



Experiment title: Study of highly-ordered anodic aluminium oxide matrices by microradian dynamic x-ray diffraction

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BM-26B

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9

Local contact(s):
Dr Kristina Kvashnina

Names and affiliations of applicants (* indicates experimentalists): W.G. Bouwman* (Delft), A. Petukhov*, D. Byelov* (Utrecht), A. Snigirev* (ESRF), V. Abramova*, K. Napolskii*, A. Eliseev* (Moscow), N. Grigorieva*, A. Chumakov*, A. Vasilieva*, S. Grigoriev* (St. Petersburg)

Report: (max. 2 pages)

The experiment was devoted to the study of structure and order of the Anodic Aluminum Oxide (AAO) membranes, which are prepared by the two-step anodization technique. An extended set of samples with different radii of the pores and different periodicity was prepared to study the influence of the preparation procedure on the structure and order of the membrane. This experiment was performed using the microradian setup, which was built and aligned during the preceding experiment 26-02-392. This allowed us to save a significant amount of beamtime. In this report we shall present a few preliminary results of the experiment.

Figure 1a shows a microradian diffraction pattern measured from an Al_2O_3 membrane of about 80 μm of thickness, with about 35 nm of pore's diameter and about 100 nm of distance between the pores. The diffraction pattern is identified as one scattered from the 2-dimensional hexagonal lattice of the channels. Up to forth-order reflections have been clearly detected, suggesting the presence of strong correlations in the channel positions over significant distances.

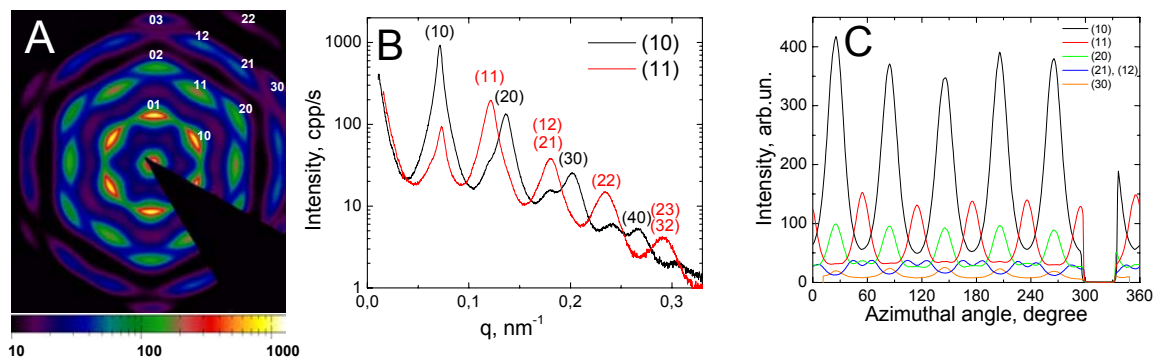


Figure 1 Microradian diffraction pattern from a 50 microns thick alumina membrane (A). Panel B presents the radial profiles of the scattered intensity along the 10 (black) and the 11 (red) directions. The hk indices for a number of reflections are given. The azimuthal variation of the intensity for several reflections is shown in panel (C).

Figure 1b presents the q -dependence of the scattered intensities (after subtraction of the detector offset of $I_{\text{off}} = 97.19$ cpps/s) with the wavevector q parallel to the principal orientations (10) and (11), respectively. The positions of the peaks ($q_{10} = 0.0696 \text{ nm}^{-1}$, $q_{11} = 0.1205 \text{ nm}^{-1}$ and $q_{20} = 0.139 \text{ nm}^{-1}$) correspond very well to the hexagonal order of pores with the distance of 105 nm between them. The radial profile of the diffraction peaks (see also Fig. 2c) has a Lorentzian shape and its half-width $\delta q = 0.004 \text{ nm}^{-1}$ corresponds to a correlation length of the hexagonal structure that spreads over a distance of $\delta L \sim \pi/\delta q = 800 \text{ nm}$. One can see that in spite of a rather large-scale periodicity of the structure, the microradian setup is able to resolve the peak profile in great detail. As illustrated in Figure 1c, the hexagonal interchannel order is extended

over distances comparable to the size of the irradiated area of the sample¹. One can also see a significant broadening of the peaks in the azimuthal direction (Figure 1c), which is induced by fluctuations of the bond-orientational order. The Half-Width at Half-Maximum of the (10)-reflections runs in the azimuthal direction is about 8 degrees for reflections of different order. The intensities of the reflections are found to be related as: $I_{10} : I_{11} : I_{20} : I_{21} : I_{30} = 37 : 14 : 9 : 2.7 : 1$. Furthermore, the diffraction pattern was found to be very sensitive to the sample orientation. Sample rotation by as little as a fraction of a degree can significantly affect the relative peak intensities.

To demonstrate that the x-ray diffraction in the alumina membranes is very strong and switches to the dynamic regime, several patterns were measured without the beamstop to allow for a direct comparison between the direct beam and the diffracted peaks (see Figure 2). Although the direct beam seems to be much brighter, one has to take into account that the power scattered into the six <10> reflections is distributed over much larger area on the detector. Our preliminary estimates show that the integrated intensity of one of the (10) reflection is 9.5 times larger (almost tenfold!) than that of the rest of the direct beam. Moreover, we found that sample rotations, which reduce the intensity of the diffracted peaks, lead to an increase of the direct beam intensity by as much as 62(!) times. This clearly shows that the diffraction is in a highly dynamic regime.

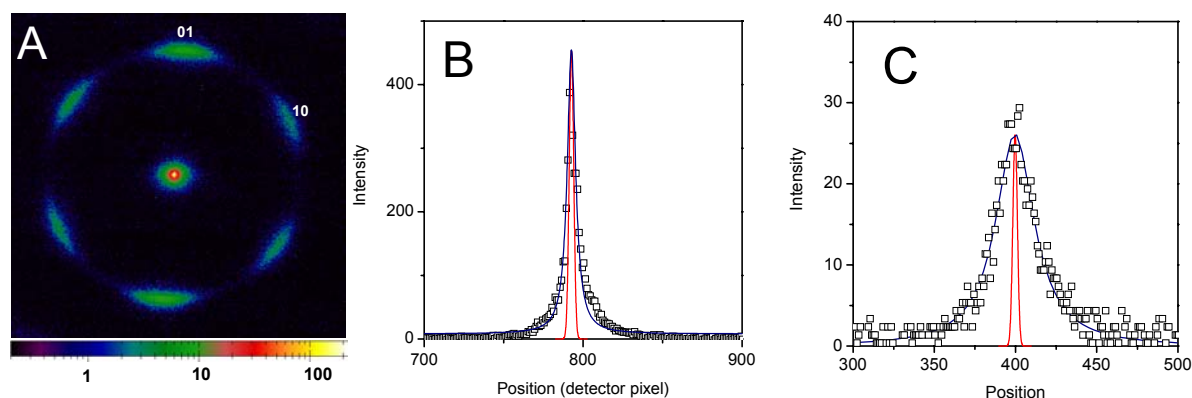


Figure 2. A microradian diffraction pattern measured without the beamstop is shown in (A). Panel B presents the profile of the direct beam passed through the alumina membrane (black squares) in comparison with the profile of the direct beam passed through a thin aluminium foil (red curve). For comparison, the radial profile of the (10) reflection is shown in (C). The red curve presents the instrumental resolution function (the same profile as that shown by the red curve in (B) but displaced to the (10) peak position).

Interestingly, the direct beam passed through the sample has a profile, which is distinctly different from that of the direct beam (measured after passing through a thin aluminium plate to reduce its intensity). The two profiles are compared in Fig. 2 b. One can clearly see that not only the diffracted peaks (Fig.2 c), but also the direct beam broadens. This can be related to fluctuations of the density of the channels in the membrane on the scale much larger than the structure period. At the same time, the dynamic character of the diffraction can also play a role. More data analysis and further experimental studies are needed to clarify this direct beam broadening.

In addition, we have performed a preliminary in-situ study of the channel growth process during electrochemical reaction. Unfortunately, due to the beamtime limitations we did not manage to vary the x-ray photon energy in order to vary the scattering contrast in our samples. We hope to perform such a study in our future experiments.

Finally, we would like to thank our local contact Dr Kristina Kvashnina and Dirk Detollenaere for their excellent support.

¹ The beam size at the sample was determined by the aperture of the compound refractive lens (about 1 millimeter).