ESRF	**Experiment title:** **Large scale structure of Anodic Aluminium Oxide membranes.**	**Experiment number**: **MA-131**
Beamline: ID01	**Date of experiment**: from: 14 oct. 2006 to: 18 oct. 2006	**Date of report**: 10/10/2009
Shifts: 6	**Local contact(s)**: Dr. Gerardina Carbone	*Received at ESRF:*

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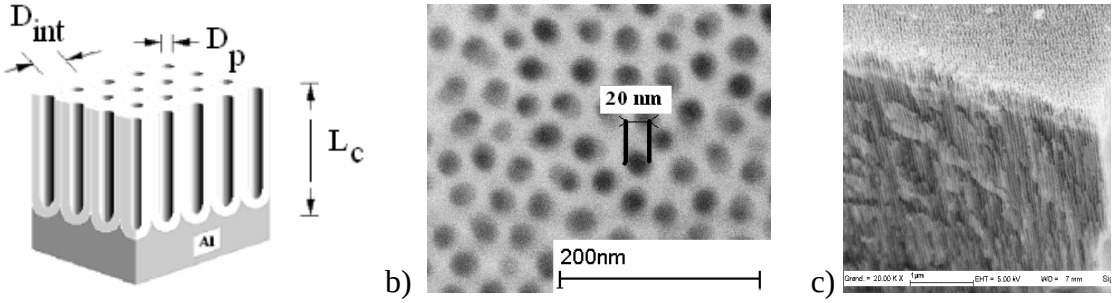
Report:

The purpose of this experiment was to **fully characterize the topology of our home made AAO membranes.** AAO are made by fairly mono-disperse oriented parallel cylindrical pores (Figure 1). The membrane morphology is described by the pore diameter, D_p, the inter-pores distance, D_{int} and channels length, L_c.

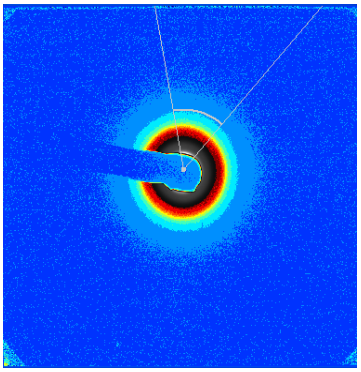


a) b) c)

Figure 1 a) *Schematic drawing of a Aluminium Anodised Oxide membrane (adapted from* **[1]***). The alumina (Al_2O_3) porous matrix, in white, is obtained by anodization of a centimetres square, few millimetres thick, aluminium plate. The membrane morphology is described by the pore diameter, D_p, the inter-pores distance, D_{int} and channels length, L_c.* ***b)*** *Scanning Electron Microscope (SEM) image of a LLB made AA0 membrane. Here, the pore diameter is 20 nm.* ***c)*** *3D SEM view of an actual LLB made AAO membrane showing the macroscopic alignment of the cylindrical pores in the bulk of the membrane (scale is 1μm).*

AAO membranes have been prepared following the two-step anodization process described by Fukuda and Masuda. [2]. The main anodization parameters are: the constant output voltage, the anodization duration, the temperature and the nature of the electrolyte. In this study, we have used the anodization parameters described by Wade and Wegrowe [3]: high purity aluminium plates (30 mm*30 mm* 2 mm) have been electropolished prior to anodization using a constant dc voltage. After chemical leaching of the preformed porous anodic alumina (Al_2O_3) film in a mixture of phosphoric acid (6 wt %) and chromic acid (1.8 wt %), the final anodization is performed under the same conditions. The final membrane (30 mm*30 mm on each side of the aluminium plate) is supported by the residual aluminium core. The AAO membrane thickness, on each side of the residual aluminium, depends on the anodization duration. At the end of the synthesis process, membranes are left several hours in distilled water then dried under vacuum.

SAXS experiments have been performed with the AAO membranes surface perpendicular to the beam so that the pores axis was alongside the incident beam. For all the membranes measured, the scattered intensity is then isotropic, making possible a circular grouping. The signal shows a series of peaks (Figure 2). SANS experiments (PAXY spectrometer, LLB, France) have also been performed on the very same AAO membranes with the surface perpendicular to the beam (Figure 3a). After isotropic grouping, the SANS spectrum exhibits only two peaks while as we expected the SAXS spectrum thanks to its better Q resolution exhibits three peaks.

a) 

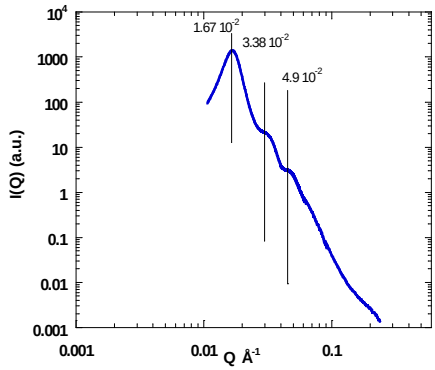
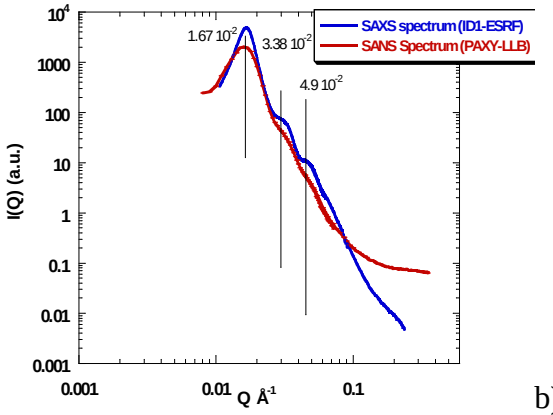
b) 

Figure 2 *a) isotropic 2D image of a AAO membranre measured on ID01 with the pore axis parallel to the incident beam b) After isotropic grouping, SAXS spectra exhibits three peaks at 1.67 10^{-2} $Å^{-1}$, 3.38 10^{-2} $Å^{-1}$ and 4.9 10^{-2} $Å^{-1}$.*

a) 

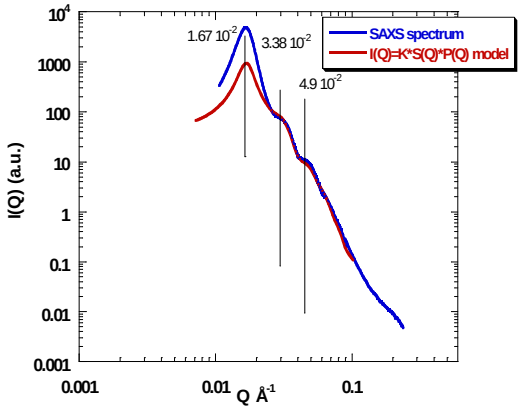
b) 

Figure 3 *a) SANS et SAXS spectra measured on the same AAO membrane. The SANS spectra exhibits only two broad peaks. b) The scattered intensity can be well modelized thanks to our model ($I(Q) \approx K .P(Q).S(Q)$ where P(Q) is the form factor of an oriented cylinder, S(Q) is a Perkus Yevick function). The morphology parameters extract from this model $D_{int} \approx 39$ nm $D_p \approx 20$ nm are in good agreement with the SEM measurements.*

In SANS or in SAXS, the scattered intensity is given by the general relation: $I(Q) \approx K .P(Q).S(Q)$ where K is the "contrast", S(Q) the structure factor and P(Q) is the pore form factor. The peaks measured can then be related to either P(Q) or to S(Q). While P(Q) is purely related to the shape of a single pore, S(Q) is only related to the spatial arrangement of the centers of the pores. We have recently shown [4] by a concurrent SEM and SANS study of AAO membranes that the intense and broad peak at small Q originates from a pure S(Q) contribution. Q* the position of this peak is actually a direct measurement of the inter-pores distance: $D_{int}=2\pi/Q^*$.

Here, we manage to go further: we adjust our experimental signal by modelizing the structure factor thanks to a Perkus Yevick function and by considering the form factor of an oriented cylinder given by $P(\mathbf{Q},\alpha)=\left(\frac{\sin(\mathbf{Q}H\cos(\alpha))}{\mathbf{Q}H\cos(\alpha)}\frac{2J_1(\mathbf{Q}R_p\sin(\alpha))}{\mathbf{Q}R_p\sin(\alpha)}\right)^2$ where H is the half length of the cylinder, R_p the pore radius and α the angle between the pore axis and the Q vector (Figure 3 b). Such model allows us to extract directly the AAO morphology : the pore diameter, D_p and the inter-pores distance, D_{int} with a good agreement with the SEM measurements.

We have also measured the anisotropic spectra obtained by tilting and rocking a membrane by respect to the incident beam in order to check the validity of our membrane modelization. This part is in progress.

Conclusion

Thanks to the SAXS measurements we have been able to fully characterize the morphology of our homemade AAO membrane. Here we propose a simple model that provides a direct statistical measurement (over the whole sample at the difference of the SEM) of D_{int} and P(Q) of the pore radius R_P.

References

[1] F. Li and al, *Chem. Mater.*, 10, 2470 (1998) [2] K. Fukuda and H. Masuda, *Science*, 268, 1466 (1995).
[3]. T.-L. Wade and J.-E. Wegrowe, *Eur. Phys. J. Appl. Phys.* 29 (2005). [4] K. Lagrené and J.-M. Zanotti, *Eur. Physical Journal- ST*, 141, 227-233 (2007).