Artur Ciesielski *PhD, HDR, CNRS Research Director (DR2)*
Nanochemistry Laboratory, Institut de Science et d'Ingénierie Supramoléculaires (I.S.I.S.)
Université de Strasbourg & CNRS, 8 allée Gaspard Monge
F - 67000 Strasbourg, France

Strasbourg, 11th October 2023

DISSERTATION REVIEW REPORT

It is an honour for me to serve on the PhD committee of the candidate Ms. Jiaxin Li. I have not been involved in the scientific work and have based my judgement reflected in this report solely on the written thesis. This report was prepared in response to the letter of prof. dr hab. inż Mirosława El Fray, Chairwoman of the Discipline Council of Materials Engineering of West Pomeranian University of Technology in Szczecin, from 16th August 2023.

Thesis title: Carbon-based Materials for High Performance Energy Storage Devices / *Materiały oparte na węglu do wysoko wydajnych urządzeń do magazynowania energii*
PhD Candidate: Jiaxin Li
Supervisor: dr hab. Xuecheng Chen

GENERAL EVALUATION

Originality of dissertation topic, relevance to the field, and possible applications

In the face of escalating global energy demands and mounting environmental concerns, the quest for sustainable energy storage solutions has taken centre stage in scientific research and technological innovation. This thesis highlights the paramount importance of studying new materials for energy storage systems in addressing these pressing challenges. Traditional energy storage technologies, such as lithium-ion batteries, have significantly advanced our ability to harness and utilize energy efficiently. However, they still face critical limitations, including limited energy density, finite cycle life, resource scarcity, and environmental impacts. A doctoral dissertation written by Jiaxin Li was submitted in the form of a classical PhD thesis. It was correctly assigned to the discipline of Materials Engineering (according to the Regulation of the Minister of Education and Science of 1 Oct. 2022 on the fields of science and scientific disciplines and artistic disciplines, Journal of Laws of 2022, pos. 2202, from 1 Oct. 2022). In her thesis, Jiaxin Li discusses various carbon-based nanomaterials that were developed from different carbonaceous precursors through rational strategies and applied in electrochemical energy storage devices including lithium-ion batteries, zinc-ion capacitors, and supercapacitors.

Tél. : +33 3 68 85 51 60 Fax : +33 3 68 85 51 41 ciesielski@unistra.fr

Detailed assessment of the scientific content, chapter-wise

Chapter 1 introduces the context of the study by highlighting the growing concern over fossil fuel consumption, climate change, and the need to transition to renewable energy sources. It emphasizes the role of electrochemical energy storage (EES) technologies in enabling the widespread adoption of renewable energy, focusing on lithium-ion batteries (LIBs), zinc-ion capacitors (ZICs) and supercapacitors. The chapter briefly traces the historical development of LIBs and their key components, including cathode materials, anode materials, and electrolytes. It also mentions the challenges associated with LIBs, such as limited lithium resources. The chapter then introduces the concept of ZICs as a promising alternative energy storage technology, highlighting their safety, abundance, and potential applications. The chapter provides a broad overview of the components and working mechanisms of ZICs, distinguishing between capacitor-type and battery-type materials. It hints at the challenges and opportunities in the field of ZICs and sets the stage for the subsequent chapters' discussions on various aspects of this technology. Finally, the chapter introduces the history and development of supercapacitors, which have been marked by significant milestones. Additionally, it underscores the pivotal role of enhancing porous carbon materials in propelling supercapacitor technology forward, resulting in improved performance, increased energy density, and extended lifespan.

Chapter 2 includes comprehensive information on the materials and chemicals employed, characterization methods utilized, and electrochemical assessments conducted for LIBs, ZIBs, and supercapacitors. This includes the inclusion of equations crucial for evaluating their performance.

In **Chapter 3**, we delve into the production of an environmentally friendly material known as Co_3O_4@void@C and its performance assessment as an anode material for LIBs. By recycling waste plastic materials (waste face mask-PP, plastic jar-PE, and foam sheets-PS) and using catalytic carbonization in the presence of spherical Co_3O_4 as the catalyst at 800°C, combined with a partial etching of Co_3O_4, Co_3O_4@void@C nanomaterials are synthesized. As control experiment, the same material without the void is used (Co_3O_4@C). The PhD candidate demonstrate that void space in the Co_3O_4@void@C releases the stress generated by the volume increase of Co_3O_4 during Li^+ ion diffusion, leading to an excellent electrochemical performance. When employed as anode materials, these nanomaterials exhibit an impressive capacity of 1190 mAh g^{-1} and maintain stable cyclic performance (capacity retention of 1066 mAh g^{-1} after 100 charge/discharge cycles).

In **Chapter 4** the PhD candidate shows the synthesis of a nanostructure composite combining carbon nanotubes (CNT) and tin dioxide (SnO_2) and N-doped carbon (CNT@SnO_2@CN_x). This synthesis addresses a swelling issue like that encountered with pristine SnO_2, effectively mitigated by the inclusion of a void space. This void space is generated using a sacrificial template, specifically meso-SiO_2. As a control experiment, the PhD candidate evaluates how the electrochemical performance is influenced by either carbon or N-doped carbon serving as the outer layer of the composite. CNT@SnO_2@CN_x unique nanostructure demonstrates improved performance in LIBs, with a specific capacity of 1087.5 mAh g^{-1} at a current density of 0.1 A g^{-1}, even after 100 cycles, and 533.6 mAh g^{-1} at 5 A g^{-1}.

Tél. : +33 3 68 85 51 60 Fax : +33 3 68 85 51 41 ciesielski@unistra.fr

In **Chapter 5,** an innovative approach to upcycling polyethylene terephthalate (PET) bottle waste into a porous carbon material is presented. First PET is converted into a metal organic framework (MOF) (*i.e,* MIL-53(Al)) by using a hydrothermal method, which undergoes a carbonization process. Notably, this method achieves an impressive yield of 22%, nearly double the yield reported in other carbonization processes. This unique "accordion-like" porous carbon structure includes micro/mesopores and a remarkable specific surface area (SSA) of 1712 m^2 g^{-1}. In a three-electrode supercapacitor setup, it exhibits a capacitance of 391 F g^{-1} at 0.5 A g^{-1} and demonstrates excellent rate capability, retaining 73.6% of its capacitance at 20 A g^{-1} in a 6M KOH electrolyte. Furthermore, in ZICs, it showcases a high capacitance of 335 F g^{-1} at 0.1 A g^{-1}, maintain 92.2% capacitance after 10,000 cycles, and offer a superior energy density of 150.3 Wh kg^{-1}.

In **Chapter 6**, the PhD candidate presents the synthesis of highly monodisperse zeolitic imidazolate frameworks-8 (ZIF-8) derived N-doped porous carbon materials (CZ-Y), where Y is the particle size (nm). By exploring different reaction temperatures, the PhD candidate studies the effect of pore size distribution (PSD). SSA functional groups and the overall electrochemical performance. CZ-150 is identified as the ideal particle size for porous carbon derived from ZIF-8, which successfully enhances the rate of ion diffusion and reduces the ion transport distance. When employed as a cathode material in ZICs, CZ-150 exhibits a gravimetric capacity of 292 F g^{-1} at 0.2 A g^{-1}, with 100% capacitance retention even after 10,000 cycles. Interestingly, the PhD candidate uses ex situ XRD characterization to shed light onto the charge storage mechanism.

In **Chapter 7**, the synthesis of a novel cathode material for ZICs is presented. This material consist in glucose-derived N,P co-doped 2D hierarchical porous nanosheets (GNPC). While mesoporous serve as the effective channels for the fast ion transport, co-doped N and P act as additional active sites as well as increase the conductivity of the carbon material. As part of control experiments the PhD candidate explores the 2D hierarchical porous nanosheets lacking heteroatom doping, those solely doped with N, and those solely doped with P. GNPC nanosheets, characterized by their large specific surface area, abundant micro/mesopores, and N and P dopants, demonstrate a capacitance of 167 F g^{-1} in a symmetric supercapacitor using 1M Li_2SO_4 as electrolyte. In addition, when assembled into ZICs, GNPC displays a capacitance of 401 F g^{-1}, a high energy density of 180 Wh kg^{-1}, and a power density of 85 W kg^{-1} at 0.1 A g^{-1}. Impressively, these nanosheets exhibit a remarkable capacity retention of 95% over 10,000 cycles at a current density of 5 A g^{-1}.

In **Chapter 8**, the synthesis of N-doped porous carbons derived from freeze-dried banana flesh (ACBS-x) through a low-temperature carbonization process followed by KOH activation is presented. The pore size distribution is adjusted via the tuning of the ratio KOH/carbonized banana sheets (CBS) (namely x=2,4,6 and 8). ACBS-6 material exhibits the largest specific surface area (2335 m^2 g^{-1}) and a well-distributed pore size ranging from 0.9 to 1.2 nm. In a three-electrode supercapacitor system using 3M KOH as the electrolyte, ACBS-6 displays a high capacitance of 264 F g^{-1} at a current density of 1 A g^{-1}. Furthermore, in a two-electrode system employing 1 M $EMIMBF_4$ electrolyte, ACBS-6 reaches a maximum specific capacitance of 155 F g^{-1} and an energy density of 49 Wh kg^{-1}.

Tél. : +33 3 68 85 51 60 Fax : +33 3 68 85 51 41 ciesielski@unistra.fr

The responsibilities of a reviewer also encompass identifying any inaccuracies, incorrect wording, or typographical errors in the manuscript. The manuscript has undergone thorough editing, and aside from a few minor errors, I did not come across any significant issues. The following is a list of questions that could be discussed during the public defence of the PhD thesis:

Chapter 1. In page 3, high work safety and no pollution are mentioned as advantages of LIBs. However, in page 14 it is mentioned that one of the main disadvantages of LIBs is the use of flammable organic electrolytes. The scarcity of lithium is also mentioned as one of the main disadvantages of LIBs. However, the second generation of LIBs do not use lithium metal as anode.
Chapter 3. i) The PhD candidate claimed in page 40 that a large content of defects in Co_3O_4@void@C is beneficial for the fast charge transport in the electrolyte. However, the presence of defects is usually considered detrimental for the electrochemical performance as it reduces the ionic conductivity of the material. ii) As a curiosity, has the PhD candidate explored if there is any correlation between the void size and the electrochemical performance?
Chapter 4. Has the PhD candidate assessed the performance CNT@SnO_2@CN_x with and without the void space in a similar manner to Chapter 3?
Chapter 5 discusses the electrochemical performance comparison of two control materials, CP and CPMH, for which the acronyms have not been provided, making it challenging to follow the discussion effectively.
Chapter 6. Although the PhD candidate always reported specific capacitance values (in F/g), during the chapter capacitance and capacity and used interchangeably.
Chapter 7. In page 96 the PhD candidate claims that the N,P co-doping of 2D hierarchical porous nanosheets leads to an increase of the electrical conductivity of the pristine material. However, as shown in the Nyquist plots in page 92, what it is actually increasing is the ionic conductivity. To further prove that the electronic conductivity is also increasing, other characterization such as 4 point probe measurements should be performed.
Chapter 8. The conclusions from Figure 8.6 are not clear. The linear fittings which employ only four data points, appear to be inaccurate.

Writing quality and clarity

The entire PhD thesis is characterized by its clear and high-quality writing. It is remarkably free of typographical errors, with concise and easily comprehensible sentences. The introduction and review of the current state-of-the-art are founded on valuable and up-to-date literature. The research objectives and resulting goals are well-defined. The conclusions put forth are not only noteworthy but also logically derived and indispensable. The explanations are rooted in extensive research and comprehensive analyses. The figures and tables are thoughtfully presented and appropriately discussed.

Concluding remarks

The doctoral dissertation prepared by PhD candidate Jiaxin Li is of very high quality. It reveals valuable results obtained with thorough experimental work. The well-designed objectives have been fulfilled and correctly argued. This original work represents advancements in designing electrode materials for lithium-ion batteries. zinc-ion capacitors and supercapacitors with enhanced electrochemical performance via facile and effective by optimization of the diverse physicochemical properties of carbon-based nanomaterials. It aligns with the demands of advanced materials and lays a robust groundwork for potentially expanding their synthesis methods.

Altogether, I asses the doctoral dissertation, prepared by Jiaxin Li, a PhD candidate supervised by Prof. Xuecheng Chen, as very good. Therefore, I conclude that it fulfils all the provisions specified in Act of 20 July 2018 "*Law on higher education and science*", Journal of Laws 2021, pos. 478, with further changes (Ustawa z dnia 20 lipca 2018 r "*Prawo o szkolnictwie wyzszym i nauce*" Dziennik Ustaw 2021, poz. 478 z pózniejszymi zmianami). Hence, I strongly recommend it for presentation before the relevant committee.

The doctoral dissertation exhibits a commendable level of technical excellence in its writing. It is skilfully composed, rendering the content accessible to both professionals and the general readership. Notably, the introduction and discussion sections are meticulously crafted and indispensable. The execution of experiments and measurement techniques is both accurate and well-organized. The devised experiments are compelling and substantiate the acquired results, which are comprehensively elucidated. The PhD candidate has also demonstrated adeptness in interpreting outcomes obtained through diverse methodologies. The provided descriptions and conclusions are praiseworthy, coherent, and pivotal, grounded in valuable research and conducted with the utmost scientific rigor.

The PhD candidate has already gained considerable scientific achievements. The results discussed in doctoral dissertation were published in high- and medium-tier peer-reviewed journals with an average (over 6 published articles) IF of 6,71 (and MNiSW points of 80, yet those are irrelevant outside of Poland). 4 more manuscripts are being prepared by the candidate. Jiaxin Li also presented two posters at two international conferences. Unfortunately, no information is given on the oral dissemination activities of the candidate, which is certainly the only weak point in her CV.

Ciesielski

Tél. : +33 3 68 85 51 60 Fax : +33 3 68 85 51 41 ciesielski@unistra.fr