Supporting Information

Understanding Pore Rearrangement during Mild to Hard Transition in Bilayered Porous Anodic Alumina Membranes

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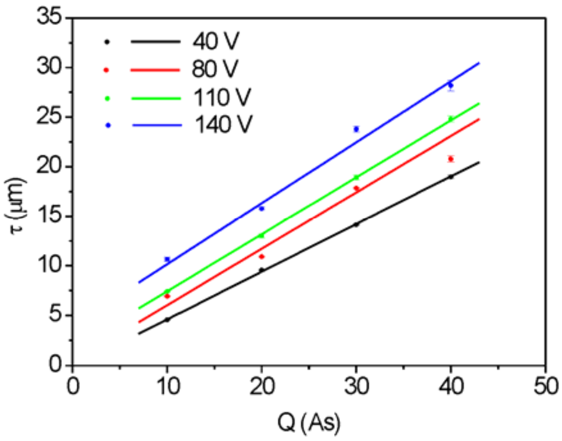

Figure S1. Template thickness (τ) as a function of the total electrical current charge (Q) for each one of the anodization voltages (i.e. 40, 80, 110 and 140 V) together with their corresponding linear fittings (equations are shown in **Table S1**). The sample area is 0.7 cm^2.

Table S1. Growth rates and linear fittings after carrying out the calibration processes.

Anodization Voltage (V)	Growth Rate ($\mu m \cdot (A \cdot s)^{-1}$)	Linear Fitting (τ versus Q)	Correlation Coefficient (R)
40	0.48	τ (µm) = 0.48·Q (A·s) + 0.24	0.99977
80	0.57	τ (µm) = 0.57·Q (A·s) + 0.31	0.98583
110	0.58	τ (µm) = 0.58·Q (A·s) + 1.66	0.99993
140	0.63	τ (µm) = 0.63·Q (A·s) + 3.74	0.99245

In the course of this work it has been used the standard image processing package ImageJ (public domain program developed at the RSB of the NIH, USA) to measure the geometric characteristics of the different types of bilayered nanoporous anodic alumina templates.

In order to estimate both the number of filled and empty pores, the following image process was applied by using ImageJ:

First, two thresholds of each SEM image were obtained, one of them for filled pores and the other for empty pores. Then, selecting suitable threshold limits made it possible to discern between filled pores (N_{FP}) and empty pores (N_{EP}). Subsequently, each pore was outlined by ellipses and the number of each type of pores was automatically counted. A schematic diagram showing the image treatment process is presented in **Figure S1**.

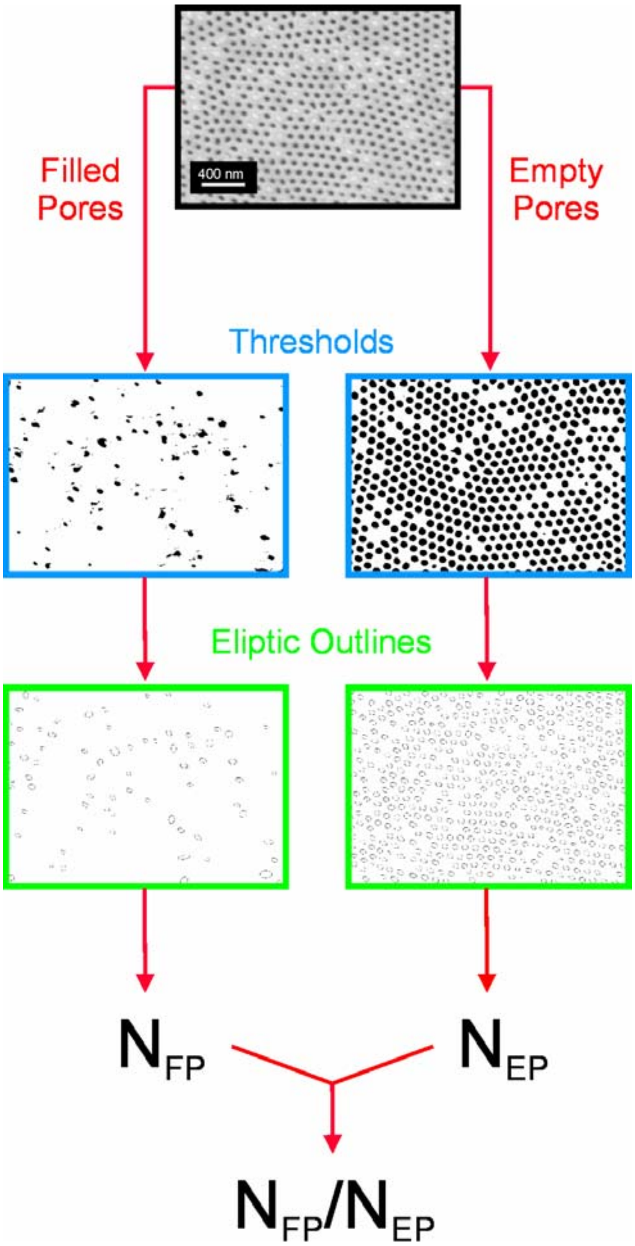

Figure S2. Schematic diagram showing the image analysis process carried out to estimate N_{FP}, N_{EP} and N_{FP}/N_{EP}.

The ANOVA table (**Table 4**) was calculated from the equations shown in **Table S2**, where SS is the sum of squares of the corresponding source, DF denotes the degree of freedom of such source, MS corresponds to the mean square of the corresponding source, F_0 is the test statistic of that source, a and b denote the total number of levels corresponding to R_v and V_{HA}, respectively, and n is the total number of replications.[28]

The strategy for testing the hypotheses H_0, H_1 and H_2 was to compare the value of F_0 calculated from the ANOVA table to the value of the F-distribution for a significance level of 95% (i.e. 0.05) with the corresponding value of DF(Source) and DF(Error) (i.e. $F_{(0.05;\ DF(Source);\ DF(Error))}$). In this way, the tested null hypotheses (i.e. H_0, H_1 and H_2) associated with each case enumerated in section 3 (i.e. cases i, ii and iii) were rejected if:

i) H_0: $F_{0\text{-}Rv} \geq F_{(0.05;\ DF(Rv);\ DF(Error))}$

ii) H_1: $F_{0\text{-}VHA} \geq F_{(0.05;\ DF(VHA);\ DF(Error))}$

iii) H_2: $F_{0\text{-}Rv \cdot VHA} \geq F_{(0.05;\ DF(Rv \cdot VHA);\ DF(Error))}$

Source	SS	DF	MS	F_0
R_v	$SS_{R_v} = \frac{1}{bn}\sum_{i=1}^{a} y_{i..}^2 - \frac{y_{...}^2}{abn}$	$a-1$	$MS_{R_v} = \frac{SS_{R_v}}{a-1}$	$F_{0-R_v} = \frac{MS_{R_v}}{MS_E}$
V_{HA}	$SS_{V_{HA}} = \frac{1}{an}\sum_{j=1}^{b} y_{.j.}^2 - \frac{y_{...}^2}{abn}$	$b-1$	$MS_{V_{HA}} = \frac{SS_{V_{HA}}}{b-1}$	$F_{0-V_{HA}} = \frac{MS_{V_{HA}}}{MS_E}$
$R_v \cdot V_{HA}$	$SS_{R_v \cdot V_{HA}} = \left(\frac{1}{n}\sum_{i=1}^{a}\sum_{j=1}^{b} y_{ij.}^2 - \frac{y_{...}^2}{abn}\right) - SS_{R_v} - SS_{V_{HA}}$	$(a-1)(b-1)$	$MS_{R_v \cdot V_{HA}} = \frac{SS_{R_v \cdot V_{HA}}}{(a-1)\cdot(b-1)}$	$F_{0-R_v \cdot V_{HA}} = \frac{MS_{R_v \cdot V_{HA}}}{MS_E}$
Error	$SS_E = SS_T - \left(\frac{1}{n}\sum_{i=1}^{a}\sum_{j=1}^{b} y_{ij.}^2 - \frac{y_{...}^2}{abn}\right)$	$ab(n-1)$	$MS_E = \frac{SS_E}{ab(n-1)}$	
Total	$SS_T = \sum_{i=1}^{a}\sum_{j=1}^{b}\sum_{k=1}^{n} y_{ijk}^2 - \frac{y_{...}^2}{abn}$	$abn-1$		

Table S2. Equations of the different parameters for the ANOVA table in a 3^2-factorial design.[28]