EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Mxene swelling in polar solvents for energy storage devices.	**Experiment number**: MA-5034
Beamline: BM20 (C04)	**Date of experiment**: from: 10 October 2021 to: 13 October 2021	**Date of report**: January 2022
Shifts: 9	**Local contact(s)**: Christoph Hennig	*Received at ESRF:*

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Report:

The project suggested experiments with powder XRD study of Mxene ($Ti_3C_2T_x$) immersed in several liquid polar solvents. It is known that certain kinds of Mxenes swell in polar solvents with significant expansion of inter-layer distance. However, so far only swelling in few solvents and only at ambient conditions was studied. The experiments were performed with cooling below freezing point (-120^{0}C lowest) and with heating to +50-90^{0}C. The freezing point of solvents is easily detected by XRD as new peaks from solid solvents appear. The main purpose was to find if any significant changes in swelling state or phase transformation exist in Mxenes upon cooling of heating excess of polar solvents. Experiments were performed in glass capillary filled with $Ti_3C_2T_x$ and excess of solvent. The Mxene material was syntehsized few days before the experiment in order to avoid posisble degradation effects related to material storage. Two synthesis batches were prepared to ensure that material is as expected. The materials were first tested at ambient temperature and the better batch selected for temperature experiments. High quality experimental results were obtained for Mxene immersed in water, methanol and dymetylsofoxide (DMSO). The most interesting results were obtained with DMSO and this part of experiment was expanded to include several heating-cooling cycles. Additional experiments were also performed with 2:1 H_2O: DMSO mixture. The mixture has significantly lower freezing point compared to pure water and pure DMSO and thus the temperature range was increased.

Some examples of results are shown below. The major part of the sample showed good swelling in methanol with d(001)=17.6Å at 300K and much weaker reflection with d(001)=14.1Å which is related to part of material not expanding due to swelling (**Figure 1**). The results of this experiment demonstrate that no significant change of swelling state is observed in Mxene immersed in methanol upon cooling down to 172K. No changes were observed also in process of heating up to 333K.

Similar results were obtained also for experiments with cooling of Mxene immersed in water and DMSO. Except for small gradual shift of d(001) no changes in a swelling state were found during the cooling to temperatures below freezing points of solvents.

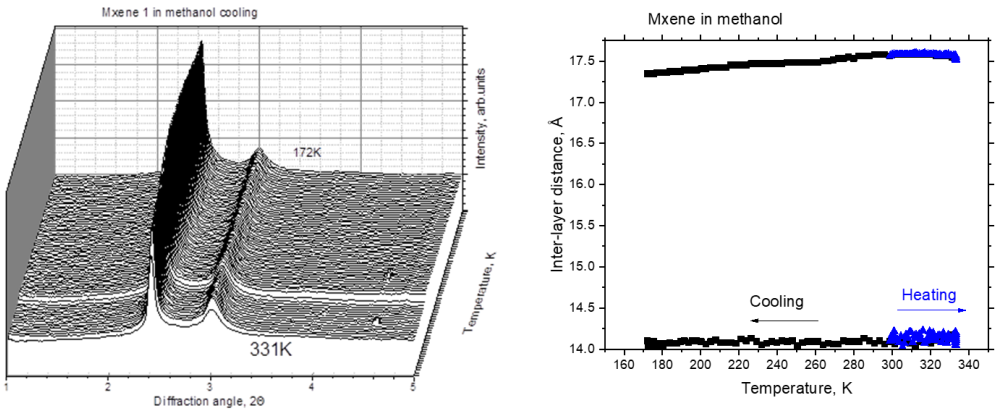

Figure 1. Temperature depend swelling of Mxene 1 in methanol: Low angle part of XRD patterns recorded from Mxene 1 in methanol recorded during cooling from 333K to 172K (left panel). b) temperature dependence of d(001) observed in the temperature cycling experiment performed with heating from ambient temperature to 333K and cooling from 333K to172K (right panel).

However, experiments with heating revealed interesting anomalies related to the change in swelling state. Thechange in swelling state is especially clear for Mxene immersed in DMSO where sharp transition was detected. According to preliminary analysis, the transition corresponds to change in the swelling state related to insertion of additional layer of DMSO solvent molecules (**Figure 2**).

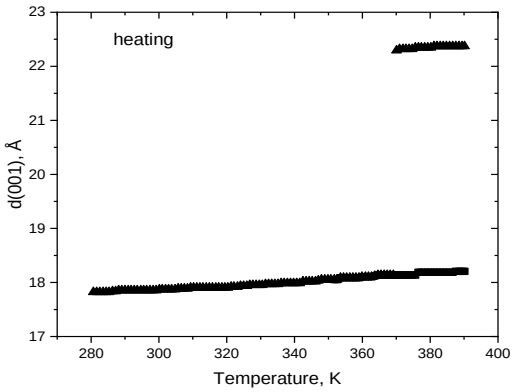

Figure 2. Temperature dependence of d(001) for Mxene immersed in excess of DMSO.

This transition is found to be irreversible and expanded phase preserves after cooling back to ambient temperature. The transition is also not complete even at highest temperature. Most likely the incompleteness of the transition is related to some inhomogeneousity of the material itself. Similar kind of incomplete transitions were observe dpreviously in ur experiments with graphite oxides immersed in ethanol. The expanded Mxene-DMSO phase is also found to be stable upon cooling down to Strong changein a swelling state was also observed upon heating of Mxene in water and in H_2O: DMSO mixture at similar temperature. Experiment with Mxene immersed in water were performed also swith lower X-ray intensity to ensure absence of beam induced degradation. The data for these experiments are processed and plotted. The data obtaine dduring experiment will be published in 2022, the work with manuscript had already started. It I splanned to submit the paper until summer 2022.