Experimental report

10/08/2022

Proposal:	**1-04-214**	**Council:**	10/2020

Title: Ion Adsorption on Planar Graphene Electrochemical Double Layer Capacitor Electrodes

Research area: Chemistry

This proposal is a new proposal

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Samples:
Graphene coated silicon wafer
hexadecenoate anion C16 TAB cation in Acetonitrile

Instrument	Requested days	Allocated days	From	To
FIGARO	3	3	31/08/2021	03/09/2021

Abstract:

All across our devices - phone to regenerative braking, electrical energy storage is becoming more important, particularly as part of the exploitation of renewable resources. Electrochemical double layer capacitors (EDLCs) are a high power energy storage device that operate by charge separation across the double layer at the electrode/electrolyte interface. Hence, we need to further our understanding of the structure of the electrolyte ions at the electrode surface to improve these devices.

Graphene is one of a number of carbons used for EDLC electrodes. This proposal aims to investigate the interactions and ‘absorption’ of ions on graphene substrates utilising the unique capability of neutron reflection to study surface structures of organic molecules on carbon surfaces in-situ and resolve cations and anions using h-/d-contrast. The structures adopted with and without applied potential will be studied.

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The aim of this experiment was to study the behaviour of a model supercapacitor double layer electrode using neutron reflectometry. In this case, we considered supported graphene electrodes on metal current collectors.

A custom electrochemical cell was designed, produced and used successfully during the experiment, as shown in figure 1. It used two silicon blocks with conductive carbon coatings as electrodes, separated by a PTFE spacer. In an advance from previous experiments, it also allowed the use of a pseudo-reference electrode. The cell was symmetric allowing us to utilise the ability of Figaro to strike to sample with the neutron beam from above or below and hence observe the positive and negative electrodes with a single applied potential. This avoids the need to cycle the potential, which can lead to changes in structure.

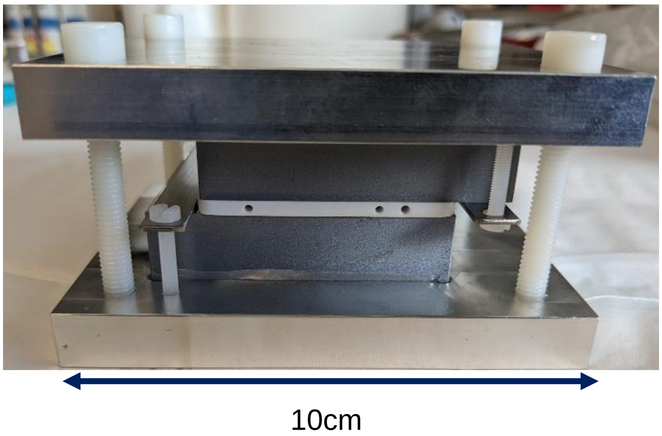

Figure 1: Photo of custom electrochemical cell

Three types of electrodes were prepared for the experiment, which consisted of a thin conductive coating supported by silicon: a) graphene, b) graphene on gold, and c) gold. Initially, we characterised each of these electrode coatings in hydrogenated and deuterated acetonitrile. Two of these systems seemed to have data as we might expected. However, this analysis revealed that for the graphene on silicon substrates, there was evidence of a thin layer (around 15 Å) of hydrogenated material on the graphene surface. This was attributed to PMMA polymer, which is used by the graphene manufacturers when transferring the graphene onto a silicon substrate.

Although the manufacturer claimed that all polymer was removed, this very thin layer of residue is undetectable by most other techniques. However, using neutrons which are very sensitive to thin layers, we were uniquely able to detect the polymer layer.

We considered several methods to remove the polymer. After each treatment, the surface was re-characterised by reflectometry to see if it was successful. Importantly we were able to identify that the most successful technique for removing the polymer was careful UV/ozone treatment (which has been shown in the literature to remove PMMA). The neutron data was particularly nice, figure 2 shows an evolution of polymer removal with increased duration of

UV treatment. This is evident in the decrease in depth of the fringes, particularly the first trough at 1.5 x 10^{-2} Å^{-1}.

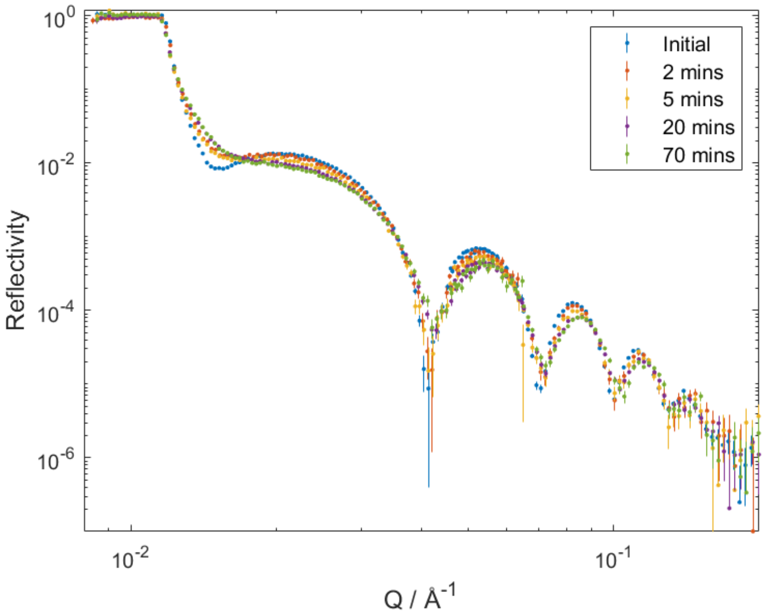

Figure 2: Reflectometry data for a graphene on gold electrode exposed to UV/ozone for increasing amounts of time (2 minutes to 70 minutes).

Once the electrode surfaces had been characterised, we added electrolyte solutions in non-aqueous solvents (tetrabutylammonium tetraphenylborate in d-acetonitrile) and investigated the effect of applying potentials to the cell. The electrodes were characterised in the electrolyte solution with no applied potential, and then positive and negative potential. Importantly, we were able to see some reversible changes with potential as we had hoped. This is attributed to the reversible formation of adsorbed double layers of ions at the electrode surfaces. However, not all the carbon-based electrodes showed this effect. Hence further work is required to investigate these interesting differences.

In conclusion, we successfully characterised graphene electrode surfaces using neutron reflectometry and studied their electrochemical response. Using this technique gave us unique insights into the polymer layer on graphene, left over from its transfer onto silicon. We were able to determine that UV/ozone is a successful method for decreasing the amount of polymer on the surface. In addition, we were able to see reversible changes to the reflectometry profile with applied potential, which is likely to be due to the reversible formation of an electrical double layer at the electrode surface.