ESRF	**Experiment title:** **In-situ study of channel self-organisation in Anodic Aluminium Oxide matrices**	**Experiment number**: 26-02-414
Beamline: BM-26B	**Date of experiment**: from: 10-06-2008 to: 13-06-2008	**Date of report**:
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Electrochemical anodization of aluminium foils leads to formation of extended pores in the growing aluminium oxide layer. At certain conditions the effective repulsion between the pores leads to their self-organisation into a hexagonal structure. This process allows one to fabricate membranes with periodically-ordered system of long pores with a well-defined diameter. This experiment was devoted to in-situ study of the self-organisation process. A special electrochemical cell was constructed to reduce the x-ray adsorption and to allow for a permanent electrolyte exchange through the cell. The aluminium foil was simultaneously acting as the exit window of the cell. The investigation is performed for a number of electrolyte compositions and anodization voltages.

To increase the intensity of the transmitted x-ray beam we have used a somewhat higher x-ray photon energy of 15 keV. A set of 9 compound refractive lenses was installed on a lens goniometer allowing to tune two translational and two rotational degrees of freedom. The electrochemical cell for in-situ studies was mounted on a sample goniometer. Photonic Science VHR CCD camera (22 micron pixel size) was used as a SAXS detector .

As we have shown in our previous experiment, the microradian x-ray diffraction setup at DUBBLE allows to resolve in great detail the radial and azimuthal profile of the diffraction peaks of many diffraction orders (*hk*). These profiles allows us to obtain information about the positional and bond-orientational order, respectively.

Fig. 1 presents an example of the collected data for anodization at 40V in 0.3M solution of oxalic acid $(COOH)_2$. The time passed after the beginning of the first and the second anodization is indicated. One can clearly see growth of the x-ray diffraction intensity upon pore growth. Moreover, the self-organisation of the pores can be seen to lead to reflection sharpening in both radial and the azimuthal directions. Yet, detailed analysis of the large data sets is needed to draw quantitative conclusions from this study.

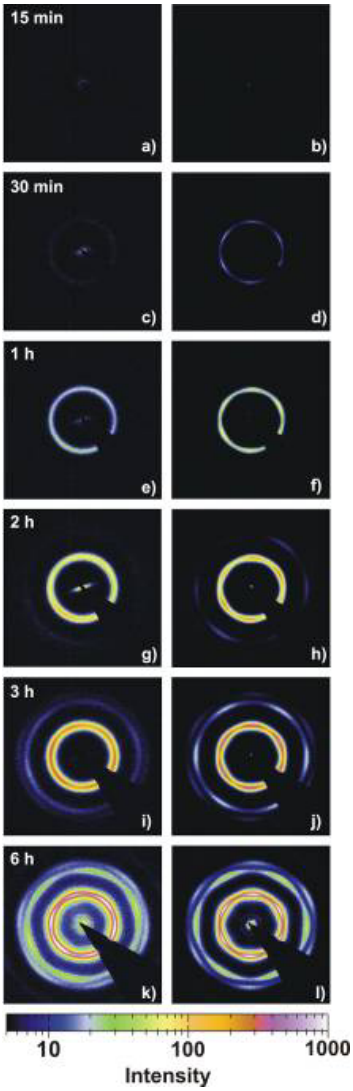

Fig. 1 Development of the microradian diffraction patterns during the first (left) and second (right) anodization. The pore separation is 105 nm.

Moreover, in the present experiment we have discovered that in addition to the two order parameters discussed above, one can also quantitatively determine the width δq_z of the reflections along the film normal z, which is related to the structural correlations along the beam. Interestingly, the reflections are found to be much sharper in the z direction, than the other directions.

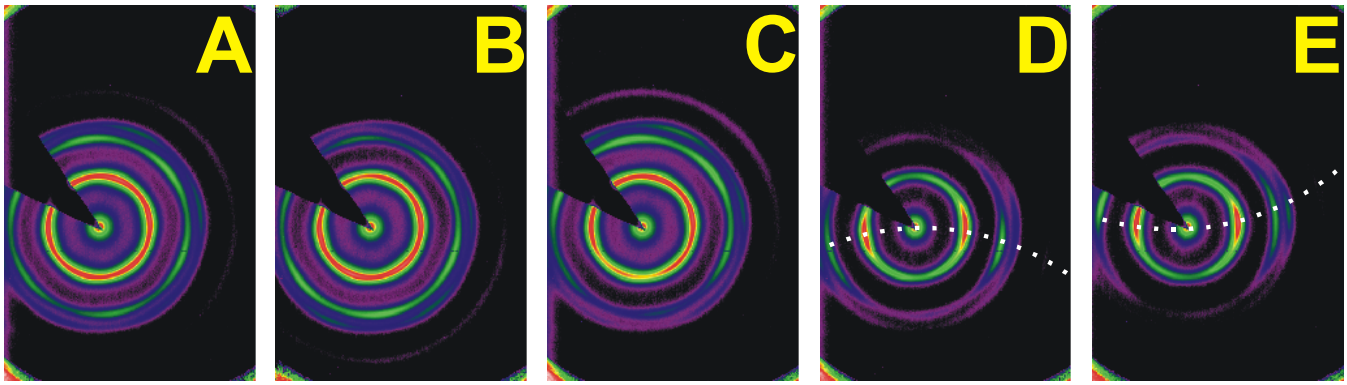

Fig.2. Diffraction patterns otained after 8 hours of the second anodization of an aluminum foil in 0.3M H_2SO_4 at 25V. The pattern are recorded at normal incidence (A), and after rotation by +0.2° (B), -0.2° (C), +0.5° (D), and -0.5° (E) around horizontal axis normal to the beam. The white arcs in (D) and (E) highlight the cross section of the Ewald sphere by a plane containing sample reflections. The pore separation is 65 nm.

Figure 2 presents a set of diffraction patterns measured with slightly different sample orientations during the *in-situ* experiment. One can see a very high sensitivity of the pattern to the orientation of the membrane. Moreover, a careful inspection of the patterns reveals a nontrivial effect of the pattern assymetry, which was earlier observed only in perfect crystals of colloidal hard spheres [1]. At positive rotation angles the reflections in the bottom part of the detector are stronger than those in the upper part. The situation is reversed at negative rotation angles.

This effect is further illustrated in Fig. 3, where the profile of the scattered intensity in the vertical directions in patterns B and C of Fig. 2 are presented. The assymetry is caused by the curvature of the Ewald sphere, which is extremely tiny at our small diffraction patterns (e.g., the first-order ring has a diffraction angle $2\theta \approx 10^{-3}$ radian). In this case the deviation of the Ewald sphere from a plane is as small as $\delta q = (2\pi/\lambda)(2\theta)^2/2 \approx (2\pi/\lambda) \times 10^{-6}$! Yet, the curvature effect is well visible in Figs. 2D and 2E. The white dotted arcs highlight the cross section of the Ewald sphere by a flat plane of the sample reflections. To observe such an effect, the reflections must be extremely sharp in the z direction, i.e. δq_z should be comparable to δq [1]. This suggests that the pore structure possesses very long correlation length along the pores. In other words, the pores have very long persistence length, of the order of tens of micrometres.

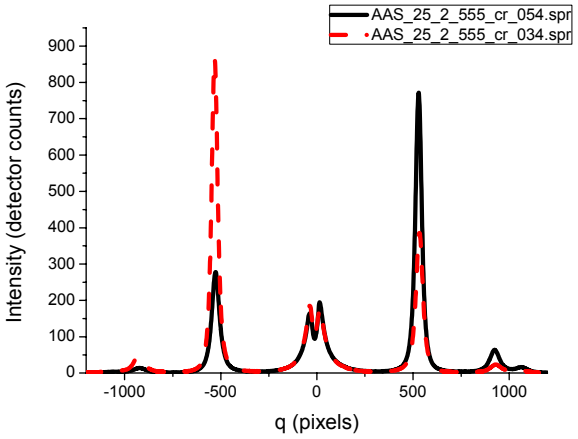

Fig. 3 The vertical profiles of the scattered intensity in Fig. 2B and 2C, represented with the black drawn line and the red dashed line respectively.

We believe that analysis of our present results will shed light on the development of the order parameters in the net of growing pores. Finally, we would like to thank K. Kvashnina and D. Detollenaere for their excellent support.

References.

[1] A.V. Petukhov et al., Phys. Rev. Lett., **88**, 208301 (2002).