

XRD analysis of freeze-cast, calendered free-standing MXene film - Rigaku

Date: 2021-10-07

Tags: XRD Texture Freeze-cast Rigaku 18/08/2021 Synth Nanoplexus 400 2021 Calendering Aerogel Article 2

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Goal : Attempt to quantify variation in crystallographic texture with coupled θ : 2θ scans of a freeze-cast, calendered Ti_3C_2 MXene film in various orientations.

Procedure :

Sample preparation

The sample preparation is as described in [\[Experiment\] Calendering of freeze-cast MXene aerogel](#) and associated experiments. In summary, $\text{Ti}_3\text{C}_2\text{T}_z$ aqueous suspension is freeze-cast at a concentration of 45 mg/mL, which should result in MXene particle basal plane alignment \parallel to the freeze-plate. The resulting freeze-dried aerogel cuboid of pure $\text{Ti}_3\text{C}_2\text{T}_z$ of dimensions 21.5 x 14.9 x 15.0 mm is then calendered, with compression along the longest axis, \parallel to the freeze-plate (21.5 mm) to a thickness of 1.00 mm. The compression should result in more dense MXene particle basal plane alignment with the largest plane of the sample cuboid (14.9 x 15.0 mm). Hence, the compressed aerogel dimensions can be associated with the dominant lattice parameter axes, such that 14.9 x 15.0 x 1.00 mm = x, y, z = a, b, c. Sample density post-compression is 0.982 g cm^{-3} compared with either 1.27, 3.8, 4.3 or 5.2 g cm^{-3} , which correspond to the maximum densities of aligned $\text{Ti}_3\text{C}_2\text{T}_z$ nanoparticles in a freeze-cast and calendered aerogel, a vacuum-filtered film, a blade-coated film and that derived from theory, respectively. This suggests the compressed aerogel still consists of a maximum of 81% pores.

Measurements are performed 50 days after the initiation of the MXene synthesis.

Instrument set-up

| | |
|------------|---|
| Geometry | Bragg-Brentano |
| Goniometer | SmartLab (In-plane) with θ 2θ Z cradle and xy-20mm attachment |

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| | |
|----------------------------------|--|
| Detector | Hypix-3000 2D-detector [38.5 mm x 77.5 mm, 385 x 775 pixels, pixel size = 100 μ m x 100 μ m] at 350 mm |
| X-ray source | CopperLine Focus X-ray tube with nickel K α absorber (0.02 mm) |
| X-ray generation power | 1.2 kW = 40 kV x 30 mA |
| Radiation | K α_1 = 0.1540598 nm, K α_2 = 0.1544426 nm, K α ratio 0.5, K β = 0.1392250 nm |
| Incident beam optics | CBO & CBO-f parallel beam, 0.1 mm collimator and 5 ° Soller |
| Diffacted beam optics | None |
| 2 θ start:finish:step / ° | 3:70:0.02 or 0.07 |
| Dwell time / s | 1.4 or 2.4 |

The configuration is captured in a photograph uploaded as IMG_1637.JPEG, where the sample orientation is defined as 'Edge' in the table below, such that ϕ , the axis aligned vertical to the sample holder is ϕ to the smallest sample dimension, such that observed reflections should be predominantly of type (hk0) for the reasons outlined earlier on sample preparation. The sample of dimensions 15.0 x 14.9 x 1.00 mm is measured in two orientations, as listed in the table below. Hence, the 'Flat' orientation refers to when z // the smallest sample dimension, when predominantly (00l)-type reflections are expected to be observed.

Results :

| Filename | Orientation | Dwell time / s | Step size / deg | Osc (ϕ) | Tilt (χ) / deg |
|--|-------------|----------------|-----------------|----------------|-----------------------|
| Ti3C2_MXENE_Film_Freeze_theta2theta_Test_100umColl_2D | Flat | 1.4 | 0.07 | Y | 0 |
| Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_Test_100umColl_2D | Edge | 1.4 | 0.07 | Y | 0 |
| Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_Test_100umColl_2D_Longer | Edge | 2.4 | 0.02 | Y | 0 |
| Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_Test_100umColl_2D_Chi20_NoOSC | Edge | 1.4 | 0.07 | N | 20 |
| Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_100umColl_2D_Chi15_OSC | Edge | 2.4 | 0.02 | Y | 15 |

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| | | | | | |
|---|------|-----|------|---|----|
| Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_100umColl_2D_Chi30_OSC | Edge | 2.4 | 0.02 | Y | 30 |
| Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_100umColl_2D_Chi45_OSC | Edge | 2.4 | 0.02 | Y | 45 |
| Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_100umColl_2D_Chi60_OSC | Edge | 2.4 | 0.02 | Y | 60 |
| Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_100umColl_2D_Chi75_OSC | Edge | 2.4 | 0.02 | Y | 75 |
| Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_100umColl_2D_Chi90_OSC | Edge | 2.4 | 0.02 | Y | 90 |

Files suffixed with _Theta_2-Theta.txt contain xy columnar data of 2θ vs intensity, .ras files are raw outputs from the diffractometer, .raw files are the TOPAS-legible equivalents of the .ras files, converted using PowDLL Convertor and .png are images of the plotted data.

The first four scans in the above table were used to test for the most appropriate measurement parameters, hence the variation in dwell time, step size and oscillation. The conditions in the third scan were found to be suitable to use for the latter six scans when tilting through χ . Files named FCCompressed_ChiTilt_Edge.png and OverlayLongChiStepScans.png display overlaid plots demonstrating the variation in the diffraction patterns when tilting through χ , produced in OriginPro 2017.

Rietveld refinement to the edge-oriented, untilted ($\chi = 0^\circ$) diffraction pattern (Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_Test_100umColl_2D_Longer) using the method refined in earlier experiments/analyses (see [\[Experiment\] XRD analysis of vacuum-filtered MXene film - PANalytical X'Pert Pro](#) or [\[Experiment\] Quantitative Phase Analysis \(QPA\) of MXene synthesis product PXRD patterns](#)) where jEdit is used to interface with Topas v5, and to produce the plot in Ti3C2_FCCalendarEdge_0.982gcm-3.png. The uploaded .inp file is the jEdit/TOPAS input file used to refine the structure (based on a model of 10wt% HF direct-etched Ti_3C_2 (<https://pubs.acs.org/doi/abs/10.1021/acs.chemmater.5b04250>)), whilst the .out, MXene_hklm_d_Th2_IScaled.txt and Yobs_Ycalc_and_Difference.txt files are output as a result. The output files can be used in conjunction with XRD_TOPASfits_allphasehkl.py uploaded to Github to reproduce the plot. $R_{\text{WP}} = 10.89$ and $R_{\text{Bragg}} = 1.65$.

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Important findings are that the broad diffracting region between 30 and $50^\circ 2\theta$ appear to be well defined by the refined structure, as has been seen previously when performing QPA. The peak at $60.52^\circ 2\theta$, which regularly was poorly fit in QPA, corresponds to the prismatic (1 1 0) reflection. The two other reflections in close proximity, which appears to fall within the breadth of the peak, are the (1 1 2) and (0 1 14) reflections with scaled intensities of 2.64 and 0.40, respectively, less than the 4.45 intensity calculated for the (1 1 0). This finding is not at all unexpected considering the predicted anisotropy of crystallite/nanoparticle orientation (texture) of the sample due to the processing route. The considerable mismatch in peak breadth between observed and calculated values for the (1 1 0) reflection is also easily explained, as the .inp file assumes isotropic crystallite size, and hence no anisotropic broadening is accounted for. We would expect the (1 1 0) peak, corresponding to the presence of prismatic planes perpendicular to z , to be narrower due to the less notable size-broadening (as compared with the (002) as the diffracting domain/crystallite size should regularly attain the minimum length of $1\ \mu\text{m}$, below which the broadening phenomenon is observed, based on knowledge of the particle size-distribution from a MXene synthesis of this type. Conversely, we would expect the (002) peak to be broader as we anticipate regular restacking on the order of less than a micron lengthscale to be less probable. A more advanced structural definition is required to model crystallite dimension anisotropy such as the use of second rank tensors or a multidimensional distribution of lattice metrics.

The plot shown in Ti3C2_FCCalendarEdge_0.982gcm-3_ChiOverlay.png has the three consistent peak locations marked with solid vertical lines and annotated hkl values, whilst the dotted lines correspond to those with scaled intensity > 1 from Rietveld refinement to the untilted ($\omega = 0^\circ$) diffraction pattern. With regards the shift in observed intensity whilst rotating around ω , the regularity of the (1 1 0) and (0 0 10) suggests that in fact, despite the processing, there is no measurable preferential orientation around the rotation axis. No comment can be made around the change in (0 0 2) intensity, as any changes are lost in the increased air scatter

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at the lower range of $< 30^\circ 2\theta$ values with increasing λ .

Conclusions:

The highly porous aerogel returns too few consistent reflections to interpret crystallographic texture via conventional means (pole figure derivation) as only three reflections, capable of being indexed to the $P6_3/mmc$ space group appear consistently all diffraction patterns. This methodology is unsuitable for this sample type.

Attached files

IMG_1637.JPEG

sha256: df89b726f509ddba23ceb4c53b9972ab52312ef75d5bf4a53e0bf62fe936aa3e



Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_Test_100umColl_2D.ras

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Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_100umColl_2D_Chi90_OSC.ras

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Ti3C2_MXENE_Film_Freeze_EDGE_theta2theta_100umColl_2D_Chi15_OSC.ras
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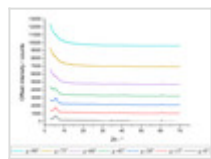
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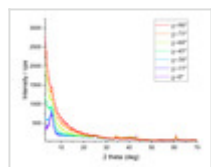
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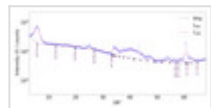
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MXeneFilm_NoNegPO_Rigaku.out

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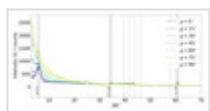
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Link: <https://frankel-elab.manchester.ac.uk/experiments.php?mode=view&id=101>