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DISSERTATION REVIEW REPORT

It is an honour for me to serve on the PhD committee of the candidate Mr. Xiaodong Xu. 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: Methods of recycling of solid wastes into hierarchical porous carbon materials for electrochemical energy storage
PhD Candidate: Xiaodong Xu
Supervisor: prof. dr. hab. Ewa Mijowska
Assistant supervisor: dr. Xin Wen

GENERAL EVALUATION

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

Amidst the increasing global energy needs and growing environmental issues, the pursuit of sustainable energy storage solutions has become a prominent focus in scientific research and technological advancement. Commercially available porous carbon materials, particularly activated carbon, have been regarded as highly promising electrode materials due to their significant specific surface area, excellent conductivity, and abundant ion-accessible sites. Nevertheless, they frequently demonstrate unsatisfactory electrochemical performance characterized by low capacity and limited rate capability. This thesis highlights the paramount importance of generating new carbon-based electrode materials from diverse green sources, including biomass, flame retardants, and polymers as well as the fine-tuning of their physicochemical properties to meet the ideal electrode characteristics required for energy storage devices. A doctoral dissertation written by Xiaodong Xu 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 his thesis, Xiaodong Xu discusses various carbon-based nanomaterials that were developed from different carbon precursors (biomass, flame retardants, and polymers) through rational and straightforward strategies and applied in electrochemical energy storage devices including supercapacitors and lithium-ion batteries.

Detailed assessment of the scientific content, chapter-wise

Chapter 1 of the thesis provides an introduction to the critical importance of energy in human development and the environmental concerns associated with fossil energy consumption. It highlights the need for alternative and sustainable energy sources such as solar energy, wind energy, nuclear energy, and electrical energy. Supercapacitors and lithium-ion batteries are introduced as key components of modern electrical energy storage and conversion systems, with a focus on their development, mechanisms, and applications. Additionally, the chapter discusses the role of carbon nanomaterials and their composites in enhancing the performance of energy storage devices. The research objectives of the thesis are outlined, emphasizing the optimization of physicochemical properties of porous carbons for improved electrochemical performance in supercapacitors and lithium-ion batteries, using various carbon precursors and synthesis methods.

Chapter 2 provides an extensive overview of the materials and chemicals used, characterization techniques applied, and electrochemical evaluations carried out for supercapacitors and LIBs. This encompasses the incorporation of essential equations for performance assessment.

In **Chapter 3**, we delve into the fabrication of hierarchical porous carbon (HPC) material from biomass waste (*i.e.,* wolfberry fruit). The PhD candidate uses different amounts of $SnCl_2$ (catalyst) to modulate the final specific surface area (SSA) and pore size distribution of HPC. Interestingly, after the synthetic procedure, the catalyst is recycled with a recovery rate higher than 95%. The optimal biowaste-derived carbon exhibits a substantial SSA of 1423 m^2 g^{-1} and impressive electrochemical performance, including a high specific capacitance (365 F g^{-1}), excellent rate capability (75%) in a 6M KOH electrolyte for a three-electrode cell. Additionally, in supercapacitors, it demonstrates exceptional cycling stability (96.4% of capacitance retention over 10,000 cycles) and a significant energy density (23.2 Wh kg^{-1}) in a 1M Li_2SO_4 electrolyte.

In **Chapter 4** the PhD candidate shows the fabrication of a N-doped porous carbon by an eco-friendly approach involving milk colloidal (biomass) and $CaCO_3$ nanoparticles. $CaCO_3$ serves a pivotal dual role, acting both as a rigid template for building the 3D continuous architecture and as an activator for pore formation through the release of CO_2 during the thermal decomposition process. The PhD candidate optimizes the weight ratio between milk and $CaCO_3$ nanoparticles in order to obtain the highest surface area and porosity and therefore the highest electrochemical performance. This resulting porous carbon exhibits impressive characteristics, including a high SSA of 1351 m^2 g^{-1}, a relatively substantial nitrogen content (6.22 at%), and a promising specific capacitance of 430 F g^{-1} as observed in a three-electrode system with a 6 M KOH electrolyte. It also demonstrates a favourable energy density of 33.6 Wh kg^{-1} and maintained 93.8% capacitance retention after 10,000 cycles in a 1M Li_2SO_4 electrolyte for supercapacitors.

In **Chapter 5,** the synthesis of a N,P co-doped 3D porous carbon is presented. In an analogous manner to the previous chapter, $CaCO_3$ nanoparticles are employed as rigid templates and activators for pore formation. Differently, the precursor material is based on intumescent flame retardants (IFRs), which are rich in both N and P heteroatoms. By following a self-assembling and self-activation method and by optimizing the weight ratio between IFRs and $CaCO_3$ nanoparticles, the optimal IFR-derived carbons exhibit a significant SSA of 851 m^2 g^{-1}, relatively high N and P contents (6.79 at% N and 2.66 at% P), and demonstrate impressive electrochemical performance when used as electrodes. In particular, in a 6 M KOH electrolyte for a three-electrode cell, they achieve a specific capacitance of

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407 F g^{-1} at 0.5 A g^{-1}. In an $EMIMBF_4$/PC electrolyte for supercapacitors, they exhibit an energy density of 62.8 Wh kg^{-1} and a capacitance retention of 84.7% after 10,000 cycles.

In **Chapter 6**, the PhD candidate presents the synthesis of amino-resin derived hierarchical porous carbons (ARHPCs). The precursor polymer of amino resin is chosen due to its inherent porous nature as well as its high N content. The primary innovation here resides in the utilization of $CuCl_2$ as an exceptionally efficient activation agent. This agent not only effectively preserves the nitrogen-doped content within the ARHPCs structures but also facilitates the generation of micropores, resulting in a material with a substantial SSA. Specifically, after the optimization of the mass ratio between $CuCl_2$ and the amino-resin, the resulting ARHPCs exhibit an outstanding SSA of 2245 m2 g-1, a substantial micropore volume of 0.79 cm^3 g^{-1}, and a noteworthy nitrogen content of 7.15 at%. ARHPCs also demonstrate excellent electrochemical performance, achieving a specific capacitance of 522 F g^{-1} in a three-electrode system with 6 M KOH electrolyte, impressive cyclability with a capacitance retention of 93.6% after 10,000 cycles, and a promising energy density of 35.5 Wh kg^{-1} in Li_2SO_4 electrolyte for supercapacitors.

In **Chapter 7**, the fabrication of a hybrid material that combines 3D porous hollow carbon sphere/porous carbon flake (HCS/PCF) and nano-SnO_2 particles is presented. The green precursor of this material consists of a combination of common commercial plastic goods (PP, PVC, PE and PS). In order to improve the electrochemical performance of the highly conductive and porous HCS/PCF, the PhD candidate incorporates pseudocapacitive SnO_2 particles of different morphologies to create a core@shell structure. The PhD candidate examines the impact of particle morphology (spherical, cubic, flaky, and blocky SnO_2 morphologies) on the overall electrochemical performance, a factor that is often disregarded. The SnO_2@HCS/PCF anodes with spherical and cubic SnO_2 morphologies exhibit exceptional electrochemical performance in terms of long-term cycling stability and remarkable reversible specific capacities in LIBs. Even after 400 cycles, the average capacity lost for these anodes amounts to approximately 0.048% and 0.05% per cycle, respectively, at a current density of 1 A g^{-1}. Moreover, at a current density of 5 A g^{-1}, the reversible specific capacities of SnO_2@HCS/PCF anodes with spherical and cubic SnO_2 morphologies amount to 0.4496 and 0.4981 Ah g^{-1}, respectively, throughout 1000 charge/discharge cycles.

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 the Introduction, the role of graphite and different carbon-based materials as anode materials in LIBs has been described. However, there has been no discussion regarding cathode materials for LIBs. What are the essential characteristics (i.e., physicochemical properties) that dictate whether a material is better suited for use as a cathode or an anode material?
Chapter 3. Could the PhD candidate comment on the performance variability when different batches of wolfberry fruits are used?
Chapter 4. In page 52, Figure 4.9c, it can be seen that the coulombic efficiency at the lowest current density (0.5 A g^{-1}) is relatively low, around 60%. Is this due to the overcharging of the electrodes? How the coulombic efficiency at low current densities could be increased?
Chapter 5. In page 54, the PhD candidate claims that 3D materials are preferred as electrode materials due to the re-stacking problem of 2D materials. However, 2D materials possess shorter channels which allow faster ion diffusion as well as improved electrode-electrolyte interaction.

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Chapter 6. The PhD candidate claimed in page 77 that the resulting copper (from the $CuCl_2$ catalyst) was eliminated by post-treatment. However, what is the recovery yield?

Chapter 7. In page 89, Figure 7.4, it is not very clear the morphology of some SnO_2 nanoparticles. While spherical morphology is clear, the cubic could also be octahedral. In this case, it would be better to compare with scanning electron microscopy characterization.

Writing quality and clarity

The PhD thesis as a whole stands out for its clear and high-quality writing. It is remarkably free from typographical errors, featuring concise and easily comprehensible sentences. The introduction and the review of the current state-of-the-art are firmly rooted in valuable and up-to-date literature. The research objectives are well-defined and the resulting goals are precisely outlined. The conclusions presented are not only noteworthy but also logically derived and indispensable. These explanations are deeply 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 Xiaodong Xu 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 green-based electrode materials for supercapacitors and lithium-ion batteries with enhanced electrochemical performance via facile and effective optimization of the diverse physicochemical properties of carbon-based nanomaterials, namely specific surface area, hierarchical porosity, and heteroatom content. 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 Xiaodong Xu, a PhD candidate supervised by Prof. dr. hab. Ewa Mijowska and co-suppervised by dr. Xin Wen. 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 4 published articles) IF of 9.08 (and MNiSW points of 115, yet those are irrelevant outside of Poland). 4 more manuscripts are recently submitted by the candidate. Xiaodong Xu also presented one poster and delivered one presentation at two international conferences. Impressively, Xiaodong Xu also possesses two patents.

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