Experimental report

09/09/2024

Proposal: 1-04-250 **Council:** 4/2023

Title: In situ SANS for Probing Ions Adsorption in Pillared Graphene-based electrodes for Supercapacitors

Research area: Materials

This proposal is a resubmission of 6-07-105

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Samples: Graphene based materials

Instrument	Requested days	Allocated days	From	To
D22	2	2	12/09/2023	13/09/2023
			28/09/2023	29/09/2023

Abstract:

We have developed pillared graphene-based materials (PGM) showing promising interest for supercapacitors (SCs) applications. To reach higher storage performances these materials need to be optimized further. For this purpose, it is necessary to investigate the adsorption processes at play in these bi-phasic graphene-based materials, and more precisely to be able to identify the different scales of porosity accessible to electrolytic ions diffusion and adsorption. we need to use SANS techniques for their scattering contrast advantage to reveal, by in situ SANS, the diffusion and electro adsorption of organic electrolyte ions in material pores of different sizes as a function of the potential applied.

In situ SANS for Probing Ions Adsorption in Pillared Graphene-based electrodes for Supercapacitors

Experimental team: Y. Ben Cherifi, F. Duclairoir, S. Pouget, L. Porcar and H. Mendil-Jakani

The aim of this *in-situ* SANS experiment was to gain insights into the **adsorption** and **desorption mechanisms** of **electrolytic ions** before/during/after **static polarization** (-1.3V and +1.5V) of **pillared graphene-based materials** (PGM) with inter-graphene sheet distance ($d_{spacing}$) modulated by the nature of the intercalant/pillar molecule (**Fig.1**) formulated as electrodes for supercapacitors. We have examined the pore size dependent adsorption of hydrogen-containing cations (tetraethylammonium (TEA^+) (Φ_{TEA+} (0.7 nm) ~ $d_{spacing}$ (0.75 nm)) and tetrahexylammonium (THA^+) (Φ_{THA+} (1 nm)> $d_{spacing}$) and boron-containing anions (BF_4^-), utilising the high neutron scattering cross-section of hydrogen (H) and the high neutron absorption cross-section of boron (B). It was anticipated that the adsorption of TEA^+ would be associated with an increase in the scattering intensity. Conversely, the adsorption of BF_4^- was expected to be associated with a decrease in the scattered intensity (BF_4^- anions contain approximately 20% of neutron-absorbing ^{10}B).

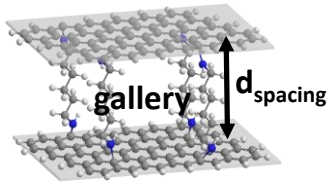

Fig.1. *Scheme of Pillared Graphene Materials – PGM Pillar = alkyl diamine with 6C*

Electrochemical cell design and sample preparation.

- To achieve these goals, we developed an *ad hoc* electrochemical cell compatible with SANS specifications. **Fig.2a** and **2b** show the conceptual scheme and the prototype of the cell. It consists of a three-electrode electrochemical cell with two neutron-transparent aluminium windows acting as current collectors and a silver reference electrode. The cell design facilitates beam centering, beam attenuation reduction and beam interaction only with the working electrode. **Fig.2c** shows the cell mounted on the D22 beamline.
- In order to attribute the observed variations in intensity to the adsorbed species, it was ensured that the only source of hydrogen in the system was the cations present within the electrolytic media. Accordingly, deuterated acetonitrile (d-ACN) was employed as the solvent.

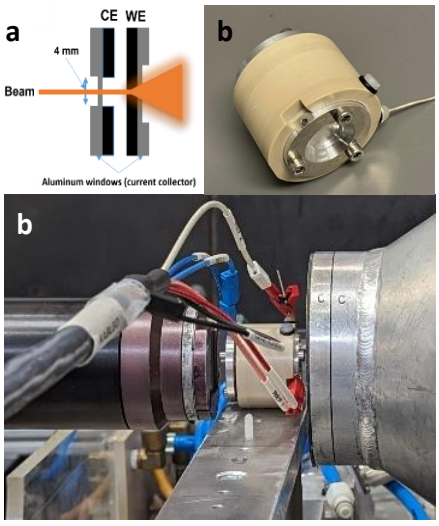

Fig.2 a. *Conceptual scheme and* ***b.*** *prototype of the electrochemical cell* ***c.*** *Cell mounted on the D22 beamline*

Main results.

In a previous *in situ* SAXS experiment conducted at the D2AM-CRG beamline at the ESRF, it was observed that the polarization of the PGM electrode in 1M $TEABF_4$/AN did not result in any discernible structural modifications. Consequently, the evolutions observed in the SANS profiles during polarization were attributed to a variation in contrast (Δρ), which was postulated to be the consequence of the evolution of the relative proportion of cations and anions within the different porosity scales under polarization.

Three SANS profiles were recorded for each sample under three conditions: (i) at the open circuit voltage (OCV), which served as a reference, (ii) at **-1.3 V** vs Ag to **promote cation adsorption**, and (iii) at **+1.5 V** vs Ag **to promote anion adsorption**.

The evolution of the scattering profiles during polarization was emphasized **by normalizing the profiles to the one recorded at the open circuit voltage (OCV) (Fig.3a** and **3b).** The interpretations presented in this study are illustrated in the conceptual schemes in Fig. 3a (TEA^+) and 3b (THA^+). This scheme is relative to a sample displaying interconnected gradually decreasing porosity scales, which is in agreement with SAXS/SANS profile recorded prior to the analysis; however at this stage of the experiment other porosity distribution profiles cannot be ruled out

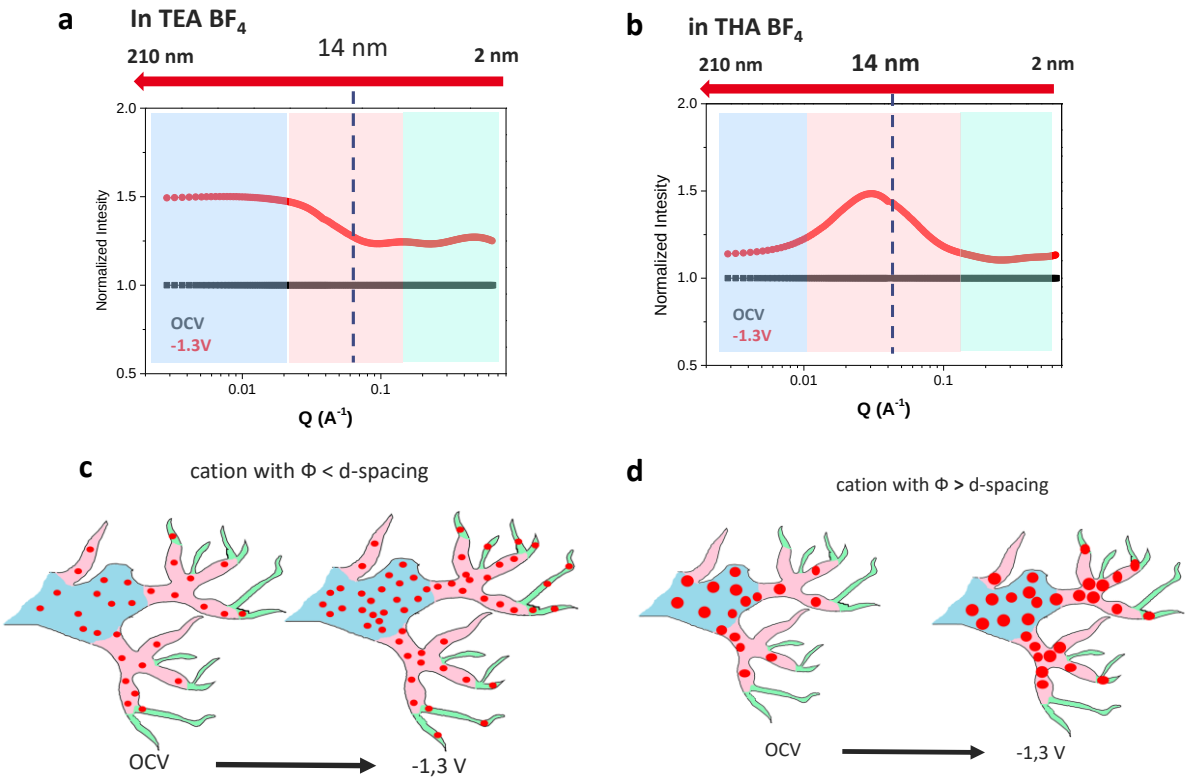

Fig.3. *Normalized scattering profiles to the OCV polarized at -1.3V in* ***(a)*** *1M $TEABF_4$ /d-ACN and in* ***(b)*** *1M $THABF_4$ /d-ACN. The curves were smoothed for clarity purpose. Schemes of the* ***(c)*** *TEA^+ and* ***(d)*** *THA^+ distribution over the different length scales of the porosity.*

The primary observations are presented below and illustrated in **Fig.3c** and **3d**.

<u>- For $TEABF_4$/d-ACN electrolyte after polarization at -1.3 V</u>

*** At low Q, (scale > 30 nm)**: the polarization at -1.3 V (red curve) induces an increase in normalized intensity compared to that recorded at the OCV across the entire scale (3 to 210 nm). This increase is attributed to the electrolyte enrichment of TEA^+ throughout all the porosity scales, with a clear increase of cation amount observed > 30 nm.

*** At high Q, (scale < 10 nm)**: the normalized intensity indicates a higher amount of TEA^+ than at OCV but lower than at high scale > 30 nm. This observation supports the hypothesis that a size-based restriction is at play below 10 nm.

*** At intermediate Q:** the normalized intensity decreases, which indicates that the smaller porosity (below 32 nm) accommodates a lower relative quantity of TEA^+ than the larger porosity, which may be explained by a geometrical/structural restriction.

- For $THABF_4$/d-ACN electrolyte after polarization at -1.3 V

*** At low Q, (scale > 80 nm):** an increase in normalized intensity is observed compared to that recorded at the OCV, indicating an enrichment of THA^+, but less than that observed for TEA^+ at -1.3V.

*** At high Q, (scale < 10 nm)**: the normalized intensity is lower than in the case of TEA^+ despite the higher hydrogen content in THA^+ compared to TEA^+, indicating that less cations reach this porosity.

*** At intermediate Q scale:** a clear bump is observed and is likely caused by the accumulation of large cations (THA^+) within this porosity scale (from ~ 8 nm to ~ 63 nm). This accumulation impedes the diffusion of these cations to smaller pores.

Our findings indicate that in the PGM sample, THA^+ ions are concentrated in the porosity region around 14 nm. This suggests that these ions are limiting in accessing the smallest porosity. This blocking effect is not observed with $TEABF_4$, as TEA^+ cations are distributed throughout the entire porosity range.

These studies demonstrate, for the first time, that the mesoporosity is active in transport and storage mechanisms within pillared graphene materials. Furthermore, these insights facilitate comprehension of the observed ion-sieving phenomenon at a local scale by ssNMR [1]. Indeed, the adsorption of THA^+ is already restricted in the mesoporosity before it even reaches the galleries.

The results obtained at 1.5 V were analyzed in a similar manner, yet a discernible trend was not readily apparent. This analysis has to be reconsidered since this absence of trend may be explained by a concomitant co-ion (TEA^+) desorption observed when the small BF_4^- is preferentially adsorbed.

This *in situ* SANS experiment constituted a significant part of Dr. Yassine Ben Cherifi's PhD thesis, which was successfully defended in early 2024 [2]. It will also play a pivotal role in a forthcoming publication.

These unprecedented results raise the question of the possibility of observing the desolvatation of ions within the electrochemical double layer (inner and outer Helmoltz planes up to the bulk of the porosity). Such question will be the basis of a future ANR project.

References

[1] Lee et al., Revealing Electrolytic Ion Sorption in Layered Graphene Galleries through Low-Temperature Solid-State NMR Chem. Mater. 2023, 35, 10, 3841–3848

[2] Advanced Characterization of Graphene-Based Materials for Supercapacitors, Yassine ben Cherifi, PhD thesis, Grenoble Alps University, 2024