



## Letter

# Anodization of dual-layer laminated aluminum foils: A facile route to through-hole porous anodic alumina templates



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## ABSTRACT

Porous anodic alumina (PAA) film with through-hole structure has been widely employed as a template or host material for the development of nanostructures. However, the fabrication of complete through-hole PAA film in a controlled and reproducible way is still a challenge to date. Here, we report a facile method to fabricate the through-hole PAA templates. A dual-layer laminated aluminum foil rather than the generally used single-layer aluminum foil was employed to achieve this goal. The idea behind this approach is to transfer the oxide barrier layer to the second-layer foil of the dual-layer aluminum foil, thereby directly obtaining a PAA film with no barrier layer in the first-layer foil. A qualitative explanation for the transition behavior of anodization voltage of the dual-layer aluminum foil during galvanostatic anodization was given. Also, this study may aid a deeper understanding of the mechanism for PAA formation.

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## 1. Introduction

Porous anodic alumina (PAA) templates have been used heavily in the field of nanofabrication due to their adjustable pore diameters, high aspect ratio of nanochannels, ease of preparation and low cost. A variety of nanostructures such as nanotubes [1–3], nanowires [4,5] and nanowells [6] composed of metals, semiconductors, polymers, and other materials can be fabricated using the PAA templates. Generally, PAA templates can be used only after unoxidized aluminum and a thin barrier layer of alumina located on the base of nanopores are removed to make the pores open. The most popular way to obtain the through-hole PAA templates is to etch away the unoxidized aluminum base by using  $\text{HgCl}_2$  or  $\text{CuCl}_2$  solutions and then to dissolve the exposed barrier layer by using  $\text{H}_3\text{PO}_4$  solutions, thus opening up the closed ends of the nanochannels of PAA [7,8]. However, this chemical etching method suffers from the contamination of heavy metal ions which may influence the properties of the resulting nanomaterials, and is also very time-consuming. Another approach to the through-hole PAA templates is to perforate the barrier layer by progressively lowering the anodizing voltage [3,9,10]. Because uniform barrier-layer thinning occurs only when a very small voltage decrement is applied in a single step, this approach is also tedious and time-consuming. To overcome these limitations, an efficient method

was proposed to detach the PAA from the barrier layer by using a short time voltage pulse in a perchloric acid solution [11,12]. Although the detachment and the barrier layer dissolution could be completed in a very short time, the method was considered to be somewhat dangerous and not easy to handle. Up to now, the detachment and pore-opening processes still remain elusive though considerable progress has now been made in this field [13–16]. A facile route to the through-hole PAA templates is highly desirable.

In this Letter, we propose an alternate way to solve the above-mentioned issues. Our strategy is to transfer the barrier layer to another layer of aluminum. That is, a dual-layer laminated aluminum foil is chosen for the anodization process instead of a single-layer aluminum foil commonly used. The barrier layer of PAA can be transferred to the next-layer foil after the first-layer aluminum foil is fully oxidized, leaving behind a barrier layer-free PAA layer in the first-layer foil. Therefore, the through-hole PAA templates can be obtained directly from the first-layer foil.

## 2. Experimental

High-purity ( $\geq 99.99\%$ ) aluminum foils of 60  $\mu\text{m}$  thickness were employed as received. The aluminum foils were firstly electropolished using the same procedure as described previously [17]. A dual-layer laminated aluminum foil was fabricated with two electropolished aluminum foils under a pressure of 10 MPa for 30 min using an oil press. The galvanostatic anodization of the dual-layer aluminum foils were performed at a high current density of 50  $\text{mA cm}^{-2}$  in 0.7 M oxalic acid solution. All anodization experiments were carried out in a conventional two-electrode cell with a Pt mesh as cathode, which was similar to the setup described in Ref. [18].

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One side of the dual-layer foil with a circular area of 18 mm diameter was exposed to the electrolyte which was rigorously stirred during anodization. The electrolyte temperature was kept at about 30 °C. The voltage–time responses during anodizing were recorded automatically by a computer measurement system [19]. The morphology of the PAA film was characterized by field-emission scanning electron microscope (FE-SEM, Hitachi S-4800).

### 3. Results and discussion

Fig. 1 displays a typical voltage–time response for galvanostatic anodization of the dual-layer aluminum foil. In the initial period of anodization (Fig. 1, inset), the curve shows a typical voltage–time behavior of generally galvanostatic anodizing during the formation of PAA, which is characterized by an initial linear voltage rise, followed by curving to a maximum value and then a decrease to a steady-state value [20,21]. In the subsequent anodization process, evolution of anodization voltage can be divided into four stages: voltage gradually arises with time (before point A); voltage quickly increases to a maximum (points A–B); voltage steeply drops to a minimum (points B–C) and again voltage slowly increases with time at a similar rate as the first stage (after point D). Given that the anodization must start from the side in contact with the electrolyte, the voltage–time response in the first stage distinctly corresponds to anodization of the first-layer aluminum (next to the electrolyte) in the dual-layer aluminum foil. The trend toward slow rise of the voltage–time curve in the first stage is also consistent with anodization behavior of the single-layer foil [17]. Moreover, the time duration of the first stage (from the initial to point A) is about 1884 s, in reasonable agreement with the time required for complete oxidation of the first-layer foil ( $<60\ \mu\text{m}$ ), because the thickness of the PAA films formed under the high electric field for 30 min is around  $65\ \mu\text{m}$  [17]. Therefore, a rapid increase in anodization voltage after point A implies that the aluminum anodic oxidation has reached an interfacial region between the dual-layer laminated aluminum foils.

In fact, the electropolished aluminum foils still have an uneven surface at the microscopic level as schematically illustrated in Fig. 2a, although a mirror-finished surface can be seen clearly with the naked eye for the as-electropolished foils [22]. While two electropolished aluminum foils are pressed to each other, an interfacial region between the dual-layer foils is inevitably formed. In this interfacial region, the atomic density of aluminum is distinctly different from that of bulk aluminum layer, which is higher in some areas (dense) or lower somewhere else (sparse) (Fig. 2b). In this case, an imbalance in the mechanical stresses associated with the

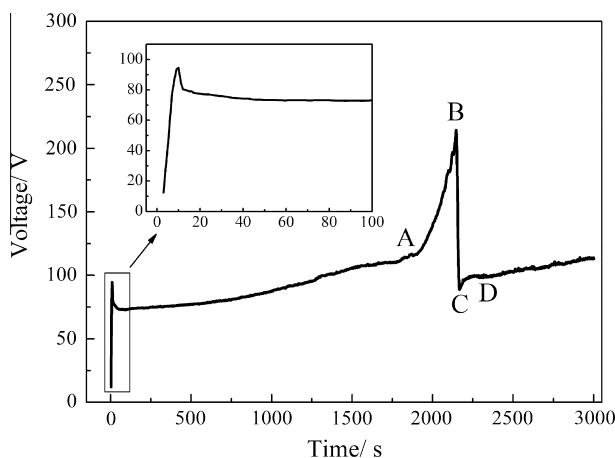


Fig. 1. Voltage–time response for the dual-layer aluminum foil anodized at  $50\ \text{mA}\ \text{cm}^{-2}$  in 0.7 M oxalic acid solution. The inset shows the voltage–time transients in the initial period of anodization.

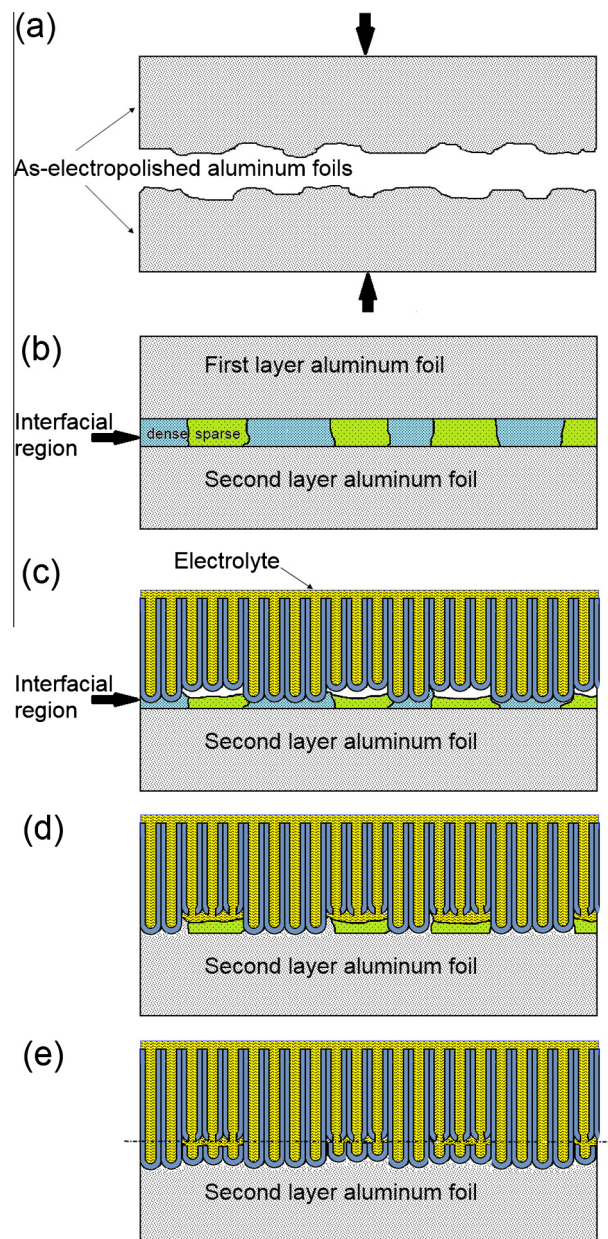


Fig. 2. Schematic diagram illustrating qualitatively the anodization process of the dual-layer foil and the fabrication procedure of through-hole PAA templates.

volume expansion [23] at the metal/oxide interface during anodization would occur because of the nonuniform distribution of aluminum atoms, when the growth of PAA film reached the interfacial region. The imbalance of the resulting stresses may lead to delamination of the barrier layer at the bottom of the pores from the underlying aluminum substrate in some areas, e.g., “sparse” zones, resulting in some gaps between them as illustrated in Fig. 2c. These gaps should block the anodization current for oxide growth. In other words, the area through which the anodization current can flow becomes smaller. This in turn is equivalent to increasing the anodization current density under the condition of galvanostatic anodization. Consequently, the anodization voltage in the voltage–time curve of Fig. 1 quickly increases (points A–B) owing to the increase of the effective current density [17].

On the other hand, since the roughness of the electropolished aluminum surface was typically between 20 and 30 nm on a lateral length scale of  $10\ \mu\text{m}$  [22], the above-mentioned gaps should also

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