EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Combined XRD and XRF study of Mxene based microsupercapacitors under conditions of operation.	**Experiment number**: MA-5897
Beamline: ID22	**Date of experiment**: from: 27 October 2023 to: 30 October 2023	**Date of report**: 13 Dec.2023
Shifts: 9	**Local contact(s)**: Catherine Dejoie	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Alexandr Talyzin,* Department of Physics , Umeå University, Sweden

Report:

The goal of this project was to study *in situ* MXene synthesis using reaction of T_3AlC_2 (MAX-phase) with LiF/HCl. This method is very common and provides "clay-like" $Ti_3C_2T_x$ Mxene. The reaction occurs as an etching Al from MAX phase structure with formation of 2D layers of Mxene. Water washing is also essential step in the synthesis as it removes acid from Mxene interlayers and assists in termination of 2D layers surface with functional groups. So far, only the reaction products were studied using *ex situ* methods. The structural changes due to etching of Al from MAX phase, possible intermediate phases, effects of lattice expansion and swelling are not possible to study using *ex situ* characterization. The synthesis is sufficiently simple to allow *in situ* XRD study at slightly elevated temperatures (40-60^0) inside of plastic capillaries.

Following the experiment plan, we performed set of in *situ* synthesis experiments at ID22 with progressively increased temperature of reaction (40^{0}C to 60^{0}C). Special cell was designed for the experiment allowing to mix LiF and HCl over the precursor MAX phase directly inside of plastic capillary. Glass capillaries can be used in these experiments due to reaction with hydrogen fluoride. Using plastic capillaries creates some problems due to strong and non linear background. Over broad range of angles. However, background is not a problem at low angle region where the most important reflections from MAX phase and Mxene are found. Another problem is bubbles which for in process of reaction, especially within first minutes. Evolving bubbles move the whole powder sample and provide strong noise in terms of absolute intensity of diffraction peaks. Some plastic net

was used to reduce sample movements. The temperature of capillary was controlled using Cryojet stream. As expected, the reaction was visibly easy to detect due to some bubbles evolving in first few minutes. However, no changes in the structure of material were observed by XRD during this stage of reaction. First signs of new MXene phase were detected after about 30 min.

Figure.1 shows results of first experiment started at 313K. Due to the rather slow rate of transformation the temperature was increased to 323k and later to 333K. As it follows from these data, the reaction is still slow but kinetics is improved at higher temperatures. Nevertheless, even after ~6 hours the transformation was not complete.

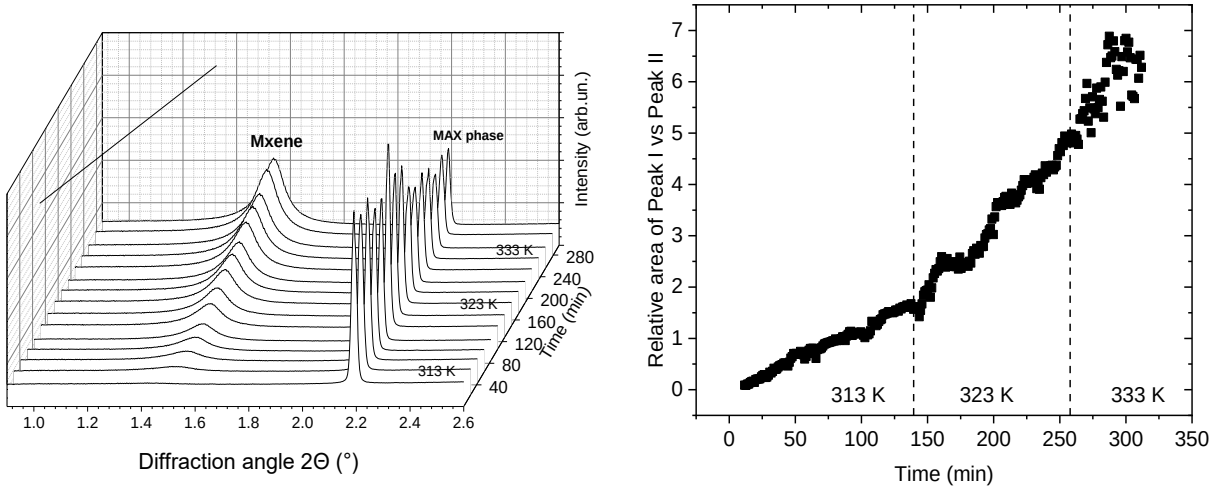

Figure 1. Low angle part of selected XRD patterns recorded during reaction of MAX phase with LiF/HCl (left): Integral intensity ratio for (001) reflections from MXene formed in the process of reaction and precursor MAX phase.

Separate experiments were performed next with new samples for prolonged periods of time at 313, 323 and 333K. Preliminary analysis of data is shown in the Figure 2. The data were obtained using batch fitting, some "bad points" will be later checked manually and possibly corrected.

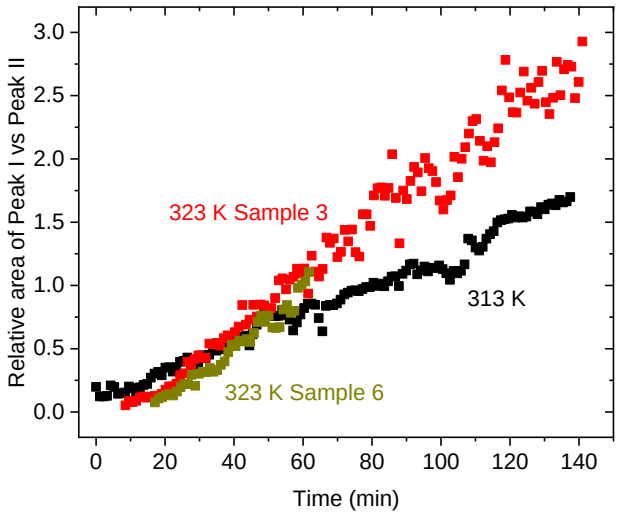

Figure 2. Plot of relative integral intensity for (001)-reflections of Mxene : MAX phase vs reaction time. Clearly the kinetics of reaction is faster at 323K.

Additional experiment was performed with materials exposed to the reaction *ex situ* for 12 hours at 318K and for 19 hours at room temperature. In this case amount of etching solution is significantly larger and the reaction is more complete. Separate experiment was also performed with water washing of reaction products. Water was added to capillaries and XRD data recroded during certain period of time.

Preliminary analysis of recorded data shows the value of *in situ* XRD experiments. We are first to record XRD patterns directly in process of etching and before washing the reaction products with water. The c-lattice expansion observed for MXene directly in LiF/HCl is different compared to dry MXene material after water washing and in water immersed (swollen) state. We expect that analysis of XRD data will provide novel information about the mechanism of reaction and will be used as a core for high quality publication.