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Highlights

- ▶ Ordered PAA membranes (D_{int} from 220 to 350 nm) have been fabricated. ▶ D_{int} depends linearly only on the first anodizing voltage (U_1). ▶ Activation energy (E_a) is yielded from the growth rate versus temperature. ▶ Addition of ethanol decreases growth rate and pore opening.
- **b** Decoupled second voltage influences pore opening with constant D_{int} .

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Improved two-step anodization technique for ordered porous anodic aluminum membranes

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ABSTRACT

We report on an improved two-step anodization technique through combining the first hard anodization in $C_2H_2O_4$ with the second mild anodization in H_3PO_4 , which successfully overcome the drawbacks of irregular top surfaces in the conventional two-step hard anodization in $C_2H_2O_4$ and disordered pore arrays in the two-step mild anodization in H_3PO_4 . The key success of our method is the strong guidance effect of the first hard anodization on the second mild anodization. Highly-ordered (both top and bottom surfaces) porous anodic aluminum (PAA) membranes with interpore spacing from 220 to 350 nm have been realized under anodizing voltages from 100 to 150 V. The interpore spacing is only determined by the first anodizing voltage, while the pore diameter can be manipulated in the second step by adding ethanol in the H_3PO_4 electrolyte, changing the H_3PO_4 bath temperature, and altering the second anodizing voltage. The bath temperature for the steady growth of ordered structures can be expanded up to 20 °C, from which the average activation energy can be yielded. The present novel two-step anodization approach is simple, efficient, and cost-effective. It expands the self-ordering regime of PAA membranes, which is of great value for applications in diverse areas of nanotechnology.

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40 1. Introduction

While the anodic aluminum has been used as anticorrosion or 41 47 decoration coating to improve the mechanical properties of aluminum, the porous anodic aluminum (PAA) is now widely employed 43 in nanoscience and nanotechnology as membrane for its self-or-44 dered uniform cylindrical pore size and pore density. PAA has been 45 extensively used as template, mask, or host materials to synthesize 46 47 various nanostructures in the form of nanopores [1,2], nanowires [3], nanotubes [4,5], and nanodots [6], which are all functional 48 materials for developing nanoscale devices. Besides, PAA has also 49 50 been employed in the field of studies on fluidic dynamics in nanoholes [7,8], separation filters [9], DNA translations [10], and pho-51 tonic crystals [11]. These versatile applications benefit from the 52 special physical characteristics of the PAA films, which can be fab-53 ricated through relatively simple anodization processes. 54

However, problems still exist in the current fabrication techniques of the PAA films. In general, there are two typical methods for the fabrication of PAA films: a pre-patterned anodization [12] and self-organized two-step anodization [1]. The pre-patterned anodization leads to an ideal hexagonal, square, and triangle

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arrangement of pores in the final structure [13], and the size of mold/stamp used for aluminum pre-patterning can be designed by the need of PAA. Nevertheless, the preparation of the master mold is time consuming and is usually based on expensive lithography techniques [12]. On the other hand, the two-step anodization is much simple and low-cost. But regular self-ordered pore structures occur only in quite small processing windows. The difficulty lies in the limited structural features of PAA such as pore diameter (D_P) , interpore spacing (D_{int}) , and regularity, which strongly depend on the chosen electrolyte and anodizing conditions. Self-ordered pore formation can be obtained for three major regimes at the following anodizing voltages: 25 V at H₂SO₄ for $D_{int} = 60 \text{ nm}$ ($D_P = 22 \text{ nm}$), 40 V at $C_2H_2O_4$ for $D_{int} = 100 \text{ nm}$ ($D_P = 45 \text{ nm}$), and 195 V at H_3PO_4 for $D_{int} = 500 \text{ nm}$ ($D_P = 176 \text{ nm}$) [1,14-17]. When the anodization of aluminum is carried out outside those self-ordering regimes, the degree of PAA regularity will decrease significantly.

It is therefore essential to form well-ordered PAA films with a vide range of pore diameter and interpore spacing, which can be manipulated in various ways. The importance of high electric field rows alumina has been noticed and high electric field can induce self-ordering pore arrays [18]. Hard anodization has been proposed to expand the ordered regime in H_2SO_4 at 27–80 V for D_{int} from 72 to 145 nm (D_P from 22 to 83

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84 50 nm) [19], and in $C_2H_2O_4$ at 100–150 V for D_{int} from 220 to 300 nm (D_P from 40 to 60 nm) [20]. Hard anodization in H₃PO₄ is 85 86 different from those in H₂SO₄ and C₂H₂O₄, which maintains the 87 anodizing potential at a self-ordering voltage of 195 V while mod-88 ulating the current density (1500–4000 A/m²) to obtain highly-ordered pore arrays [21]. What is more, highly-ordered cell 89 90 arrangements of porous alumina films were realized in malonic acid at 120 V and tartaric acid at 195 V having 300 nm and 91 92 500 nm pore intervals, respectively [22].

93 However, the PAA films obtained in H₂SO₄ using hard anodiza-94 tion have poor mechanical properties because of a high density of 95 cracks and structural defects, which are not stable enough for real-96 life application [19]. Hard anodization in C₂H₂O₄ results in PAA films with self-ordered array of uniformly sized parallel channels 97 98 with cylindrical shape closed at the pore bottoms [20], where 99 irregular top surface with "pore in pore" structures [23] cannot 100 be exclusive in C₂H₂O₄. To obtain ordered arrays with both regular 101 top and bottom surfaces, the irregular top surface needs to be de-102 tached by ion beam polishing which is time consuming and diffi-103 cult to control.

104 We find alternating the electrolyte type in the second anodiza-105 tion can reduce the current density to be small enough to avoid the irregular top surface, where the self-arrangement effect is weak 106 and the guidance effect of the first anodization will be the leading 107 factor to keep ordered pore arrays. On that basis, we propose an 108 109 improved two-step anodization, taking advantages of hard anod-110 ization for high growth rate and ordered bottom pore arrays in 111 $C_2H_2O_4$ for the first step and mild anodization for regular top arrays in H₃PO₄ for the second one. We have demonstrated that well-or-112 dered PAA films with D_{int} from 220 to 350 nm (D_P from 90 to 113 250 nm without pore broadening after pore formation) can be fab-114 ricated at anodizing voltages of 100–150 V, taking advantage of the 115 guidance effect of the first hard anodization for the ordered pore 116 arrangement in the second mild anodization of H₃PO₄, and working 117 118 temperature as high as 20 °C to enhance the growth rate. We have 119 carried out a detailed investigation on the effects of ethanol per-120 centage, bath temperature, and decoupled anodizing voltages on 121 the formation of PAA films, from which three easy methods to 122 manipulate the pore diameter/interpore spacing have been found.

123 2. Experimental details

124 2.1. Materials

High purity (99.999% purity) aluminum foils with a thickness of
 0.2 mm were used as the starting material. Prior to anodizing a
 piece of round aluminum foil with 20 mm diameter was degreased
 in acetone and rinsed in distilled water. A working surface of the
 sample was 1.5 cm² and the rest of aluminum plate was insulated.

130 2.2. PAA films formation under conventional two-step approach

For the normal two-step anodization, the first anodization was 131 carried out in $0.3 \text{ M} \text{ C}_2\text{H}_2\text{O}_4$ with a 1:4 volume mixture of ethanol 132 and water as solvent at -5 °C, 140 V for 20 min or 5 wt.% H₃PO₄ 133 water-based electrolyte at 5 °C, 140 V for 3 h, with the second 134 anodization carried out under the same conditions as the first step. 135 After removing the remaining aluminum on the backside, detach-136 137 ment of the barrier layer was conducted in a 5 wt.% H₃PO₄ solution 138 at 30 °C for 2 h. Both the first and second anodizations were conducted with vigorous stirring in a 2 L large glass beaker, cooled by a powerful circulating system. A $\frac{90}{20}$ cm² size graphite electrode 139 140 141 was used as a cathode. The voltage source was an Agilent N5752A 142 DC power supply, and the real current was recorded by a Keithley 143 2400 source meter.

2.3. PAA films formation under improved two-step approach

To obtain self-ordered PAA films with continuously tunable 145 interpore spacings from 220 to 350 nm at anodizing voltages from 146 100 to 150 V, we propose here an improved two-step technique, 147 taking advantages of the first hard anodization in $C_2H_2O_4$ [20] 148 and the second mild anodization in H₃PO₄ [17]. The first anodiza-149 tion was carried out in the electrolyte of $Q.3 \text{ M} \text{ C}_2\text{H}_2\text{O}_4$ with a 1:4 150 volume mixture of ethanol and water as solvent at a constant volt-151 age ranging between 100 and 150 V, -5 °C for 20 min. After the re-152 moval of the preformed oxide by a mixture of 6 wt. H₃PO₄ and 153 1.8 wt.% H₂Cr₂O₄ at 60 °C for 4 h, the second anodization was per-154 formed in 5 wt.% H₃PO₄ water-based electrolyte or an ethanol-155 water mixture with a constant temperature from -5 to 20° C, un-156 der the same or a little differentiated anodizing voltage as used in 157 the first step for 3 h. Other experimental parameters were the 158 same as those of the conventional approach. 159

2.4. Characterization

The morphology of the formed membranes was observed by a 161 field emission scanning electron microscope (FE-SEM, FEI Sirion 162 200). The PAA membranes were sputtered with gold for 45 s prior 163 to characterization. The imageJ software [25] was used for estima-164 tion of the interpore spacing, pore diameter, and thickness by ana-165 lyzing the FE-SEM images. The current density was the real current 166 divided by the size of the working surface of anode and the growth 167 rate was the thickness divided by the anodizing time. Porosity P 168 was determined by $P = \frac{\pi}{\sqrt{3}} \left(\frac{D_{\rm p}}{D_{\rm int}} \right)^2$, with $D_{\rm P}$ pore diameter and $D_{\rm int}$ 169 the interpore spacing. 170

3. Limitation of the conventional two-step approach

Fig. 1 presents the FE-SEM results and the corresponding cur-172 rent density-time characteristics of the PAA films fabricated under 173 the normal two-step of both the first and the second anodization in 174 the same $C_2H_2O_4$ (a-c) or H_3PO_4 (d-f) electrolytes. Although the 175 PAA films obtained by the traditional two-step anodization in 176 C₂H₂O₄ have uniform and ordered bottom surfaces and cross-sec-177 tions (Fig. 1a), there are disordered top surfaces with special "pore 178 in pore" structures as demonstrated in Fig. 1b, and the porosity of 179 the PAA is only about 3% which is too tiny to fulfill all the requests. 180 What is worse, the PAA films obtained by the normal two-step 181 anodization in H₃PO₄ have both disordered top and bottom sur-182 faces as shown in Fig. 1d and e. 183

The recorded current density-time characteristics in Fig. 1c and f can account for the irregular pore arrays obtained under the normal two-step anodization method. For both the first and the second anodization in C₂H₂O₄, the rapid drop of the current density at the beginning indicates the growth of barrier layer, while the process of the steep increase to the maxima current density corresponds to the pore nucleation and formation, and a nearly exponential decrease to the pore channel elongation (Fig. 1c). The rapid increase of the strong current density leads to more densely distributed penetration paths which are the precursors of pores [21,26]. The strengthened mechanical stress at metal/oxide interface forces the alumina cells to form regular hexagonal bottom pore arrays in Fig. 1a [27]. Nevertheless, the deep pores, as a result of rapid film growth deduced from the strong current density, make the mechanical stress at metal/oxide interface not able to totally compensate the small pores near the top surface. In fact, under the first anodization, the PAA film has already possessed ordered bottom arrays but irregular top surface. The ordered concaves on the aluminum after removing the preformed oxide guide the film growth in an orderly way under the second anodization.

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Fig. 1. (a) Bottom-view, cross-sectional view (inset), and (b) top-view FE-SEM images of PAA films anodized in 0.3 M C₂H₂O₄ at 140 V for 20 min, together with (c) the current density-time characteristics. (d) Bottom-view, cross-sectional view (inset), and (e) top-view FE-SEM images of PAA films anodized in 5 wt.% H₃PO₄ at 140 V for 3 h, together with (f) the current density-time characteristics.

But the diversified current still result in tiny pores near the top sur face. Therefore, we can observe disordered top surfaces with spon taneous "pore in pore" structures in Fig. 1b.

In the case of H₃PO₄ electrolyte, however, the small current 207 208 density in the process of pore nucleation and formation (Fig. 1f) brings about negligible elastic stress. At the initial stage of instabil-209 ity corresponding to the pore initiation and self-organization, the 210 field-assisted dissolution reaction will result in spatially irregular 211 top pore arrays in the absence of stress due to the wavelength 212 selection mechanism. The field-assisted dissolution reaction lead 213 to spatially irregular pore arrays, and when the effect of elastic 214 215 stress in the oxide layer is significant, the instability can transform from the long-wave type to the short-wave type which leads to the 216 growth of spatially regular and ordered arrays [28]. In the process 217 218 of steady anodization the current is still so small that the mechan-219 ical stress at metal/oxide interface is not large enough to compel 220 the bottom pore arrays to grow regularly. So the pore arrays 221 formed under the first anodization in H₃PO₄ electrolyte are irregu-222 lar, which cannot help the alumina cells forming ordered arrays 223 under the second anodization. While the small current of the sec-224 ond anodization analogous to the first anodization still result in the 225 irregular top (Fig. 1e) and bottom surfaces (Fig. 1d).

4. Improved two-step approach

Fig. 2a–c shows the schematic diagram of the proposal with the first and second anodization in different electrolytes. An alumina membrane was formed with small porosity, irregular top surface but ordered bottom arrays and cross-sections (Fig. 2a and d) by the first anodization in $C_2H_2O_4$. The preformed oxide was removed leaving ordered concaves on aluminum (Fig. 2b and e). The second anodization was carried out in H_3PO_4 on the basis of these concave structures where ordered pore arrays were formed with larger porosity (Fig. 2c and f).

Fig. 2f^{-h} presents the FE-SEM images of the final PAA products under the two different anodizing electrolytes. It is clear that the improved two-step anodization proposal can achieve self-ordered pore arrays with regular cross-sections (Fig. 2f), top (Fig. 2g) and bottom (Fig. 2h) surfaces. The recorded current density-time curves in Fig. 2i further elaborate the success of the improved technique. In the conventional two-step method, the nearly same current density characteristics of the first and second anodizations (Fig. 1c) and f) result in a repetition of defects (Fig. 1b and e) as mentioned before, which can be overcome through distinguishing reaction environments of the two steps. Under the present im-

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Fig. 2. (a-c) Schematic diagram of the proposal with the first and second anodization in different electrolytes, and (d-i) the corresponding experimental results for the proposal: (d) cross-sectional FE-SEM image of PAA films under the first anodization in 0.3 M $C_2H_2O_4$ for 20 min at 140 V, -5 °C; (e) top-view of aluminum after removing the preformed oxide; (f) cross-sectional FE-SEM image of PAA films under the second anodization in 5 wt.% H_3PO_4 for 1 h at 140 V, 0 °C; (g) top and (h) bottom FE-SEM images of the final PAA films, together with (i) the current density-time characteristics.

247 proved two-step anodization, the ordered concaves on the alumi-248 num due to the hexagonal bottom pore arrays of the preformed oxide serve as initial sites for pore formation in the second anod-249 250 ization (like the pre-patterning technique in Ref. [29]). The irregular top surface resulting from the rapidly changing current density 251 of the first anodization will not affect the pore formation in the sec-252 ond anodization. As no more penetration paths aroused by the 253 small current of the second anodization, the trend of Al³⁺ field-254 assisted dissolution in the anode is toward the inner corner/elec-255 trolyte interface, which implies a higher rate of Al³⁺ dissolution 256 257 at the bottom of the concaves [30]. The oxidation at the pore bot-258 tom pushes the gradually forming pore walls upwards on the con-259 caves ridges, driving the pore arrays to grow regularly and 260 mirroring the uniformity of the concaves. Therefore, we can realize 261 ordered PAA films in spite of the weak mechanical stress as a result of the small current density in the second anodization. In fact, the 262 first anodization reinforces the regularity of PAA membranes ob-263 264 tained by the second step.

265 To further confirm the strong guidance effect of the first anodization, we have extended the anodizing time to achieve PAA with 266 267 long pore channels. Although the anodization conditions employed for the second anodization step are far from the self-ordering con-268 269 dition for phosphoric anodization, we can still obtain ordered PAA 270 with long pore channels due to the strong guidance effect. For a 271 short period of time, the PAA is highly-ordered as shown in Fig. 2f. When the anodization time is extended to 3 h, the regular-272 ity maintains well (Fig. 3a). When the length of the membrane is 273 274 about $25 \,\mu\text{m}$ as presented in Fig. 3b, the regularity is generally 275 good (see enlarged Fig. 3c and d) except for the bottom part 276 (Fig. 3e).

Due to stability of the regularity using the improved two-step277approach, some experimental parameters like anodizing voltage,
content of solvent and bath temperature, can be changed to modify278the morphology of the PAA films.280

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4.1. Effect of anodizing voltage

Fig. 4a-c shows the top-view FE-SEM images of ordered PAA 282 films formed by the improved two-step anodization at various 283 anodizing voltages. It is clear that the pore homogeneity increases 284 with the anodizing voltage, especially when the voltage is higher 285 than 130 V. The sensitivity of the final PAA films to the anodizing 286 voltage results from the homogeneity of the bottom channels of 287 the preformed oxide obtained by the first anodization. As we know, 288 for the hard anodization in C₂H₂O₄, the most regular PAA films can 289 be achieved under 120-150 V [20]. This directly leads to different 290 orders of pre-patterned aluminum after removing the preformed 291 oxide which affects the pore arrangement of the final PAA. 292

Fig. 4d presents the evolution of the interpore spacing (D_{int}) as a 293 function of anodizing voltage, where a linear relationship has been 294 clearly observed. Previous studies have revealed that D_{int} achieved 295 under ordinary mild anodization and hard anodization depends 296 linearly on the anodizing voltage with a proportionality constant 297 of $\zeta_{MA} = 2.5 \text{ nm/V}$ in H₃PO₄ [14] and $\zeta_{HA} = 2.25 \text{ nm/V}$ in C₂H₂O₄ 298 [31], respectively. Our proportionality constant of 2.26 nm/V 299 (Fig. 4d) is close to ζ_{HA} , stemming from the limitation of the first 300 anodization. The concaves left on the aluminum surface impose 301 restrictions on the pore arrangement. In spite of the trend to form 302 pore arrays with a proportionality constant of $\zeta_{MA} = 2.5 \text{ nm/V} \text{ dur-}$ 303 ing the second mild anodization, the repulsive interactions are too 304

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Fig. 3. (a) Cross-sectional view of PAA formed using the improved approach at 10 °C under an anodizing voltage of 140 V for 3 h; (b) cross-sectional view of PAA formed using the improved approach at 10 °C under an anodizing voltage of 140 V for 9 h with enlarged cross-section images of the (c) top, (d) middle, and (e) bottom parts.

weak to drive the pore cells to rearrange. This phenomenon further
 confirms that the second mild anodization mirrors the uniformity
 of the concaves discussed above.

308 4.2. Effect of the addition of ethanol

It is well known that anodization in H₃PO₄ electrolyte generates 309 a lot of Joule heat in the oxide/metal interface which may disturb 310 the stable growth of the anodic oxide film. In order to accelerate 311 the diffusion of the heat that evolves from the sample, we can 312 313 add some ethanol as coolant for its high effumability and low acidity [21]. Fig. 4e-g displays the top-view FE-SEM images of the PAA 314 315 films formed at 140 V and 5 °C in H₃PO₄ electrolyte with different 316 volume ratios of water and ethanol. The added ethanol does affect 317 the morphology to some extent. When the ratio of ethanol and 318 water is 1:4, the uniformity (Fig. 4f) is slightly better than the one obtained in the absence of ethanol (Fig. 4e) with D_{int} and D_P al-319 most unchanged. However, when the ratio reaches 1:2, the mor-320 phology (Fig. 4g) is transfigured, where the size of pore opening 321 322 decreases significantly.

The deformation of the PAA films is a result of the protecting effect on the chemical dissolution process caused by the addition of

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ethanol. The vaporization of ethanol at the bottom of the channels due to the high effumability aids the agitation of electrolyte to take away the heat efficiently, preventing the increase of the localized temperature and retarding the chemical dissolution. Besides, the extremely low degree of ionization of ethanol enhances the protecting effect of the chemical dissolution. It is generally accepted that the pores are broadened by the chemical dissolution of pore walls by electrolyte during the film growth [32]. The weaker chemical dissolution will induce the smaller $D_{\rm R}$ and porosity in the presence of ethanol as shown in the inset of Fig. 4h. In contrast, D_{int} is determined by the anodizing voltage of the first anodization unaffected by the rate of chemical dissolution, retaining nearly constant under different ethanol/water ratios (Fig. 4h (inset)). The current density characteristics in Fig. 4h can further verify the function of ethanol on the growth of PAA. The weak chemical dissolution due to the addition of ethanol reduces the migration of ions $(O_{\perp}^{2-}/OH_{\perp}^{-}/Al^{3+})$ which are related to the anodizing current and growth rate, leading to the decrease of the steady current with the addition of ethanol. To ensure the steady reaction and moderate growth rate, we tend to perform the anodization in the H₃PO₄ electrolyte with a 1:4 volume mixture of ethanol and water as solvent.

4.3. Effect of bath temperature

Previous studies indicate that the anodization in H_3PO_4 electrolyte should be carried out at lower temperature compared to the anodization in other acid electrolytes [14,17], to maintain steady growth of ordered pore arrays. We have also carried out a detailed investigation on the effect of H_3PO_4 bath temperature on the morphology of PAA films under the optimal $C_2H_2O_4$ electrolyte circumstance. The top-view FE-SEM images of PAA films obtained by the improved two-step anodization at 140 V, but different H_3PO_4 electrolyte temperatures ranging from $_5$ to 20 °C have been presented in Fig. 5a–d, as well as Fig. 2g and Fig. 4f. We notice that higher H_3PO_4 electrolyte temperature does accelerate the chemical dissolution, resulting in the pore broadening. Nevertheless, the regularity of the pore arrangement has not been disturbed, keeping a hexagonal close packing structure, owing to the guiding function of the ordered pre-textured aluminum.

Fig. 5e presents the dependence of the pore diameter and the film growth rate (r) on H₃PO₄ bath temperature (T), where an exponential increase of the pore diameter and film growth rate is discernable. As we know, the reaction rate k in chemical reactions can be well described by the Arrhenius equation of $k = A \exp(\frac{1}{k})$ $(-E_a/RT)$ [33], with E_a activation energy and R = 8.31 J/(mol K) gas constant, which indicates a remarkable increase of the reaction rate with the temperature. Since the PAA film growth rate is directly correlated with the reaction rate, we can get the average activation energy of $E_a = 75.2 \text{ KJ/mol}$ from the fitted value of the growth rate curve in Fig. 5e, in good agreement with the previous calculated value of 78.6 KJ/mol [34]. Likewise the pores are broadened by the chemical dissolution of pore walls by electrolyte during the film growth, which will also abide by the Arrhenius equation. Fig. 5e displays the well fitted results for D_P, with the different fitting parameters mainly due to the difference of mechanism between the film growth (ion migration at the pore bottom) [27,35] and pore broadening (chemical dissolution of pore walls) [32].

The effect of the H_3PO_4 bath temperature on the oxide formation and growth can be further demonstrated by the current density-time characteristics of the second anodization shown in Fig. 5f. The movement of ions is quickened by the increase of temperature, leading to a relatively high rate of oxide layer formation corresponding to the current climb stage. Besides, the average steady current density (*i*) corresponding to the stable growth is 346 347

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Fig. 4. Top-view FE-SEM images of PAA films formed using the improved approach in the electrolyte with a 1:4 volume mixture of ethanol and water as solvent at 5 °C under an anodizing voltage of (a) 110 V; (b) 130 V; (c) 150 V; with (d) dependence of the interpore distance D_{int} on the anodizing voltage. Top-view FE-SEM images of PAA films formed at 5 °C and 140 V, in electrolyte with ethanol and water volume ratio of (e) 0:1; (f) 1:4; (g) 1:2; together with (h) current density-time characteristics and dependence of pore diameter (D_P), D_{int} , and porosity on the ratio of ethanol/water (inset). The anodizing time was 3 h.

also increased, exhibiting an exponential relation with the H₃PO₄ 389 bath temperature (see inset of Fig. 5f). The anodizing current is 390 caused by the migration of ions $(O^{2-}/OH^{-}/Al^{3+})$ in the barrier layer 391 392 [27,35], which is related with the reaction rate. As a result, the cur-393 rent density has a similar trend with the growth rate, both with the 394 form of Arrhenius equation. Furthermore, the growth rate (r) is the thickness of the PAA films (h) divided by the anodizing time, where 395 the thickness is expected to follow the integrated form of 396 $h = C \int_{0}^{t} i dt$ with C a constant [36]. While the evolution shown in 397 the inset of Fig. 5f is the average steady current density (neglecting 398 399 the rapidly changing part), the fitted value of average current den-400 sity about the activation energy ($E_a/R = 9128.3$ K) (Fig. 5f) is slightly larger than that of the growth rate ($E_0/R = 9046.6$ K) in Fig. 5e. 401

In general, higher H_3PO_4 bath temperature efficiently improves the growth rate and broadens the pores. Nevertheless, when the temperature is high enough, the strong chemical dissolution makes the surface turn into tip bundle structure without segregated pores [37]. Thus the temperature should be controlled under 20 °C to preserve the regular porous structure. 407

4.4. Effect of decoupled anodizing voltages

In the traditional two-step treatment, Lee and Wong [38] have proposed that the voltage in the second anodization must be the same as that in the first step because once the ordering by the first anodization was accomplished, the applied voltage in the second 412

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Fig. 5. Top-view FE-SEM images of the PAA films fabricated at 140 V under different H₃PO₄ electrolyte temperatures of (a) –5 °C; (b) 10 °C; (c) 15 °C; (d) 20 °C; together with (e) dependence of the pore diameter (D_p) and the film growth rate (r) on electrolyte temperature (T); (f) current density-time characteristics and the evolution of average current density (i) of the second anodization as a function of temperature (inset). The anodizing time was 3 h.

413 step must produce an interpore spacing that matches the remnant structures of the first step. However, we show in Fig. 6 that the 414 anodization under discriminating voltages (decoupled voltages) 415 can also achieve ordered PAA films to some extent in the present 416 417 improved two-step approach. Conditions which lead to a moderate expansion of the aluminum during oxide formation are most suit-418 419 able for obtaining hexagonal ordered pore arrays, disordered PAA 420 structures will be yielded if the difference of the two anodizing 421 voltages is too large due to the volume contraction (Figs. 6a and b) [27]. However, as already stated in Fig. 2 for our present im-422 423 proved technique, the oriented oxidation at the pore bottom 424 pushes the gradually forming pore walls upwards on the concaves ridges, driving the pore arrays to grow regularly, where ordered ar-425 rays can still be obtained under decoupled voltages. Proper differ-426 ence between the voltages will not bring about significant 427 influence on the PAA regularity (see Fig. 6c-h). 428

To further demonstrate the effect of decoupled anodizing volt-429 430 ages, we list in Table 1 the D_{int} and D_P of the PAA films obtained at different decoupled voltages, where an abnormal evolution is 431 exhibited with the second anodizing voltage. When we fix the first 432 433 anodizing voltage (U_1) , it is clear that D_{int} is almost independent of the second anodizing voltage (U_2) , while D_P decreases with the in-434 crease of U_2 . These are totally different from the wide accepted 435 phenomenon in the traditional two-step treatment that both D_{int} 436 437 and $D_{\rm P}$ increase with the applied voltages [39,40]. As we know, 438 the first step is a hard anodization, where the preformed oxide 439 interpore spacing $D_{int-1st}$ depends linearly on the anodizing voltage $[D_{\text{int-1st}}(\text{nm}) = 2.26U_1 - 7.72$ in our case and $\sim 286(309)$ nm at $U_1 = 130(140)$ V]. On one hand, the guidance of the remnant con-440 441 caves in the first anodization pushes the cells to form pore arrays 442 in the second step, the final interpore spacing D_{int} under different 443 U_2 is therefore all around $D_{int-1st}$ due to the limitation of the first 444 anodization. On the other hand, the volume expansion during oxi-445 dation increases with the applied voltage according to Jessensky et 446 al. [27]. In our situation of almost constant D_{int} under different U_2 , 447 The volume expansion can only be realized (see Table 1) by 448 expanding the oxide inward pores, i.e., the decrease of the pore 449 diameter D_P with increasing U_2 . It is clear that the present tech-450 nique has the ability to manipulate the pore diameters, while keep-451 ing constant interpore spacing and regularity, by adjusting the 452 second anodizing voltage within a certain range. 453

4.5. Advantages of the improved two-step approach

Based on the above experimental facts and discussion, we can 455 find that the improved two-step approach has significant advanta-456 ges compared to the conventional two-step anodization. Firstly, it 457 realizes the formation of ordered PAA membranes with the inter-458 pore spacing ranging from 220 to 350 nm under the voltages from 459 100 to 150 V in the H₃PO₄ electrolyte. It overcomes the "pore in pore" structure on the top surface caused by the conventional two-step hard anodization in C₂H₂O₄ and breaks the limitation that ordered PAA cannot be obtained in H₃PO₄ electrolyte under anodizing voltage smaller than 160 V [17].

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Fig. 6. Top-view FE-SEM images of PAA films fabricated using the improved two-step approach under decoupled first anodizing voltage (U_1) and second anodizing voltage (U_2): (a) $U_1 = 130$ V, $U_2 = 90$ V, (b) $U_1 = 130$ V, $U_2 = 100$ V, (c) $U_1 = 130$ V, $U_2 = 110$ V, (d) $U_1 = 130$ V, $U_2 = 120$ V, (e) $U_1 = 130$ V, $U_2 = 140$ V, (f) $U_1 = 140$ V, $U_2 = 110$ V, (g) $U_1 = 140$ V, $U_2 = 120$ V and (h) $U_1 = 140$ V, $U_2 = 130$ V. The anodizing time was 3 h.

Table 1	
Effect of decoupled two-step anodizing voltages on D_{int} and D_{P} .	

U ₂ (V)	<i>U</i> ₁ = 130 V		$U_1 = 140 \text{ V}$	
	D _{int} (nm)	$D_{\rm P}({\rm nm})$	D _{int} (nm)	D _P (nm)
110	284.8	167.3	311.6	239.3
120	287.7	148.9	310.4	156.9
130	286.4	109.2	304.8	128.1
140	283.2	100.2	308.7	117.2

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Secondly, due to the highly ordered concaves on the aluminum in the improved approach, we can change some experimental conditions to control the parameters of the PAA films without sacrificing the regularity. We have demonstrated that $D_{\rm int}$ can be continuously modulated by changing the first anodization voltage U_1 . D_P can be easily manipulated with the percentage of ethanol in the electrolyte, the bath temperature in the second anodization, and the second anodizing voltage during the growth of oxide. In contrast, broadening of the pores can only be realized by chemical dissolution in H₃PO₄ after the formation of PAA films in the conventional method.

Thirdly, the efficiency of the PAA formation is much improved. It usually takes hours for the first step using mild anodization to obtain ordered arrays, while tens of minutes are enough for the hard anodizatoin in the present technique. Since our anodization can be carried out in a wide region of bath temperature from -5 to 20 °C, higher temperature does benefit to the improvement of the growth rate, and the activation energy can also be yielded from the evolution of growth rate as a function of temperature.

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485 5. Conclusions

486 In this study, we have addressed the limitation of the PAA membranes with interpore spacing from 220 to 300 nm yielded 487 by the conventional two-step anodization approach [20], where 488 hard anodization in C₂H₂O₄ results in irregular top surface with 489 "pore in pore" structure and mild anodization in H₃PO₄ leads to 490 491 pore arrays with both irregular top and bottom surface. An im-492 proved two-step anodization technique has been proposed taking 493 advantages of the first hard anodization in C₂H₂O₄ and second mild anodization in H₃PO₄. The hard anodization offers faster 494 oxide growth and improved ordering of the bottom pore arrays 495 496 and the mild anodization keeps the order of the first anodization while overcomes the "pore in pore" structure of the top surface. 497 We have realized efficient growth of the ordered pore arrays with 498 interpore spacing from 220 to 350 nm via tuning the anodizing 499 voltage from 100 to 150 V in a wide temperature range from 500 –5 to 20 °C. 501

We have carried out a detailed investigation on the effects of 502 the anodizing voltage, addition of ethanol, H₃PO₄ bath tempera-503 ture, and decoupled anodizing voltages. It is found that the inter-504 505 pore spacing is determined only by the first anodizing, which 506 increases linearly with the first anodizing voltage by the proportionality of 2.26 nm/V. The interpore spacing is independent of 507 the second anodizing voltage, the percentage of ethanol in H₃PO₄ 508 electrolyte, and the bath temperature. The addition of ethanol re-509 510 duces the anodizing current and the pore size in a way that higher ratio of ethanol weakens the chemical dissolution thereby de-511 creases the current and the pore size. The existence of ethanol also 512 513 strengthens the heat dissipation to keep the steady growth of the 514 films.

515 The growth rate and current density are found to be greater at 516 higher H₃PO₄ temperature. This is caused by the increased reaction rate as a result of accelerated ion migration. The pore size 517 is also broadened due to the enhanced chemical dissolution. Or-518 dered PAA films can further be obtained under decoupled anodiz-519 520 ing voltages. While the interpore spacing is still determined by the first anodizing voltage, the second anodizing voltage can 521 manipulate the pore diameter. The pore size decreases with the 522 increase of the applied second anodizing voltage due to the en-523 524 larged volume expansion under fixed interpore spacing with ris-525 ing voltage.

526 6. Uncited reference

527 **02** [24].

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