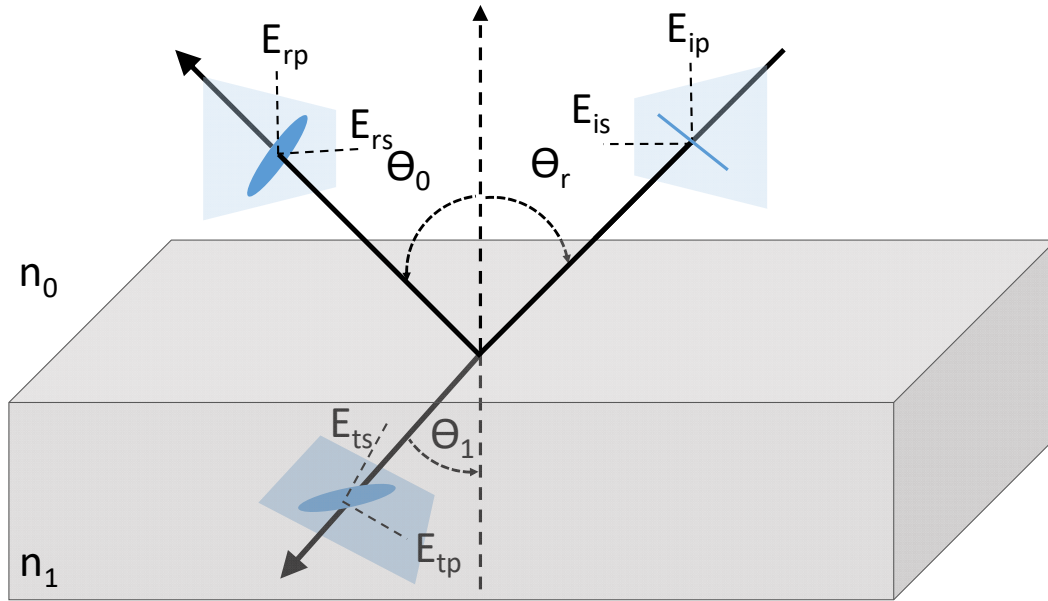


# Optical and Electrochemical Characterization of Nanoporous Alumina Structures: Pore Size, Porosity, and Structure Effect

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**Figure S1.** Scheme of spectroscopy ellipsometry measurement for a homogeneous sample.

Ellipsometry measured angles  $\Psi$  and  $\Delta$  are related to the ratio of Fresnel reflection coefficients  $\tilde{R}_p$  and  $\tilde{R}_s$  (p for parallel and s for perpendicular polarized light) by:

$$\rho = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan \Psi e^{i\Delta} \quad (1)$$

**Fresnell expressions:**

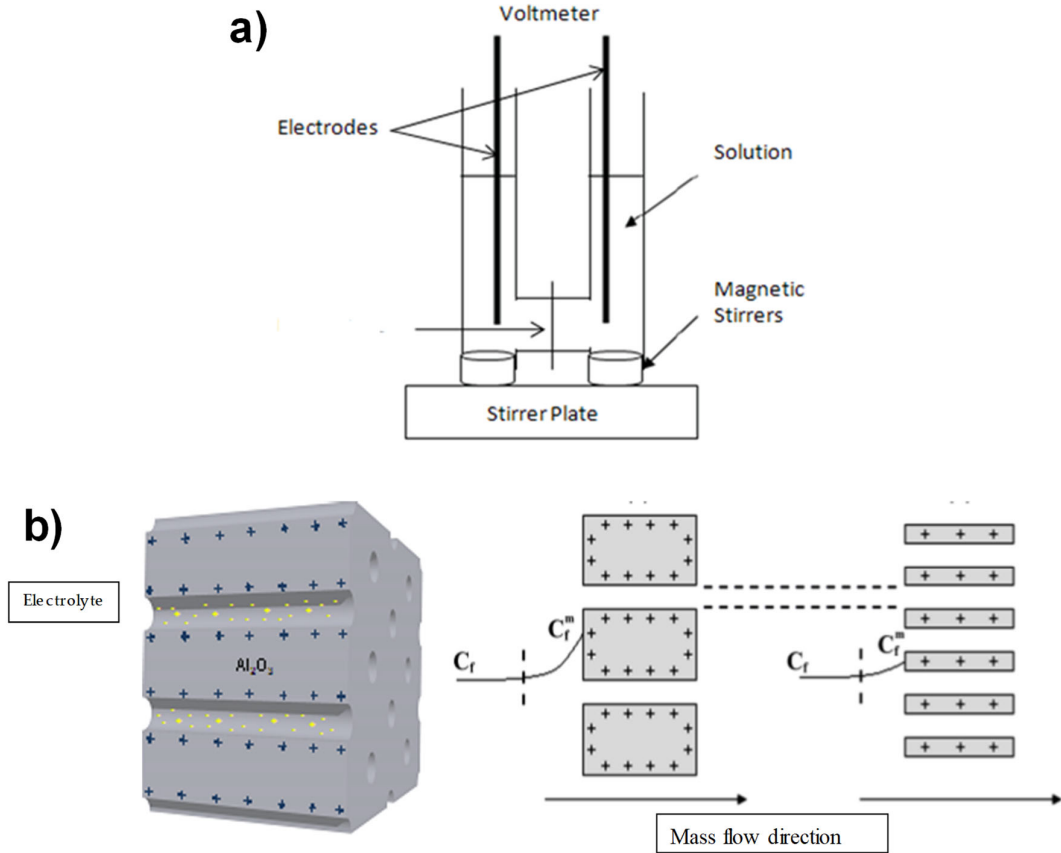
$$\tilde{r}_p = \frac{\tilde{E}_{rp}}{\tilde{E}_{ip}} = \frac{\tilde{n}_1 \cos \theta_0 - \tilde{n}_0 \cos \theta_1}{\tilde{n}_1 \cos \theta_0 + \tilde{n}_0 \cos \theta_1} \quad (2)$$

$$\tilde{r}_s = \frac{\tilde{E}_{rs}}{\tilde{E}_{is}} = \frac{\tilde{n}_0 \cos \theta_0 - \tilde{n}_1 \cos \theta_1}{\tilde{n}_0 \cos \theta_0 + \tilde{n}_1 \cos \theta_1} \quad (3)$$

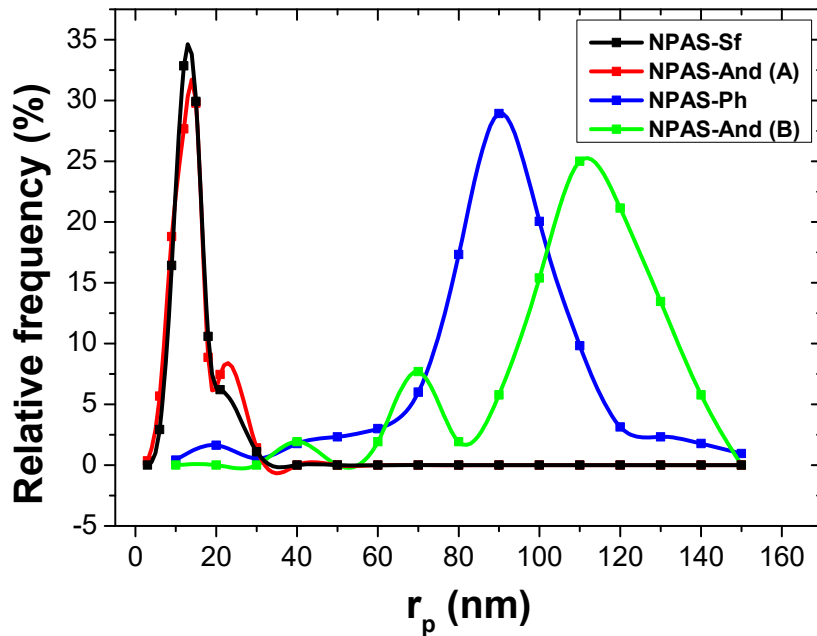
Where  $\tilde{E}$  is the incident electric field while the subscripts are: s for perpendicular, p for parallel, 0 for incident and 1 for transmitted.  $\tilde{n}$  is the complex refractive index of: 0 the incident medium (usually vacuum or air), and 1 the bulk sample.

$\theta_0$ ,  $\theta_r$  and  $\theta_1$  must fulfil two conditions:

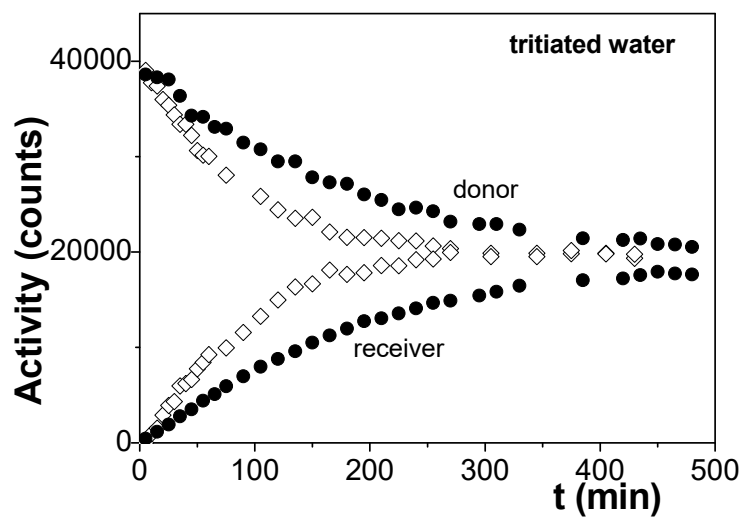
- Specular reflection:  $\theta_0 = \theta_r$
- The Snell's law has to be valid:  $\tilde{n}_0 \cdot \sin \theta_0 = \tilde{n}_1 \cdot \sin \theta_1$



**Figure S2.** Scheme of: a) electrochemical test-cell; b) solid sample/electrolyte electrical distribution and interfacial effects.



**Figure S3.** Analysis of the pore radii distribution for the studied samples.



**Figure S4.** Time evolution of tritiated water activity in donor and receiver solutions for: (●) NPAS-Sf and NPAS-And (◇).