19 March 2025

PhD contract offer

Synthesis and characterization of new biosourced hard carbons for sodium-ion batteries

General information

Workplace: Epinal and Clermont-Ferrand, France
Type of contract: PhD contract funded by ANR, in the framework of the PEPR project "Batteries"
Contract period: 36 months
Expected date of employment: 1 October 2025
Proportion of work: Full time
Remuneration: About 2200 € gross / month (minimum)
Desired level of education: Master's degree in materials science or chemistry
Experience required: -

Subject description

Hard carbons are key materials as anode for sodium-ion batteries (SIBs). This PhD thesis consists in producing new biosourced hard carbons, following the first extremely encouraging results obtained from plant polyphenols (reversible capacity 306 mAh/g at C/20, coulombic efficiency 87%) in negative electrode for Na-ion battery [1]. However, no optimization had been made. The precursors used, tannins, can be formulated to combine with furan resins and other phenolic molecules, such as phloroglucinol, all of which are bio-based, and many variables can be brought into play in the preparation to obtain hard carbons of different textures and very low specific surface area. The formulations can be converted into monoliths, aerogels, doped with heteroelements, or even 3D printed to obtain self-supporting materials with controlled porosity [2] (see Figure 1).

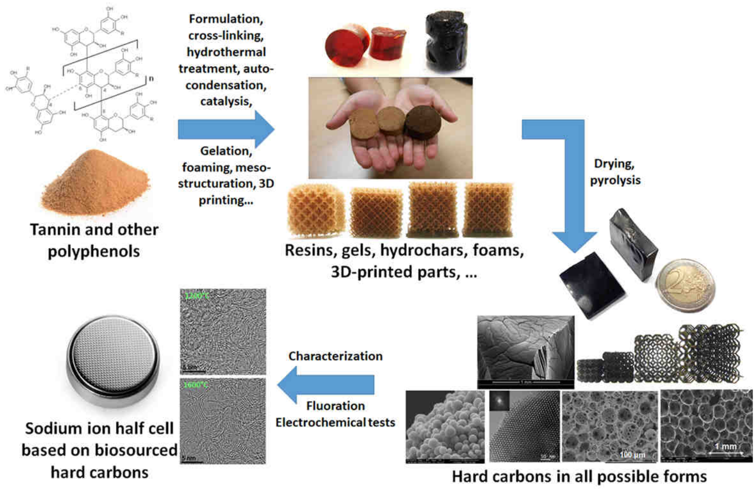

Figure 1. *Biosourced hard carbons as anode*

This thesis between IJL and ICCF therefore proposes a systematic exploration of biosourced phenolic resins and their derived carbons. To reduce the number of syntheses and associated characterizations, it will use experimental designs in multi-variable systems "monomer - cross-linking agent - phenolic/furanic substitution rate - pH - catalyst - thermal history". These systems are very complex but very well mastered by the laboratory, which to date has only tested a single derived hard carbon in a Na-ion battery, with the results mentioned above. Based on a unique experimental platform in terms of characterization, notably by adsorption with different probe molecules and its ad-hoc models, the thesis will propose hard carbons with optimized composition, texture and physical properties for the targeted application [3].

To limit the irreversible electrochemical process of hard carbons when used as anode in lithium ion battery, a surface treatment is known to be beneficial and, more particularly, the surface fluorination [4-6]. The latter can be managed by different ways. In order both to optimize fluorination level and to favor fluorination of carbon defects without creating new ones, gas-solid fluorination will be preferred. However, fluorination agent, concentration, temperature and contact time are critical parameters to discriminate. In order to delimitate quickly those parameters, TGA-MS under pure molecular gas will be used and a panel of fluorinating agents will be usable. The main criteria used to validate fluorination effect will be first the amount of dangling bond and its decrease upon fluorination. The final assessment will be galvanostatic tests comparing hard carbon with and without surface fluorination, using a coin cell configuration. The electrochemical properties of the selected surface fluorinated anode (hard carbon) and cathode will be investigated using half-cell with metallic Na. The more promising anode/cathode combination will be then studied.

Themes / Context

This thesis is part of the COFLUENSS project "COextrusion and FLUorination for ENhanced Solid state Sodium ion battery", involving 4 research units from 3 universities and the CNRS. The project is based on the observation that sodium ion batteries (SIBs), despite research dating back to the 1970s, remain less developed than lithium ion batteries (LIBs). Indeed, the mechanisms of sodium storage and solid electrolyte interphase (SEI) formation are not fully understood, requiring advanced in situ/operando characterizations and theoretical simulations. SEIs in SIBs are less stable than in LIBs, leading to secondary reactions and performance degradation. Controlling the material-electrolyte interface (MEI) and SEI is therefore crucial to improving cycle stability and electrochemical performance.

COFLUENSS therefore aims to develop an all-solid-state sodium-ion battery with a polymer electrolyte, exploiting fluorine to mitigate dendrite formation, stabilize interfaces and synthesize new electrode materials. The project focuses on:

1. **Protecting the active material surfaces against electrolyte attack and suppressing the surface degradation.** Ensuring the stability of active materials is crucial for improving the performance and lifespan of SIBs. This objective focuses on preventing degradation, which directly impacts battery efficiency and durability.
2. **Contributing to the understanding of both the side reactions at the material-electrolyte interface and the formation of the solid electrolyte interface to achieve high reversibility of sodium plating/stripping and stable interface polymer electrolyte/electrode.** A deep understanding of these interfaces is essential for enhancing battery performance and safety. This knowledge is critical for developing stable and efficient electrolytes and electrodes.
3. **Defining the most efficient route for surface and bulk fluorination and performing its up scaling.** Identifying the optimal fluorination processes is foundational for enhancing material properties and achieving the desired chemical stability in battery components. This objective is key to advancing both materials science and battery engineering.
4. **Quantifying the performance gain for optimized anode/cathode combinations.** Measuring performance improvements from optimized material combinations helps prioritize material choices and design strategies for better battery performance.
5. **Developing environment-friendly and scalable processes for (co-)extruding new generation electrolytes and electrodes at the laboratory scale.** Creating scalable and sustainable manufacturing processes is essential for transitioning from laboratory research to industrial production. This objective underpins the feasibility and environmental impact of the project.

Supervision Details

Supervision will initially take place at the IJL's Epinal site, then at the ICCF's Clermont-Ferrand site. It will be complementary in terms of skills in synthesis and characterization of bio-based hard carbons, and fluorination of these materials and associated electrochemical tests, respectively. This PhD contract will provide a rare opportunity for a highly motivated candidate to study every stage in the preparation of a sodium-ion battery anode, from the formulation of the bioresources on which the hard carbons are based, their optimization and modification, to their testing in a battery in operation.

Scientific, Material, and Financial Conditions of the Research Project

The research will be carried out in fully equipped laboratories, with a doctoral contract secured.

Research Dissemination, Publication, and Intellectual Property Rights

The results will be disseminated through publications in international journals and presentations at specialized conferences. If deemed relevant by the research team, patent applications may also be considered.

Planned Collaborations

As the proposed work is part of a consortium of 4 laboratories, interactions are to be expected with the different partners, each in its own field of expertise. Whenever necessary, leading experts will be consulted to address experimental, theoretical, or modeling-related challenges. Depending on the circumstances, additional research stays at partner laboratories in France or abroad may be considered.

References

1. Tonnoir, H., Huo, D., Canevesi, R.L.S., Fierro, V., Celzard, A., Janot, R. Tannin-based hard carbons as high-performance anode materials for sodium-ion batteries (2022) Materials Today Chemistry, 23, art. no. 10061.
2. A. Celzard, V. Fierro. „Green", innovative, versatile and efficient carbon materials from polyphenolic plant extracts. Carbon 167 (2020) 792 – 815
3. J. Jagiello, J. Kenvin, C.O. Ania, J.B. Parra, A. Celzard, V. Fierro. Exploiting the adsorption of simple gases O2 and H2 with minimal quadrupole moments for the dual gas characterization of nanoporous carbons using 2D-NLDFT models. Carbon 160 (2020) 164 – 175
4. M. Chatenet, S. Berthon-fabry, Y. Ahmad, K. Guerin, M. Colin, H. Farhat, L. Frezet, G. Zhang, M. Dubois, Fluorination and its effects on electrocatalysts for low-temperature fuel cells, Advanced Energy Materials, 2023, 13, 2204304
5. Y. Charles-blin, O. Gimello, D. Flahaut, K. Guerin, M. Dubois, L. Monconduit, N. Louvain, H. Martinez, Surface atomic layer fluorination of Li4Ti5O12: Investigation of the surface electrode reactivity and the outgassing behavior in LiBs, , Applied Surface Science, 2021, 542, 148703
6. "Composite SnOx/C fluoré pour matériau d'électrode", Inventeurs : C. Gervillie, A. Boisard, S. Berthon fabry, K. Guérin, E. Sainton disa, Demande de brevet en France N°: FR1908401 du 24/07/2019, Copropriétaires : SAFRAN - UCA - ARMINES - CNRS - SIGMA Clermont

Work context

The candidate will join two research teams specializing in materials science: the "Biosourced Materials" team at the Institut Jean Lamour (IJL, UMR CNRS 7198), housed in the premises of ENSTIB, in Epinal, and the "Fluorinated Materials" group at the Clermont-Ferrand Institute of Chemistry (ICCF, UMR CNRS 6296). Supervision will take place half at the Epinal site of the IJL (ENSTIB Campus), and half at Clermont-Ferrand site where ICCF is located. It will be complementary in terms of skills in hard carbon synthesis, optimization and characterization, and in modification of these materials by various fluorination methods, electrochemical properties and associated testing.

Skills

The candidate should have a very strong background in solid-state chemistry or materials science, but knowledge of batteries and electrochemical systems in general will be particularly appreciated. The candidate will have to demonstrate a great ease with the modern analytical techniques he/she will be trained in, to become quickly autonomous, and in particular, to deepen the physicochemical aspects involved (macromolecular synthesis, pyrolysis, grinding, electrical conductivity, surface treatment, in-depth physicochemical characterizations, electrode shaping and electrochemical testing). He/she will need to be dynamic, curious and persevering to carry out the multiple syntheses, characterizations, tests and interpretations of results, and demonstrate the ability to work in a team and in two distinct scientific environments.

Constraints and risks

The position you are applying for is located in a sector relating to the protection of scientific and technical potential. It therefore requires, in accordance with the regulations, that your arrival be authorized by the competent authority of the Ministry of Higher Education, Research and Innovation.

About Institut Jean Lamour and Institut de Chimie de Clermont-Ferrand

The Institut Jean Lamour (IJL) is a joint research unit (UMR 7198) of CNRS and Université de Lorraine. The IJL is focused on materials and processes in science and engineering, and covers activities in condensed matter physics, materials, metallurgy, plasmas, surfaces, nanomaterials and electronics. The IJL staff consists of 183 researchers/lecturers, 91 engineers/technicians/ administrative staff, 150 doctoral students and 25 post-doctoral fellows. The IJL has active partnerships with 150 companies and our research groups collaborate with researchers from more than 30 countries throughout the world. The IJL's exceptional instrument platforms are spread over 4 sites; Epinal is one of them.

The Institut de Chimie de Clermont-Ferrand (ICCF) is a Joint Research Unit (UMR 6296) under the auspices of the CNRS, the Université Clermont Auvergne and the Centre Hospitalier Universitaire de Clermont-Ferrand. The ICCF develops fundamental and applied research with strong industrial partnerships in various fields of chemistry, enabling it to respond to societal challenges linked to its three research areas: Chemistry and the Environment, Chemistry and Materials, and Chemistry for Life, with a particular focus on the design of innovative materials. The ICCF makes its technical skills, instrumental equipment and know-how available to meet the current needs of society and industry.

Application

Only high quality applications will be considered: Master 2 average ≥ 14/20, 1st quartile, international experience required. Applicants who do not meet these requirements are asked not to submit an application.

Women are especially encouraged to apply. Applications should consist of a cover letter including a motivation statement, a curriculum vitae, a list of publications, the contact details of two references, together with diploma copies and/or marks obtained during the Master degree, and send it to:

alain.celzard@univ-lorraine.fr

katia.araujo_da_silva@uca.fr

Then, interviews will be organised and visits of the labs will be possible on request.