Novel silicon-based architectures as anode materials for high-energy capacity fast charging lithium-ion batteries

Summary of the project Silicon is a promising anode material for lithium-ion batteries but its application is limited due to its low electronic conductivity and severe volume change during the lithiation/delithiation process. While both silicon-based layered structures and hollow spheres have previously been investigated as anode active materials, the application of silicon-based hollow multilshelled microspheres has not yet been studied. This project mainly aims to design microscale silicon-based anode materials with hierarchical structures composed of nanosized structures like hollow microspheres with multilayer onion-like shell nanostructure, enabling ample space for lithium storage and efficient volume expansion suppression.

Supervision This project is based on a jointly PhD supervised program between Sorbonne Université (SU, Dr. Imad Arfaoui as supervisor) and Technical University of Crete (TUC, Prof. Dimitrios Gournis (https://www.linkedin.com/in/dimitrios-gournis-61686559/?originalSubdomain=gr) as co-supervisor). Monthly meetings and/or reports will effectively monitor the progress of the project.

Position of the project within national and international context The quest for next-generation lithium (Li)-ion batteries (LIBs) demands heightened capacity, prolonged lifespan, and rapid charging capabilities. Silicon (Si)-based anode materials have garnered substantial interest due to their abundant supply, low cost, and remarkable theoretical capacity, surpassing conventional graphite by tenfold. However, their application is hindered by challenges such as poor electronic conductivity and substantial volume expansion during charge and discharge cycles, leading to the formation of a destabilizing solid electrolyte interphase (SEI) layer. This volume expansion exacerbates sluggish electrochemical kinetics and compromises the stability of the SEI layer, crucial for efficient ion transfer1. To address these limitations, nanostructured Si materials, including Si based-nanoparticles and two-dimensional (2D) Si based-nanostructures, have been explored to mitigate volume expansion and enhance ion accessibility.

These studies have so far shown very promising results regarding the application of 2D-based materials in spatially confining material expansion and enhancing large Li-ion absorption[2]. However, to achieve high-energy LIBs, several issues need further investigation such as optimization of material expansion, effective anode wetting, reduction of functional group population, and enhancing the space for Li storage capacity.

In particular, one proposed strategy to overcome volume expansion is the application of hollow nanospheres coated with mechanically stiff materials, limiting expansion inward[3]. However, the issue with these structures is that, on one hand, they require complicated and costly material synthesis, and on the other hand, the available volume for Li storage is significantly decreased compared to layered structures.

Then, one of the challenges for increasing the capacity of 2D multilayer structures to reach the highest theoretical capacity of the 2D structure is to make it possible for Li to find more space between the layers[4]. While theoretically, this should be achievable, still the best achieved capacity is at least two times smaller than the theoretical predictions. This can be attributed to the geometry of the structures. In 2D multilayer structures, a considerable portion of the space is buried inside the layered blocks, and the low Li-ion conductivity of the structure does not permit Li to efficiently occupy all the available sites and instead exploits more of the outer spaces. Hence, novel material architecture is required to permit the formation of fewer layers per layered block and maximize storage capacity to facilitate Li-ion diffusion and minimize buried space.

The present PhD project proposes the use of Si-based hollow multilshelled microspheres (HMMs) as a holistic approach to address this challenge i.e. designing microscale Si-based anode materials with hierarchical structures composed of nanosized structures like hollow microspheres with multilayer onion-like shell nanostructure. Their unique architecture combines the benefits of 2D layered systems with hollow nanospheres, enabling efficient volume expansion suppression and ample space for Li storage[5].

Objectives In this context, the present PhD project seeks the main objective to respond to the current demand of LIB technology for achieving high-energy capacity and fast-charging batteries by introducing a novel material concept as a platform for anode active materials i.e. HMMs. The study aims to understand the effects of each material and its corresponding slurry properties and parameters on determining factors such as the stabilization of the SEI layer formation, ion conductivity and diffusion, volume expansion of the structure, material stability, mechanical robustness during cycling, electrolyte-anode chemical reactions, etc.

Strategy While both Si-based layered structures and hollow spheres have previously been investigated as anode active materials, the application of Si-based HMMs has not yet been studied. This requires a detailed investigation on three aspects: materials design and synthesis, anode electrode fabrication, and battery performance testing and in-depth material characterization to define the details of the ion and electron transfer processes in these structures, their detailed role and effectiveness in each of the mentioned challenges, and the dependence of the battery performance tests on their structures and chemical compositions. Through a jointly supervised PhD thesis between SU and TUC and the use of MONARIS laboratory and School of Chemical and Environmental Engineering facilities and expertise, these objectives can be categorized under three main work packages:

1. **Design, synthesis, characterization, and optimization of HMMs.**

Hollow spheres of nanometer to micrometer dimensions define another important class of shape-fabricated materials, in which the hollow sphere's shell can be constructed from a variety of materials of valuable scientific interest and technological importance[6]. The co-supervisor has the skills in synthesizing HMM structures of various material platforms[7]. We anticipate demonstrating the fabrication possibility of Si-based HMMs materials such as Si, SiO_x, SiO_2, etc., using similar synthesis protocols[8, 9]. In this project, inorganic hollow microspheres will be developed, fully characterized and tested. Several inorganic materials based on silica, aluminosilicate and carbon based materials, with multilayer onion-like shell structure, will be obtained using both a modified self-assembly technique and CCVD methods. Initially, inorganic (silica or aluminosilicate-based nature) hollow microspheres of high thermal stability will be fabricated by the adsorption of colloidal 2D silicane or aluminosilicate (clay) layers onto the surfaces of a spherical anion exchange resin and calcination of the resulting resin–silica composite. Various 2D materials (silicas, clays etc), templates (spherical shaped templates) and experimental conditions will be used resulting in hollow spherical objects of different sizes (and/or shapes) and surface properties.

2. **Fabrication of corresponding anode slurries based on the HMMs structure, battery packaging, and performance investigations.**

Since 2021, MONARIS laboratory (SU) benefits from all the resources and experience, mainly through collaboration with QUANTUMAT (https://www.quantumat.com/index_fr.html), TUC, LCMCP (Laboratoire de Chimie de la Matière Condensée de Paris (UMR 7574 Sorbonne Université, CNRS, Collège de France) and LRCS (UMR 7314, Laboratoire de Réactivité et de Chimie du Solide, Université Amiens Picardie Jules Verne) for the fabrication of anodes and batteries as well as the performance tests of the latter.

a- Coin cell making (slurry making + slurry casting)
b- Battery testing

3. **Investigation of the relationship between performance results and the chemical and physical material properties from the perspective of material design optimization.**
   a- Morphological information (Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM))
   b- Chemical information (Infrared and Raman spectroscopies, X-ray Photoemission Spectroscopy (XPS), and Rutherford Backscattering Spectrometry (RBS))
   c- Structural information (X-ray diffraction, porosity and AFM nanoindentation measurements)

Expected results As explained, the application of Si-based HMM structures as anode active materials is anticipated to significantly enhance the specific energy capacity of Li-ion batteries. This enhancement aims to minimize capacity loss during large electric charging currents, thereby increasing charging speed and extending battery unit durability and lifetime. These outcomes are expected to be achieved through engineering the chemical and physical properties of the HMM materials, primarily based on the following expected results:

- Controlled synthesis of Si-based HMM materials such as Si, SiO_x, SiO_2.
- To adjust the number of layers and their intercalation inside HMMs, as well as the size of the HMMs themselves.
- Stabilization of the SEI layer via limiting volume expansion inside the HMM structures in order to enhance battery durability compared to 2D materials.
- To establish a model describing the formation and evolution of the SEI layer and the reasons for its stabilization in these materials.
- To improve significantly ion and electron conductivity of the structures and increase the specific energy of the batteries by providing large volumetric spaces on the surface and inside the microspheres as the HMMs contain closed sheets of well-defined and unshrinkable volumes.

Scientific environment The project will benefit from the facilities of both MONARIS laboratory (SU) and School of Chemical and Environmental Engineering (TUC), as well as their respective financial resources. Moreover, an official Research Collaboration Agreement (Ref. Sorbonne Université C23/0839) has been established between QUANTUMAT, SU and TUC. Highly motivated candidates (expecting a master degree or equivalent with excellent academic records) with a background in Physical Chemistry and Material Science are strongly encouraged to apply. Knowledge of the candidate in electrochemistry, surface characterization, and material synthesis will also be appreciated. Previous experience and knowledge in numerical simulation techniques could benefit the project and would be valuable but is not mandatory. The project entails several coherent and interconnected objectives, the answers to which could be the subject of journal publications with high ranking. Meanwhile, from a technological standpoint, we anticipate that upon the achievement and optimization of the designed materials, protection of the technology will be necessary. This protection will likely involve including the PhD student as one of the inventors. Besides, the PhD student will present his/her results via communications (oral presentations, posters) in national and international workshops and internal events (doctoral school, MONARIS seminary, …).

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