Supporting Information

Unveiling the Hard Anodization Regime of Aluminum: Insight into Nanopores Self-Organization and Growth Mechanism

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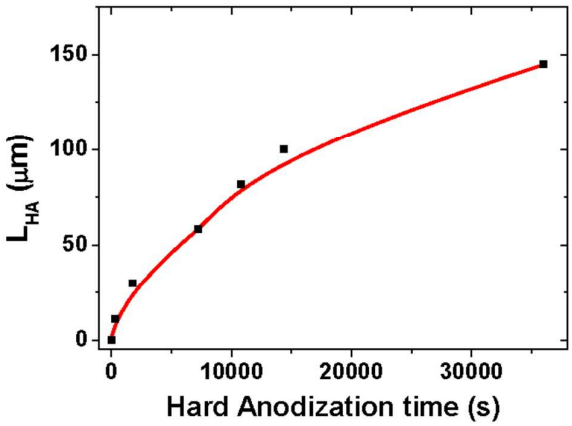

Figure S1. Thickness of the H-AAO layer, L_{HA}, as a function of the hard anodization time.

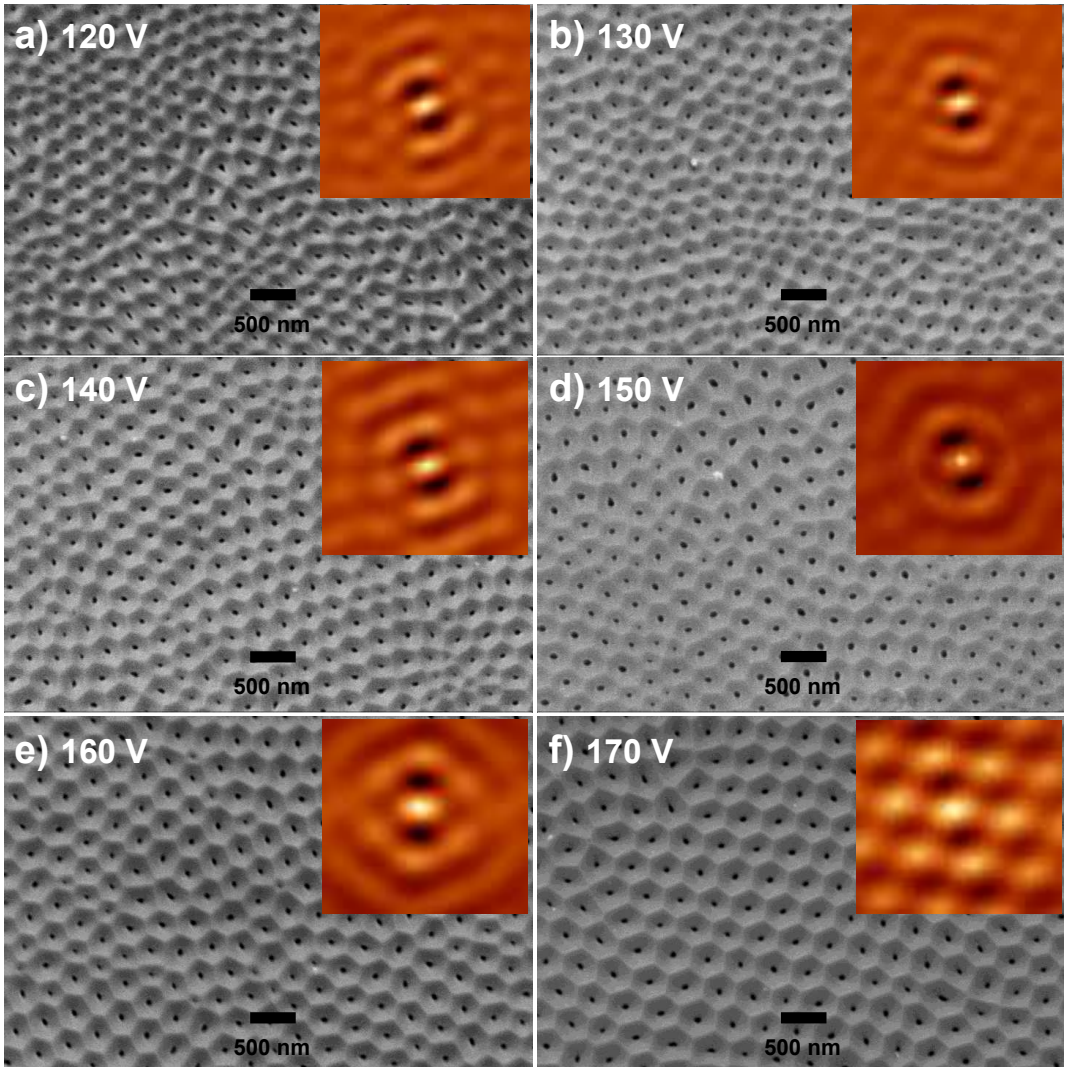

Figure S2. SEM images at the bottom surface of H-AAO membranes synthesized by hard anodization in 0.150 M oxalic acid electrolyte containing 5% of ethanol for the anodization voltages of (a) 120 V; (b)130 V; (c) 140 V; (d) 150 V; (e) 160 V, and (f) 170 V. The insets show the respective self-correlated images[1] indicating the variation of the pore ordering degree.

Relation between D_{int} and t_{BL} in the frame of the viscous flow model

According with the works of Van Overmeere et al. (2010) and D. Barkey et al. (2010), in which a electrostatic energy-induced surface instability is proposed as the mechanism controlling pore interspacing in anodic oxide films of aluminum and titanium (that is, the lattice constant of the ordered pore arrangement arises from competition between the compressive electrostriction force and the viscous resistance to oxide flow), [2, 3] the relation between lattice constant (interpore distance) and barrier layer thickness is given by:

$$D_{int} = \sqrt{\frac{4\pi^2\gamma}{\varepsilon_0\varepsilon_r}}\frac{{t_{BL}}^{3/2}}{V_{an}} \qquad \text{(a)}$$

where γ is the surface excess free energy of the oxide, ε_r is the dielectric permittivity of the anodic oxide film and ε_0 is the one of vacuum. Taking γ = 0.1 J·m^{-2}, ε_r = 8 and V_{an} = 120 V, and using equation (a), we obtain for the proportionality constant between D_{int} and ${t_{BL}}^{3/2}/V_{an}$ a value of 7.5 V·nm$^{-1/2}$, which is in close agreement with the parameter obtained from the linear fitting in Figure 6 b) (7.3 V·nm$^{-1/2}$), with coefficient of determination, R^2, of 0.96. These results indicate that the competition between electrostrictive force and viscous flow might be the underlying mechanism controlling pore ordering and interpore distance in HA of aluminum. However, systematic experiments covering a wide range of voltages and anodization times are required in order to assess the validity of this model to HA processes.

Hard anodization in ethylene glycol containing oxalic acid electrolytes

In order to verify the validity of the described method for finding the corresponding self-ordering regimes in different electrolytes basing on voltammetric curves, we have performed a study of HA of Al in 0.3 M oxalic acid electrolytes containing 50 vol.% of ethylene glycol. The voltammetry curves, presented in Figure S3 (a), indicate that the addition of 50 vol.% of ethylene glycol causes a reduction in the anodic current density in comparison with 0.3 M oxalic acid electrolyte without ethylene glycol. Furthermore, the current plateau (B* interval) is shifted in this case to higher voltage values, ranging from 150 to 170 V. The shift in the B* interval and reduction in the anodic current density with the addition of ethylene glycol can be ascribed to the increase in the electrolyte viscosity and reduction in the mass transport rate along the pore channels.[4-6]

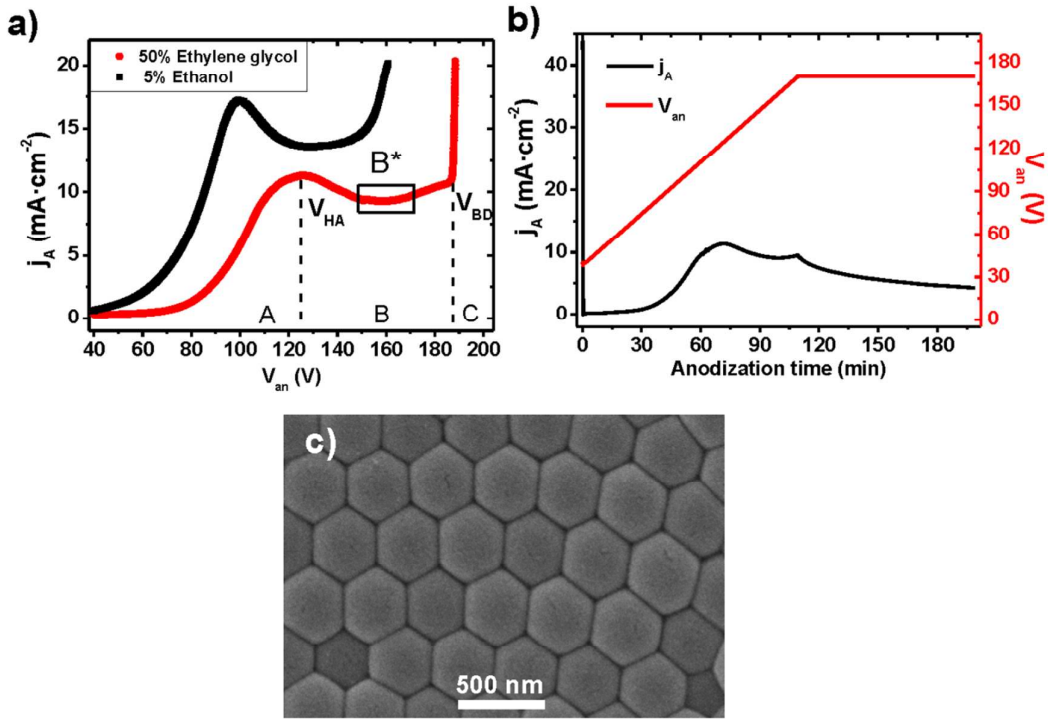

Figure S3. (a) Linear sweep voltammetry of the anodic oxidation of Al in 0.3 M oxalic acid electrolyte containing 50 vol.% of ethylene glycol. b) Current and voltage transients recorded during the fabrication of a H-AAO membrane in 0.3 M oxalic acid electrolyte containing 50 vol.% of ethylene glycol, at a HA potential of 170 V. c) SEM bottom view of the H-AAO membrane obtained from (b).

So, as a proof of concept and without any other help of additional test or further experimental determination of the best self-ordering regime in this electrolyte, one sample was produced by hard anodization at 170 V, and both current and voltage transients recorded during the fabrication procedure are shown in Figure S3 b). A

similar behavior to that of the HA processes in oxalic-ethanol electrolytes (see Figure 1 (a)) is also observed in this case. Finally, the backside of the sample was checked by SEM, as it can be seen in Figure S3 c), demonstrating that the H-AAO membrane produced in oxalic acid - ethylene glycol electrolyte also exhibits a self-ordering of its porous spatial arrangement for an anodization voltage within the range of the current plateau B*.

References

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