Introduction

Nanoporous metal membrane may be used as a permeable support for numerous applications such as gas electrodes, catalysts, chemical reactors, etc. For example, in our concern, the metal membrane exhibits several advantages such as (i) the channels of porous membrane may be used as the passageway for reactive gas, (ii) it exhibits good electrical conductivity for the electron conduction, and (iii) it exhibits sufficient strength to be used as a substrate to deposit solid electrolyte on, therefore, it might be used in the applications of solid oxide fuel cells (SOFCs).

Recently, template-assisted method has been developed mainly for the fabrications of nano-structures such as nanodots, nanorods, nanowires and nanotubes [1–4]. Based on template-assisted method, nanohole-array membranes of metal [5–8] and semiconductor [9] can be fabricated by two-step replication technique. Two-step replication process is capable of forming materials with nanoporous configuration as the porous anodic alumina (PAA) which is a typical self-organized hole-array structure [5–9]. Basically, the two-step replication consists of two parts: (i) the fabrication of negative-type poly(methyl methacrylate) (PMMA, which is usually used as the filling material due to its great chemical stability) from PAA template and (ii) the subsequent deposition of desired materials into the cavity of the PMMA negative-type matrix by electrochemical deposition (ECD) or electrophoresis deposition (EPD).

In this report, first, nanoporous PAA template with pore diameter about 100 nm was fabricated from Al foil by anodization. The effect of PMMA concentrations and molecular weights on replication of negative-type PMMA was discussed. Then, the Ni metal membranes were obtained from the negative-type PMMA template by electroplating. After removing the PMMA by acetone, Ni metal membrane could be obtained. Finally, a yittria-stabilized zirconia (YSZ) film was deposited on the Ni membrane by EPD. The 8YSZ film/nanoporous Ni metal membrane structure might be applied in the applications of thin-film SOFCs.

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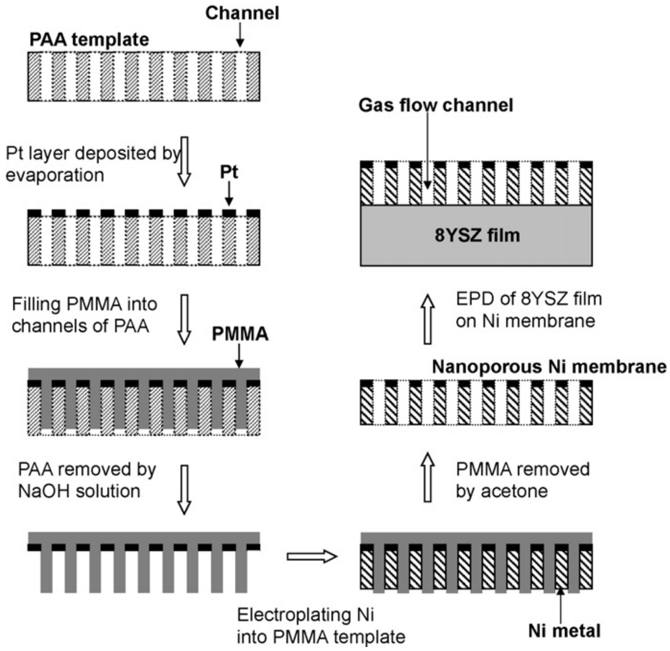

Fig. 1. Schematic representation of using two-step replication technique to fabricate nanoporous Ni membrane and 8YSZ/Ni membrane structure.

2. Experimental procedure

Nanoporous metal membrane was obtained by a two-step replication technique. The whole steps of two-step replication are represented in Fig. 1. First, the porous anodic alumina (PAA) template was obtained by anodization of Al foil (Alfa, 99.997%) under 80 V in 0.3 M oxalic acid solution with a cooling circulation bath (13 °C). The PAA template with 100 nm diametered channels was finally separate from Al foil by $HgCl_2$ and the barrier layer was removed by 10 wt% phosphoric acid solution [10]. After fabricating the PAA template, a thin Pt layer was deposited on the surface of PAA template by evaporation for 10 min. This Pt layer was used as a current collector for the subsequent electroplating process. In the first step replication, PMMA solutions (PMMA dissolved in chlorobenzene) with various PMMA molecular weights (M_w = 15,000, 70,000, and 996,000 g/mol) and various concentrations were dropped on the Pt-coated PAA template to fabricate negative-type PMMA cylindrical structure. After the evaporation of the chlorobenzene and polymerization of PMMA, the PAA template can be removed by 5 M NaOH solution and then a replicated negative-type PMMA with cylindrical structure can be obtained. After removing PAA template, the Pt layer previously coated on PAA surface can be transferred to the replicated PMMA cylindrical structure and was used as a current collector for the second step replication. In here, the second step replication was electroplating Ni into the cavity of PMMA negative-type cylindrical structure in a solution consists of $NiSO_4 \cdot 6H_2O$ (330 g/L), $NiCl_2 \cdot 6H_2O$ (45 g/L), and H_3PO_3 (35 g/L). The electroplating process was carried out at −0.9 V versus Ag/AgCl reference electrode. After Ni electroplating, negative-type PMMA cylindrical structure can be removed by acetone and the nanoporous metal membrane was obtained. Because of the nanoporous Ni metal membrane can be used as the support and electrode for thin-film SOFCs. Therefore, a film of 8YSZ was finally deposited on the metal membrane by EPD at −40 V for 5 min. The solution for EPD is an 8YSZ suspension (10 g/L) consists of 8YSZ particles (Tosol, ∼Ø200–500 μm) disperse in a mixture of acetone and ethanol (3:1, v/v). In addition, iodine (0.6 g/L) added into the suspension is helpful to increase the conductivity of 8YSZ suspension and enhance the deposition rate.

In order to understand the effect of the concentration and molecular weight (M_w) of PMMA on the fabrication of PMMA negative-type cylindrical structure, the viscosity of PMMA solution was conducted by Brookfield viscometer (DV-II+Pro). The morphologies of the PAA template, replicated PMMA negative-type cylindrical structure, nanoporous metal membrane, and the cross-sectional image of 8YSZ film/Ni membrane were observed by scanning electron microscope (Hitachi, S4100).

3. Results and discussion

3.1. Fabrication of PAA template

In order to fabricate porous metal membranes by using two-step replication technique, anodizing the Al foil to form PAA mother template is the first task. Fig. 2(a) shows the SEM top-view image of the home-made PAA template. In previous work, highly ordered PAA template can be obtained either by one-step anodization of electropolished Al foil or by repeated anodization of nonelectropolished Al foil in 0.3 M oxalic acid solution under specific voltage (40 V) [11]. However, in order to speed up the anodization process to obtain a PAA template with desired thickness (∼60 μm), the anodization in this study was carried out at 80 V. Therefore, the pores does not arrange orderly in large area and show irregular shapes (Fig. 2(a)) are

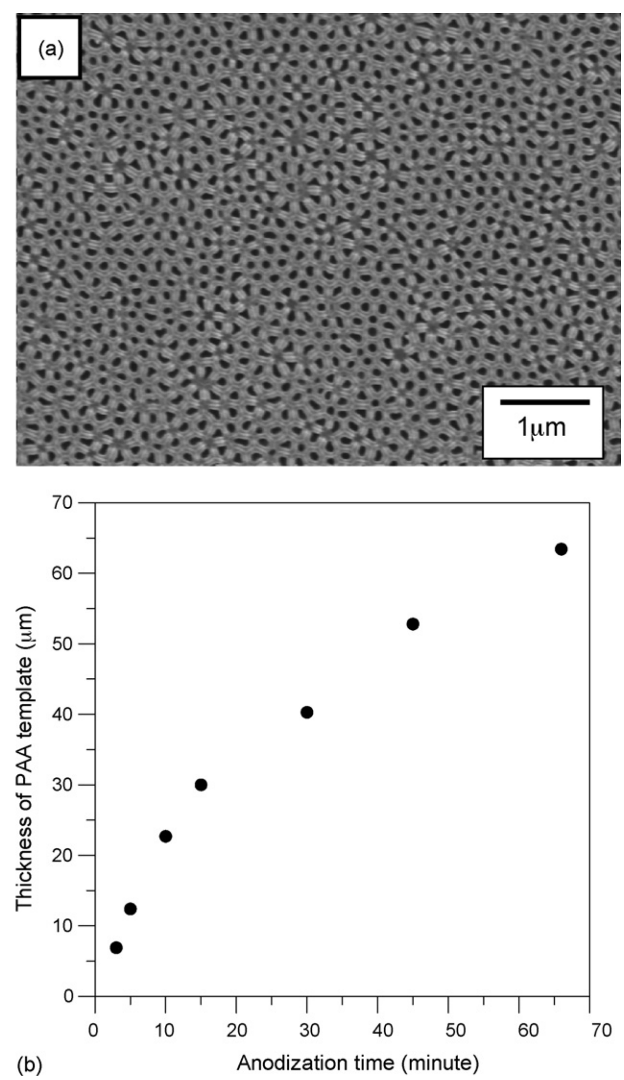

Fig. 2. (a) SEM top-view image of PAA template. (b) PAA thickness plotted as a function of anodization time.

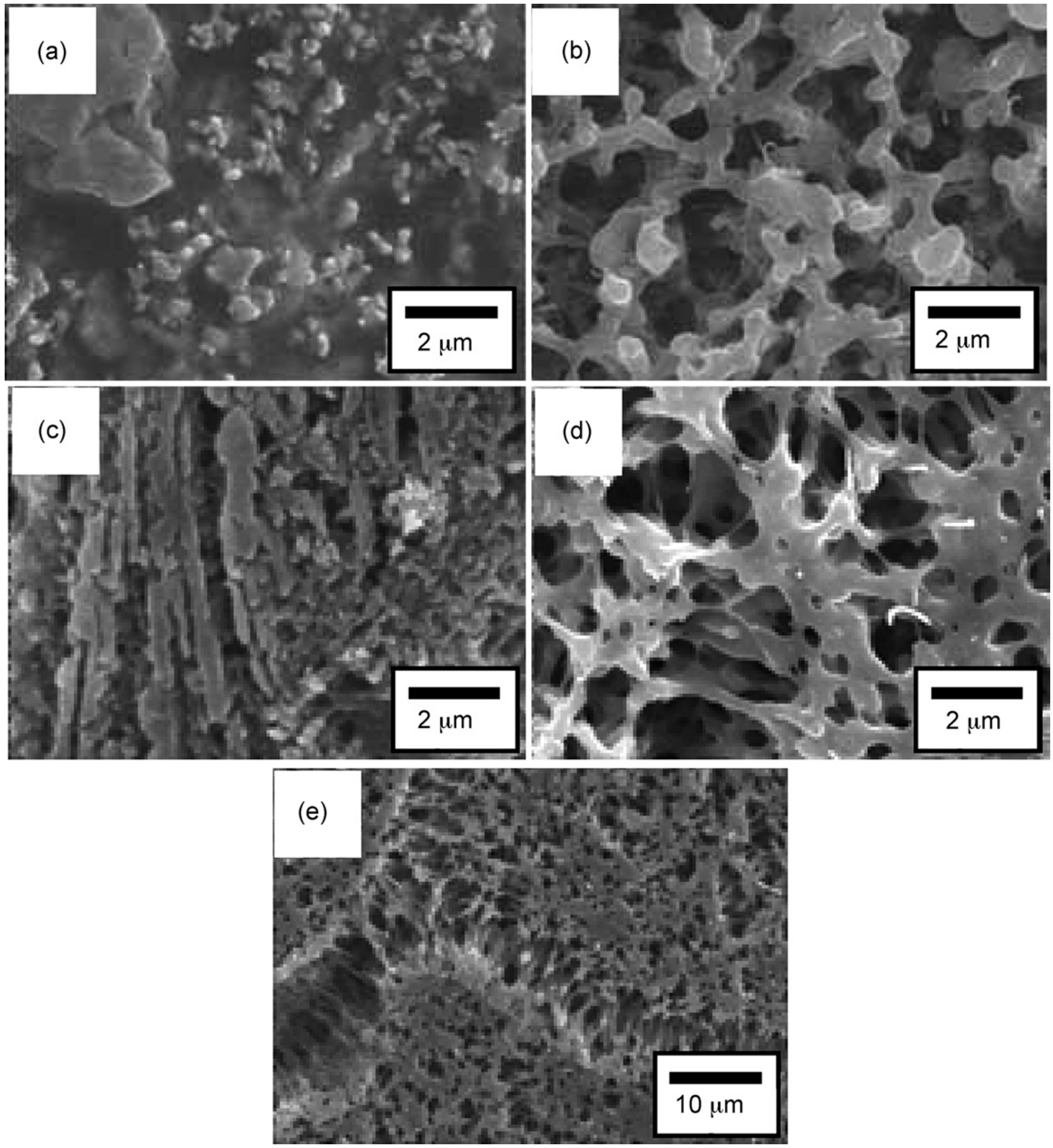

Fig. 3. SEM top-views of replicated negative type of PMMA (M_w = 15,000 g/mol) that fabricated with various concentrations: (a) 10 wt% and (b) 15 wt%. SEM top-views of replicated negative-type structures of PMMA (M_w = 70,000 g/mol) that fabricated with various concentrations: (c) 10 wt% and (d) and (e) 15 wt%.

attributed to the higher anodization voltage. After anodization, the PAA thickness was plotted as a function of anodization time (Fig. 2(b)). In this figure, the anodization could be divided into two regions. The anodization rate in the initial 10 min is about 2.4 μm/min. And then, the anodization rate reduces to about 1 μm/min when anodization period extends to 10–60 min. The decreasing of anodization rate is due to the increasing length of PAA channel which increases the diffusion path of the dissolve species and then suppresses the further anodization rate. This result indicates that the anodization rate at initial stage is not strongly affected by the length of PAA channel. However, when the length of PAA channel is longer than about 24 μm, the anodization rate is suppressed into a steady state.

3.2. Fabrication of PMMA cylindrical structure from PAA template

In order to obtain the same porous structure as PAA template, two-step replication process was accepted. In the first step replication, it is performed by filling PMMA into the pore structure of PAA mother template. In order to obtain satisfactory PMMA negative-type cylindrical structure, PMMA solutions with various PMMA molecular weights and concentrations were tried to fill the PAA template.

Fig. 3(a) and (b) shows the SEM micrographs of replicated PMMA negative-type structures by using various concentrations (10 and 15 wt%) of PMMA (M_w = 15,000 g/mol). After removing the PAA template by 5 M NaOH, the remaining PMMA does not show cylindrical structure but shows discontinuous and porous structure instead of the desired cylindrical structure. This structure could not be used for the second step replication to electroplate nanoporous metal membrane. Thus, PMMA M_w was increasing to 70,000 g/mol to prepare the PMMA solutions. Fig. 3(c)–(e) shows the SEM observations of replicated negative-type PMMA obtained from PMMA (70,000 g/mol) solutions with various concentrations. In Fig. 3(c), the PMMA cylindrical structure is still not observed by filling 10 wt% PMMA solution into PAA template. But as the PMMA (M_w = 70,000 g/mol) concentration increasing to 15 wt%, the wire-like structure gradually forms in some area (Fig. 3(d) and (e)). In these figures, because of the Van der Waals' force, the aggregation of PMMA wires can be observed. The significant improvement of replicated PMMA cylindrical structure is observed when the PMMA M_w increases from 15,000 to 70,000 g/mol, and, this result indicates that the increasing PMMA M_w is beneficial for the fabrication of replicated PMMA cylindrical structure. However, the cylindrical structure is only observed in some area and is still not satisfactory for the subsequent metal-electroplating process.

In order to obtain the desired cylindrical structure in a large area, PMMA M_w was finally increased to 996,000 g/mol. Fig. 4

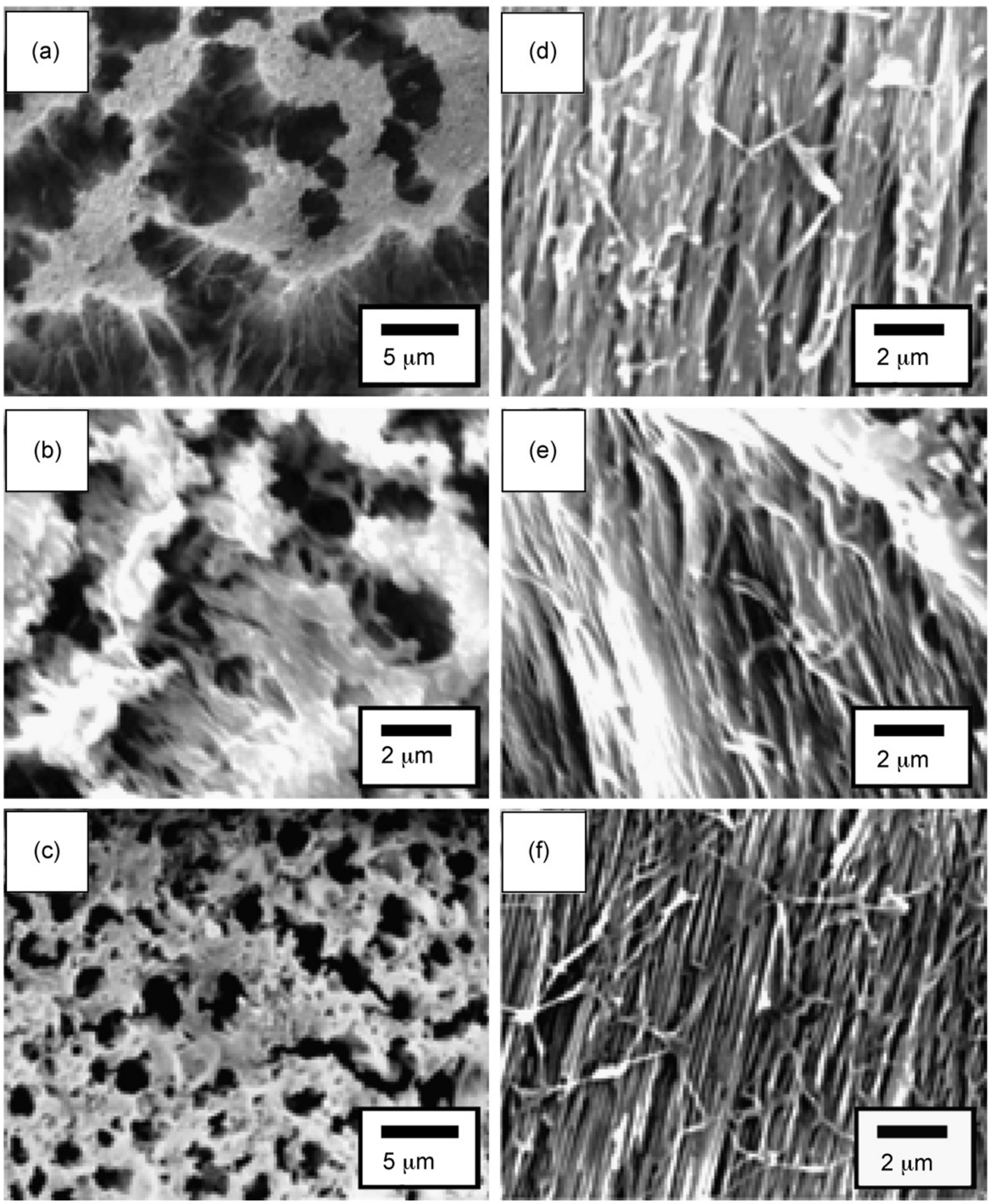

Fig. 4. Top-view images of PMMA nano-arrays fabricated at PMMA concentration of: (a) 10 wt%, (b) 13 wt%, (c) 15 wt%, cross-section images (d) 10 wt%, (e) 13 wt%, and (f) 15 wt% (PMMA M_w = 965,000 g/mol).

Table 1
The dependence of PMMA solution viscosities on various concentrations and molecular weights

PMMA concentration (wt%)	PMMA molecular weight (g/mol)		
	16,000	70,000	996,000
10	5.94	15.13	117.67
13	7.38	24.92	401.91
15	8.64	37.56	892.32

Viscosity unit: cP.

shows the replicated negative-type PMMA cylindrical structure fabricated by using PMMA with M_w is 996,000 g/mol. Fig. 4(a)–(c) are top-view and Fig. 4(d)–(f) are cross-sectional images of replicated negative-type PMMA obtained from 10 to 15 wt% PMMA solutions, respectively. From the top-view observations, the aggregation of PMMA nanowires is observed due to the Van der Waals' force between long PMMA nanowires. The cross-sectional images show that the PMMA nanowires with diameter of 100 nm was successful obtained by filling PMMA (996,000 g/mol) with various concentrations into PAA template. Because the large-area negative-type PMMA cylindrical structure was successfully obtained by using 996,000 g/mol PMMA, the subsequent electroplating (the second step replication) was carried out by using these replicated negative-type PMMA cylindrical structures as templates.

It is known that the viscosity of polymer solutions is involving many interacting variables, such as the polymer concentration and molecular weight [12,13]. In general, the viscosity can be regarded as a simple reference for the degree of molecular entanglement of polymers. Therefore, in other words, the entanglement of polymer molecules is relative to the polymer concentration and molecular weight. The viscosity of PMMA solutions with various concentrations and molecular weights was measured and shown in Table 1. In this table, the viscosity increases with the increasing PMMA concentration and molecular weight can be observed. The increasing PMMA viscosity with the increasing polymer concentration is attributed to the more molecules dissolve in the solvent that increases the chance of entanglement of molecules. Thus, the high-degree entanglement of molecules leads to the higher viscosity and higher strength to maintain the cylindrical structure. Therefore, the increasing concentration of PMMA solution is benefic to obtain satisfactory negative-type cylindrical structure.

Moreover, the molecular weight is generally based on the mass of polymer chain unit [13]. Therefore, the length of PMMA chain is relative and increasing with the M_w of PMMA. As a result of the low M_w PMMA exhibits short-chain molecules and shows low degree of PMMA entanglement, the intermolecular interaction of PMMA is too weak to maintain the cylindrical structure. Thus it forms intermittent and porous structure. As the M_w of PMMA increased, the viscosity is increasing due to the high-degree entanglement of PMMA molecules with long chain. Consequently, the stronger intermolecular interaction of PMMA is benefic to sustain the cylindrical structure, and, the desired negative-type PMMA cylindrical template can be obtained.

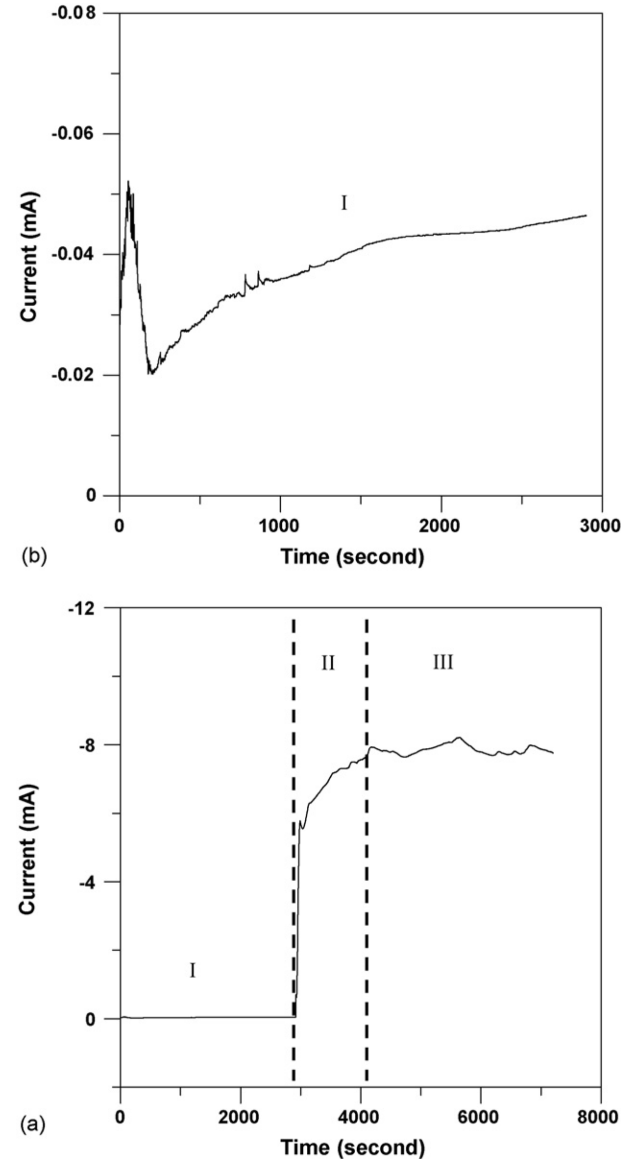

Fig. 5. The current transient curves for (a) long time and (b) short time (<3000 s) of Ni metal electroplating into the negative-type PMMA.

3.3. Fabrication of nanoporous Ni membrane and fabrication of 8YSZ film on Ni membrane

The second replication was performed by electroplating the desired material into the negative-type PMMA cylindrical structure (as a template) obtained previously. Fig. 5(a) shows the current transient curve of electroplating Ni membrane for the duration of 8000 s. In order to view closely within the initial electroplating period of 3000 s, region I of Fig. 5(a) is enlarged and shown in Fig. 5(b). The initial current transient (region I) shows a conventional electroplating behavior for filling materials into template [1,14]. The electroplating current quickly increases from −0.03 to −0.05 mA in the beginning and then drops back to −0.02 mA due to the consumption of electroplating species on the surface. Subsequently, the current slowly increases due to the electroplating species gradually diffuse to the electroplating surface. Finally, the current maintains at a

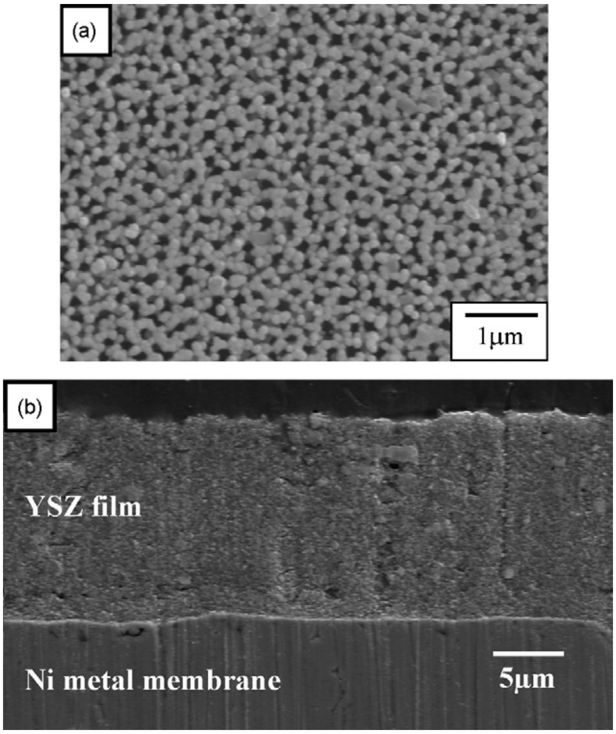

Fig. 6. (a) SEM top-view observation of Ni membrane fabricated by electroplating. (b) SEM cross-sectional image of 8YSZ film deposited on Ni membrane by EPD.

steady state due to the balance of consumption and supplement of the electroplating species. As a result, the metal is gradually deposited into the cavity of PMMA cylindrical-structured template. In region II (Fig. 5(a)), the rapid increasing current results from the interconnecting of deposited metal through the percolation point. The cavity of the replicated PMMA is filled with metal and the metal begins to form a thin and continuous metal layer over the top of replicated PMMA cylindrical-structured template. Thus, the conducting area for further electroplating is greatly enhanced and the current increases obviously. Finally, the current remains steady at ~ -8 mA as shown in region III. Based on the current transient of electroplating metal into the negative-type PMMA cylindrical-structured template, the thickness of metal hole-array membrane could be controlled.

By using the two-step replication technique, the Ni metal membrane is successfully fabricated as shown in Fig. 6(a). The nanopores observed from Ni membrane are similar to that of PAA mother template. However, some channels with diameter slightly larger than that of PAA template is due to the aggregation of PMMA wires in the negative-type cylindrical template. The nanoporous Ni membrane may be used as the substrate for YSZ thin-film deposition in SOFCs applications. The subsequent deposition of 8YSZ electrolyte on Ni membrane was carried out by EPD. Fig. 6(b) shows the cross-sectional image of the structure of 8YSZ film/Ni membrane. The thickness of the YSZ film is about 15 μm after EPD for 5 min. The YSZ film deposited by EPD is extremely dense and well adheres to the Ni metal membrane. The 8YSZ film is just coated on the surface of Ni membrane but not deposited into the channels. This result can be attributed to the 8YSZ particles are larger than the diameter of channel. The structure of YSZ film/Ni metal membrane may be used for SOFCs applications. The electrochemical property of this unique structure will be discussed in the near future.

4. Conclusion

PAA mother template fabricated by anodization Exhibits 100 nm diametered nanoporous structure. Low M_w (15,000 and 70,000 g/mol) PMMA cannot build up satisfactory negative-type cylindrical structure. The negative-type PMMA cylindrical structure was successfully obtained by increasing the molecular weight of PMMA to 996,000 g/mol. The higher molecular weight exhibits long-chain molecules and increases the degree of intermolecular entanglement. Consequently, the higher intermolecular interaction of polymers maintains the desired cylindrical structure. Nanoporous Ni metal membrane was obtained by electroplating Ni into the PMMA cylindrical template. The morphology of metal membrane is similar to that of PAA mother template. The nanoporous metal membrane may be used as electrode in SOFCs applications since the 8YSZ electrolyte can be deposited on the Ni metal membrane by EPD technique and shows well adhesive to the Ni membrane.

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