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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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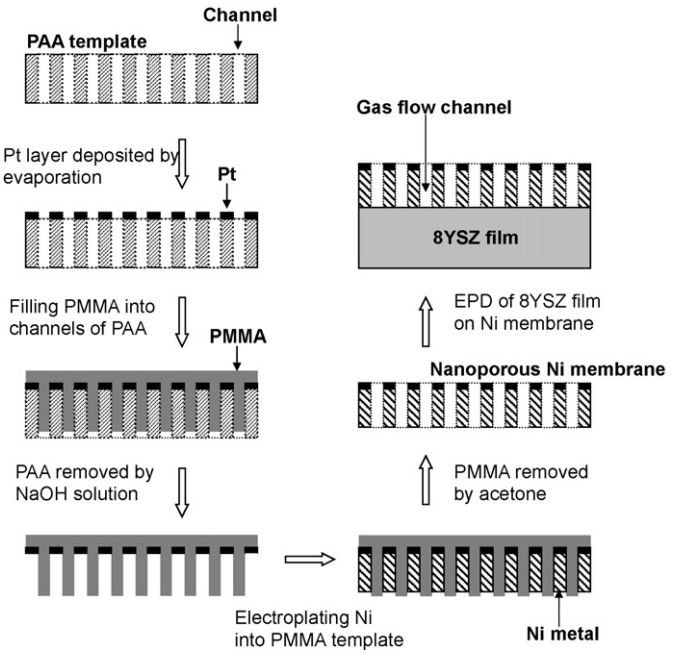

Fig. 1. Schematic representation of using two-step replication technique to fabricate nanoporous Ni membrane and 8YSZ/Ni membrane structure.

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

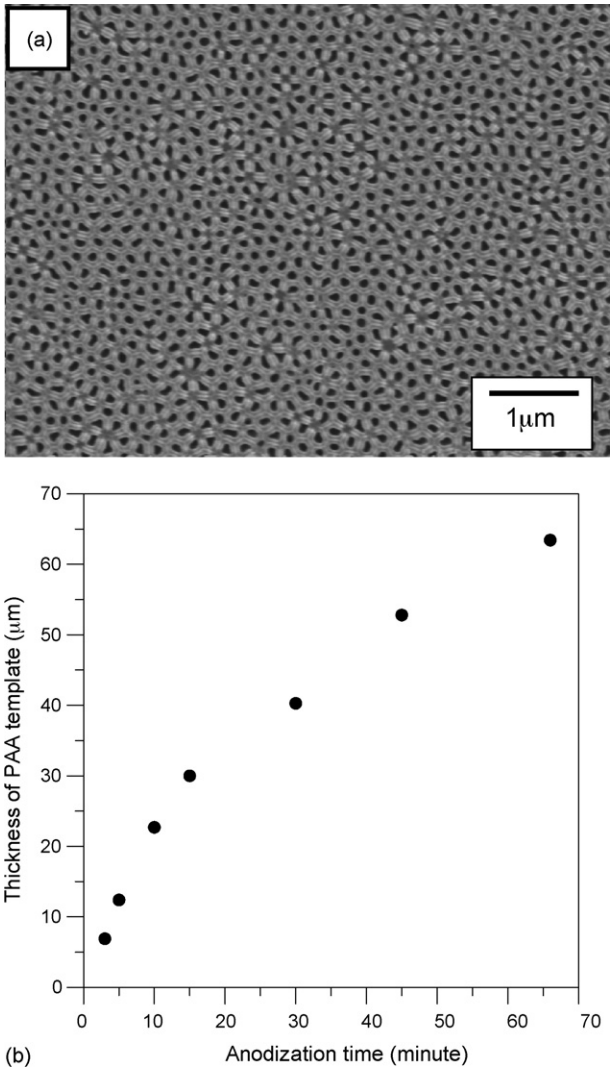

Fig. 2. (a) SEM top-view image of PAA template. (b) PAA thickness plotted as a function of anodization time.