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-5528
Beamline: ID16B	**Date of experiment**: from: 24 November 2022 to: 28 November 2022	**Date of report**: 2 Feb.2023
Shifts: 12	**Local contact(s)**: Remi Tucoulou Tachoueres	*Received at ESRF:*

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Report:

The project plan was to study structural changes and migration of electrolyte ions in microsupercapacitor electrodes under condition of the device operation. Two types of devices were prepareed for these experiments. First type is standard in-plane sueprcapacitor with Mxene electrode and gel electrolyte. Following types of gel electrolytes were used: KI and H_2SO4 in PVA-DMSO and PVA-H_2O. Iodine concentration was monitored using XRF in experiments with KI-based electrolyte. H2SO4-based electrolyte is standard in that type of supercapacitor devices and in this case it was serving as a reference in XRD experiments. Second type of microsupercapacitor devices was based on cylindrical geometry using standard glass capillaries. In the end, most of the XRD experiments had to be done using capillary-type deviced due to very strong preferential orientation of Mxene layers. The layers tend to align along the substrate and, as appeared, transmission geometry does not allow to observe most important XRD reflection related to inter-layer distance in Mxene structure using flat devices.

Summarizing results, experiments with capillary type of miscrosupercapacitors were successfully performed for all four electrolytes listed above. Typical experiment included following steps: first recording CV curve from the device installed at the beamspot, control of charging current for next steps. XRD was then recorded in the same spot in several cycles with opposing polarity, first at +0.6V and -0.6 V and next with increased potential

(e.g. 0.8V, 1.1 V, 1.2V), until detecting clear degradation of device performance. Example of data is shown in the **Figure 1.**

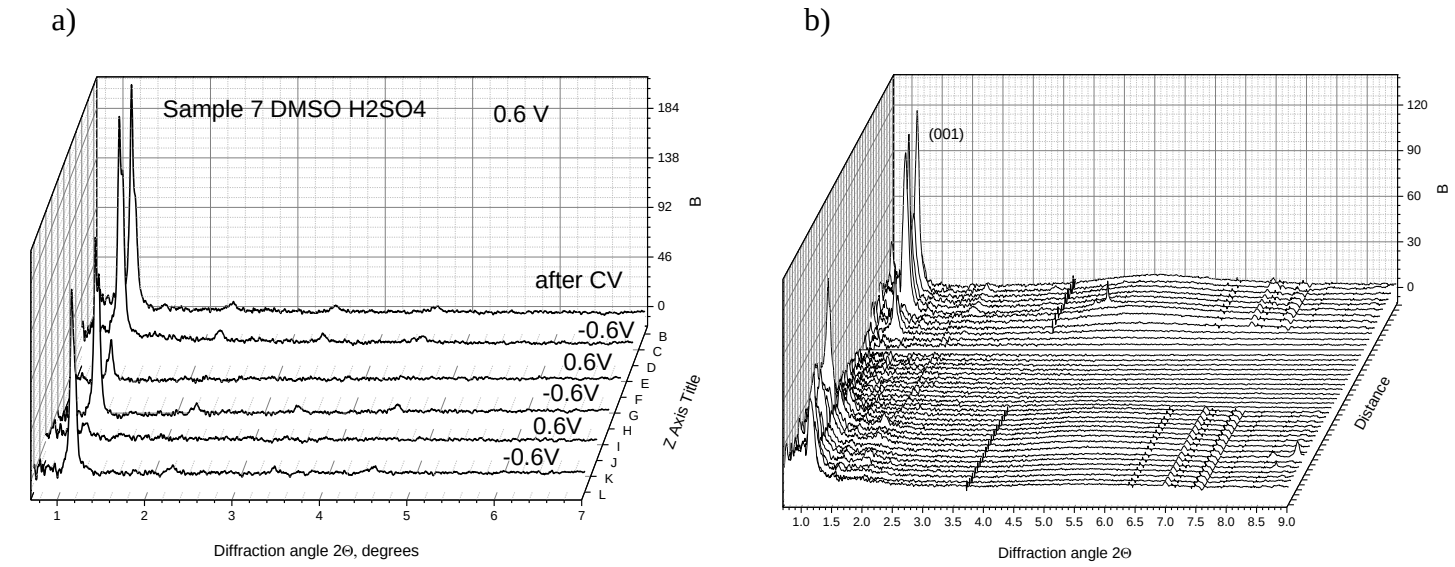

Figure 1a Intergrated XRD patterns recroded from microsupercapacitor device: a) at static conditions and reversing potential polarity (+0.6V and -0.6V). b) XRD patterns recorded in linear scan which startrs on one electrode , goes over the separator area (no peaks from the material) and finish at oppsite electrode. Recorded at -1.1V. Background subtracted.

In this particular experiment the change in intensity of (001) reflection was detected. This reflection corersponds to inter-layer distance of MXene. Figure 1b shows second type of experiment where XRD patterns were recroded in a linear scan along the capillary. The scan wa sperformed so that it crosses the separator area (no electrode) and records data from both electrodes close to separator area. The scan shows very clear some difference in d-spacing of Mxene (001) reflection on opposite electrodes. The scan was also recorded at the potential (1.1V) sufficient for degradation of material caused by electrochemical reactions. Additional XRD reflections not present at 0.6V operation were detected indicating structral changes. Exact nature of structural changes observed in these experiments and complex analysis of all experiments are under consideration at the moment. Similar data were recroded also for KI electrolytes based on DMSO and H_2O. The XRD part of experiment can be considered as successful and likely to lead to some publciation after complete analysis and, possibly, after adding data by some other methods.

XRF characterization of processes in operating miscorsupercaps revealed several issues which require further work for complete success. The thickness of gel electrolyte is difficult to control using standard procedures. The electrolyte is added as droplet over the whole area of flat in-plane device. XRF allows to detect both Ti from electrodes and Iodine in the electrolyte. However, if the thickness of electrolyte drop is too high, no change in iodine concentration was detected. When the electrolyte layer was too thin (added as thin film over electrodes), all iodine was absorbed by electrodes showing no difference after change of polarity. Yet another experiment with "intermediate thickness" showed some change in concentration of iodine over one of electrodes, but rather small. It can be concluded, that preliminary data obtained during our experiments demonstrate feasibility of using XRF for studies of microsupercaps but some improved design of devices is necessary. The main part to improve is some control over the thickness of gel electrolyte added over the device.

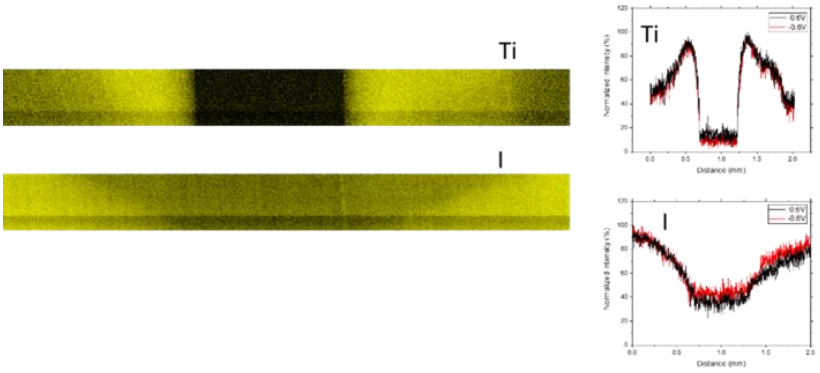

Figure 2. XRF scans showing Ti and Iodine distribution recorded on printed in plane microsupercapacitor in the area of electrode separator. The change of integrated profiles under conditions of changed polarity is shown in two diagrams, for Ti and I. Some change in the concentration of iodine can be detected on the right side.