Experimental report

Proposal: 6-07-109	**Council:** 10/2022

Title: In situ study of supercapacitors with reduced graphene oxide electrodes using neutron reflectivity.

Research area: Materials

This proposal is a new proposal

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Samples: Graphene Oxide

Instrument	Requested days	Allocated days	From	To
SUPERADAM	5	3	24/05/2023	27/05/2023

Abstract:

Graphene-related materials are promising for applications in supercapacitors (SC), devices which store charge thanks to an electrical double layer formed on the surface of the electrodes. In situ and in operando studies of electrode materials inside of electrochemical devices are important for understanding of basic processes and ways to improve SC performance. However, in situ or in operando studies of supercapacitors were never tested using neutron scattering methods to the best of our knowledge. This project suggests to perform first in operando study of supercapacitor cell with reduced Graphene Oxide (rGO) electrodes using Neutron Reflectivity (NR) method. Quantitative estimation of electrolyte ions sorption using NR will be performed first in absence of potential difference, then under conditions of fully charged supercapacitor cell with opposite polarity of applied voltage and as a function of charge/discharge cycle number. We will be able to evaluate the change in composition of rGO electrode due to sorption of ions (positive or negative depending on applied potential). The charge density change due to formation of electrical double layer will then be evaluated.

Experimental Report. Alexandr Talyzin
Proposals 6-07-109 (25 -27 May 2023) + CRG-2961 (27-29 May 2023).

Experiments were aimed on *in operando* study of supercapacitors which was never tested previously using neutron scattering methods (to the best of our knowledge). Prior to experiment we designed and tested electrochemical cell which can be easily assembled on place, filled with electrolyte and tested for electrochemical performance prior to recording neutron scattering data. The cell is assembled using two Si plates covered by thin reduced graphene oxide films (rGO) separated by 1-2 mm layer of electrolyte. The neutron reflectivity (NR) scans were recorded trough Si plates in process of supercapacitor cell operation. Our previous experiments demonstrated that Neutron Reflectivity (NR) is powerful tool to study thin films of graphene oxide (GO). Graphene oxide film thickness and chemical composition changes in process of intercalation by various polar solvents was studied. Therefore, we had extensive experience in preparation of GO films on 7 cm x 7 cm substrates with quality sufficient for NR studies. The GO films can easily be reduced by thermal treatment, thus providing films of reduced graphene oxide (rGO) which are electrically conductive and routinely used as electrode materials in electrochemical devices.

For this experiment we prepared 10 rGO films with somewhat different thickness. The films were verified first using standard NR setup and the films with best visually observed oscillations selected for next experiments. Standard experiment included characterization of rGO film on air, then with electrolyte (H_2SO_4) added. The cell was then checked for leaks and connected to potentiostat and charged-discharged several times to record electrochemical data. As expected, the cells showed typical for supercapacitors CV loop (**Figure 1**).
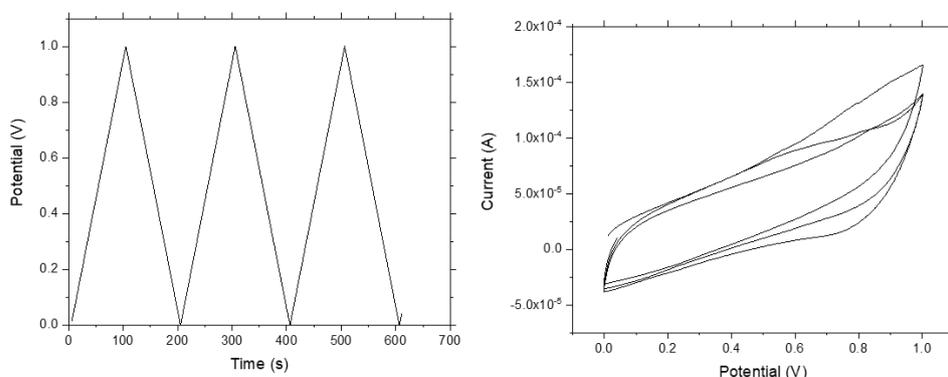

Figure 1. Example of CV data recorded from electrochemical cell with rGO electrodes.

As anticipated, the cell shows rather modest energy storage and CV loops deviating from perfect square shape. However, these deviations were expected considering design with relatively large separation of electrodes and slow kinetics of charging/discharging.
On the next step active electrode was charged at +1V. The neutron reflectivity data were then recorded from the electrode charge to +1V (with counter electrode at 0V), then at -1V and after complete discharge at 0V. Therefore, ideally full cycle consists of 4 scans. Counting two additional scans recorded prior to experiment (on air and in electrolyte), total 6 scans are required for complete characterization of one complete cycle of charge-discharge.
However, in practice some problems were experienced: leaks preventing recording complete cycle, issues with contacts or loss of electrochemical performance. Nevertheless, we succeeded

to record one satisfactory experiment. In this cell the voltage applied was decreased to +0.5 and -0.5 V.   Two cycles were recorded.
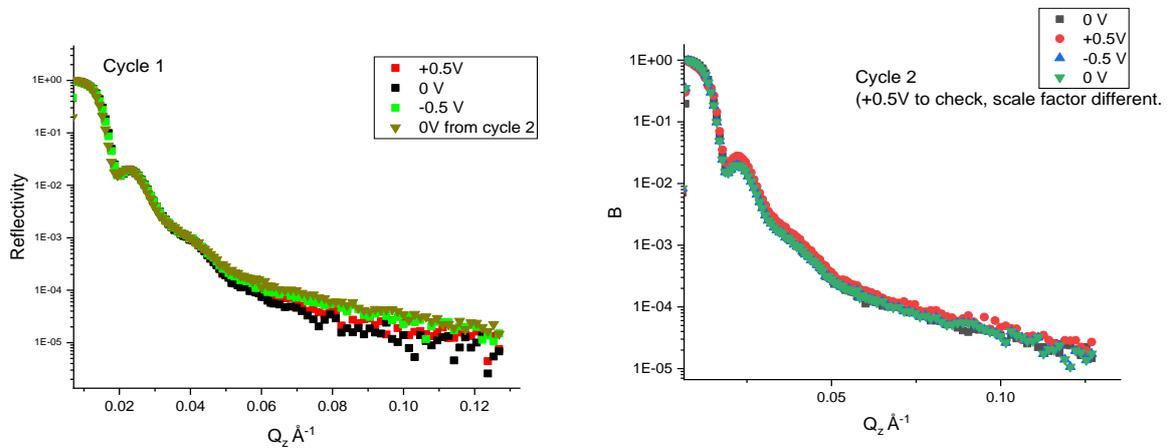

Figure 2. Preliminary data recorded using NR from rGO electrode inside of electrochemical cell with H_2SO_4 electrolyte.

As it is shown in Figure 2, NR scans recorded from rGO electrode in charged state are slightly different. Relatively small difference likely reflects non porous nature of rGO electrode and sorption of ions mostly on outer surface of film.   Therefore, rather detailed analysis is required in order to make any conclusions about processes inside of the cell. Analysis of data is in process at the moment.

Preliminary results are following:

- High quality rGO films were prepared and tested using NR. The films are found to be suitable for NR data recording with some clear oscillations present.
- Special electrochemical cell adapted to NR was designed and successfully tested in our experiments. The cell showed reasonably good electrochemical performance, it is proved that good quality NR scans can be recorded from rGO electrodes in electrolyte -filled cell, the films are also stable in process of charging and discharging.
- The changes in structure of electrodes as function of applied potential are small which is likely due to non porous nature of electrode. The films is most likely graphite-like with disordered structure. This point will be checked using XRD analysis.
- Detailed analysis of NR data is expected to reveal formation of H+ and SO_4^{2-} layers on the surface of charged rGO. The final result depends on how strong the changes in NR scans are and detection limits of the method.