PhD proposal in CEA Grenoble

Advanced Characterization of Pillared Graphene-Based Materials for Supercapacitors

PhD Summary:

The goal of the PhD project is to use advanced methods in order to characterize and explain how electrolytic ions diffuse through and adsorb at the surface of pillared graphene materials. These materials consist in graphene sheets linked together by bi-functional pillar molecule used to prevent reduced graphene oxide (RGO) sheets from restacking. In supercapacitor cells, this strategy - employed to increase adsorption active surface area in graphene sample - has been shown to be successful, as improved storage performances could be achieved with such assemblies compared to RGO. Fundamental characterization and understandings of the materials structures and ions diffusion/adsorption inside these systems will allow to study electrochemical double layer formation and eventually will provide methodologies on how to improve pillared graphene materials. Hence, multi-scale and multi-physics characterizations of the material structure and ion transport will be performed to correlate both parameters. It is noteworthy that the material is innovative as this class of pillared graphene-based materials is able to confine electrolytes in 2D dimensions, which provide a model-like structure to study 2D diffusion in lamellar porosity.

Detailed subject:

Context:

Electrochemical double-layer capacitors also known as supercapacitors (SCs), are devices that store energy through charge separation from electrolytic ion sorption on charged electrode surfaces. Graphene is a very interesting material for this application as it theoretically presents high electrical conductivities, large surface areas and mechanical flexibilities. Despite these high potentialities, graphene is showing limited capacitances (~100F/g) due to sheets partially restacking through π- π interactions. Exploring the layered structures of graphene derivatives modified with intercalant units is a strategy followed in the laboratory to avoid graphene layers restacking for enhanced ion sorption. Indeed, we synthesized a class of pillared graphene materials with varied inter-layer separation using alkyl diamines as pillars, speculating that such expanded layered structures could offer additional ion sorption sites and improve storage performances in supercapacitors (SCs). These pillared graphene materials have then been assembled into graphene hydrogel to optimize the ions transport inside electrode bulk porosity. The storage performances achieved demonstrated the success of this strategy.

Project objective:

The goal of the PhD project is to use advanced methods in order to characterize and explain how electrolytic ions diffuse through and adsorb at the surface of these materials. Theses fundamental understanding are highly interested as they will deepen the knowledge on these materials, strengthen the importance of the good storage performances achieved and provide methodologies on how to improve pillared graphene materials. Hence, multi-scale and multi-physics characterizations of the material structure and ion transport will be performed to correlate both parameters. Notably the dynamic of electrolyte confinement inside these pseudo 2D-structures will be evidenced.

Project description:

During this PhD thesis, pillared graphene architectures will be obtained using pillar molecules selected to promote the formation of graphene galleries to mechanically prevent reduced graphene oxide sheets to restack. These pristine materials will be physico-chemically (XPS, IR…), structurally (XRD, SAXS, BET) and morphologically (SEM, TEM) characterized. These combined analyses will allow to identify parameters such as porosity (closed and open), interface morphologies, nano-scale (d-spacing) and mesoscale structuration as well as surface chemistry nature and conductivity. The electrochemical evaluation of the materials will be performed in order to qualify these new systems with respect to other existing carbon material without expanded structures (ie. without 2D porosity). Combining these results to ex situ X-ray and neutron diffraction/scattering techniques (XRD, SAXS, ssNMR) characterizations will help identifying ion transport, adsorption, interactions mechanisms inside these structures. The dynamic of electrolytic ions confined inside these materials will also be addressed using QENS experiments. This in-depth understanding of pristine materials as well as cycled ones will provide fundamental knowledge and understanding, and will allow paving the way for the development of efficient materials and cells.

Technical content of the PhD project:

The tasks of the PhD will be to synthesize pillared graphene materials following procedures developed in the laboratory. Graphene assemblies with varying bulk porosity and density will be prepared. Physico-chemical (ss-NMR, XPS, TGA, SEM…) and electrochemical characterizations will be performed on all samples to allow a comprehensive comparison of the various materials. The PhD student will also perform advanced X-ray and neutrons scattering analysis on the samples to try the extract trends between samples structures and storage performances.

Outcome for the student:

This PhD project is dealing with a highly interesting societal issue, which is the electrochemical storage of energy. The student will hence be sensitive to these issues. He will also gain extensive knowledge on advanced characterization techniques applied to study energy storage processes, which is currently a very interesting skill to acquire for future research positions.

Student profil

The student should be about to graduate from a M2 Research in a topic related to chemistry, electrochemistry or material chemistry. The student should also be interested by the field of energy storage.

Contact information

Please send CV, cover letter and L3/M1/M2 marks to: florence.duclairoir@cea.fr and hakima.mendil-jakani@cea.fr.