Centrum Zaawansowanych Technologii

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Dissertation review report

Carbon-based Materials for High Performance Energy Storage Devices / Materiały oparte na węglu do wysoko wydajnych urządzeń do magazynowania energii

PhD Candidate: Jiaxin Li

The doctoral dissertation titled "Carbon-based Materials for High Performance Energy Storage Devices," submitted to me for evaluation, was conducted by Ms. Jiaxin Li under the supervision of Professor Xuecheng Chen at the West Pomeranian University of Technology in Szczecin. The main objective of the doctoral thesis was to develop new methodologies for obtaining carbon-based nanomaterials and then applying them in electrochemical energy storage devices. Undoubtedly, the research topic carried out within this work represents a creative extension of scientific research, which has been successfully conducted within the Supervisor's team. The defined tasks in the thesis possess a clearly marked interdisciplinary and cognitive character, and the research undertaken by the doctoral candidate in this area is fully scientifically justified.

Generation of carbon-based materials for high-performance energy storage devices holds immense significance in contemporary scientific research and technological development. Carbon, with its unique properties such as high surface area, electrical conductivity, and chemical stability, serves as a promising candidate for enhancing energy storage systems. The quest for sustainable energy solutions necessitates the advancement of efficient energy storage technologies to accommodate the intermittency of renewable energy sources like solar and wind. Carbon-based materials offer versatility in design and application, enabling the development of lightweight, compact, and durable energy storage devices. Moreover, their abundance and relatively low cost compared to other materials make them attractive for large-scale implementation. By delving deeper into the synthesis, characterization, and optimization of carbon-based materials, researchers aim to unlock their full potential in revolutionizing energy storage, paving the way for a cleaner and more sustainable energy future. In this context, the doctoral dissertation submitted by Ms. Jiaxin Li fits perfectly into the current trend of research in this field, and the conducted experimental work was rightly focused on attempting to solve the above-mentioned research problems. In my opinion the thesis 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

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of science and scientific disciplines and artistic disciplines, Journal of Laws of 2022, pos. 2202, from 1 Oct. 2022).

The dissertation follows a classical structure, is written in English (with an abstract in Polish), spanning 135 pages. Of these, 30 pages are dedicated to the literature review, while the discussion of the original research is written on 70 pages. Additionally, several dozen extra pages include items such as a list of abbreviations used in the dissertation, a summary of the thesis, and a list of original publications resulting from the presented research. The text concludes with an impressive bibliography containing 320 references to cited literature.

The literature review is designed to support the aforementioned research objectives, consist of 4 main chapters, and unequivocally demonstrates a very good understanding of both general and more specialized literature relevant to the doctoral candidate's own research. In my assessment, the scope of each part of the literature review introduction has been well chosen and shows that the candidate is proficient in the issues related to the dissertation topic. A detailed description of each part of the literature review introduction by the reviewer is not necessary, as the primary role of this part of the doctoral work is to logically present the current state of knowledge, as well as to clearly specify the main scientific challenges facing researchers interested in the given topic. However, I believe it is worth emphasizing the skillful arrangement of the individual subsections in the literature review introduction, from the most general ones covering basic aspects of the structure and applications of lithium-ion batteries to the description of two groups of materials relevant to the doctoral research topic, namely zinc-ion capacitors and supercapacitors, to mention the most important aspects of porous carbon materials. In summary, the literature review section has been written in clear and concise language, and serves as an excellent introduction for the reader to the research problem addressed by the doctoral candidate.

The main part of the dissertation comprises the description of the doctoral candidate's own research. This section of the thesis has been divided into six chapters, each containing a brief introduction, a description of the conducted research, and a summary/discussion of the obtained results. A sort of technical introduction to the description of the strictly scientific results collected by the candidate is Chapter 2, in which an extensive coverage of the materials and chemicals utilized, the methods employed for characterization, and the electrochemical assessments conducted for LIBs, ZIBs, and supercapacitors were described. This section also includes all equations crucial/essential for the evaluation of their performance.

Chapter 3 constitute the actual description of the doctoral student's own research. In this part of the dissertation, the production of Co_3O_4@void@C nanomaterials through the innovative method of repurposing waste plastics (such as waste PP face masks, PE jars etc.) *via* catalytic

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carbonization at 800 °C, using spherical Co_3O_4 as a catalyst was described. Here I am wondering what guided the doctoral candidate in choosing these specific waste plastics instead of others? Have the application of other synthetic polymers been also considered? The expansion of Co_3O_4 volume during Li^+ cation diffusion, is released by the vacant space/void between the inner and outer carbon layers, resulting in significant enhanced electrochemical performance in lithium-ion batteries (LIBs). In addition, the PhD candidate showed that the use of this material as an anode, resulted in the generation of system exhibiting impressive attributes, including a high capacity of 1190 mAh g^{-1} and consistent cyclic stability. The results of this research were written up in the form of a publication published in a respected journal, namely *ACS Applied Nano Materials*.

A completely different system is presented in the next chapter (Chapter 4) of this dissertation in which, the doctoral candidate presents the synthesis of a novel composite-type material incorporating carbon nanotubes (CNT), tin dioxide (SnO_2), covered by two different carbon resources, namely carbon coating and N-doped carbon. Such a set of components used as anode material ensured enhanced performance in lithium-ion batteries (LIBs), exhibiting a capacity of 1087.5 mAh g^{-1} at a current density of 0.1 A g^{-1} (this excellent performance is retained even after 100 cycles), and 533.6 mAh g^{-1} at 5 A g^{-1}. The doctoral student sequentially added each element to the material, ultimately achieving the expected nanostructure-type product. Importantly, this part of the work not only includes successful characterization of the obtained material using a wide range of analytical techniques but also describes the comparative tests that were conducted. These tests revealed differences in the electrochemical values achieved at each stage of the material production. Certainly, other forms of carbon nanotubes such as multi-walled carbon nanotubes (MWCNTs), or double-walled carbon nanotubes (DWCNTs) could be tested for such purposes. Did the doctoral candidate explore the potential application of these alternative forms?

The next chapter (Chapter 5) provides another example of the successful upcycling of plastics (polyethylene terephthalate, PET) waste in the generation of modern porous carbon nanomaterials with properties that allow them to be used as supercapacitors. Obtaining the final product was accomplished through a step involving successive transformation of PET into a metal-organic framework (precisely MIL-53(Al)), which was then subjected to a carbonization process. The hydrothermal method used by the doctoral student to synthesize these materials proved to be very effective and efficient, significantly outperforming those previously described. The final "accordion-like" carbon-based material obtained was not only characterized by an impressive specific surface area (SSA, 1712 m^2 g^{-1}) value, but also proved to be a remarkably successful supercapacitor electrode design element with excellent parameters characterizing this type of material. These results also found recognition in the eyes of the reviewers of the journal *Green*

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Energy & Environment however one question appeared while reading this part: does the doctoral candidate believe that the type of MOF material used could affect the observed electrochemical properties?

Chapter 6 describes another successful attempts to generate functional materials, this time based on a series of narrow particle size distribution of monodisperse zeolitic imidazolate frameworks-8 (ZIF-8) derived N-doped porous carbon materials. In the series of temperature-control processes the doctoral student found that porosity characteristics as well as the contents of N dopants were largely affected by its particle size. Optimization of the entire process and the acquisition of suitable reactants resulted in the discovery of the ideal particle size (CZ-150), significantly enhancing the desired properties of the tested materials. This enhancement includes an increase in the ion diffusion coefficient, facilitating rapid electrolyte ion transport over short distances and promoting a fast ion diffusion rate. Moreover, the obtained material was utilized as a cathode, achieving a gravimetric capacity of 292 F g^{-1} at 0.2 A g^{-1}, with 100% capacitance retention even after 10,000 cycles.

It seems that the experience gained during the execution of the project described in Chapter 6 was rightly used in the next, 7^{th} chapter of the submitted dissertation, in which a material consisting of glucose-derived N, P co-doped 2D porous nanosheets was studied. The hierarchical structure and the additives used in the materials resulted in an increased degree of porosity, which in turn translated into increased conductivity. As in previous projects, the doctoral student appropriately conducted several control experiments among materials differing in the type of additives used. This type of approach of actually verifying and comparing the obtained data with other materials should be appreciated especially when it comes to the preparation of doctoral thesis. The experiments performed within the frame of this project showed that materials containing both N and P performed by far the most favorably in terms of their electrochemical performance, which confirms that the research assumptions were appropriately refined.

An extremely interesting approach is described in the last experimental chapter (Chapter 8) of this work concerning the synthesis and electrochemical application of N-doped porous carbon materials derived from freeze-dried banana flesh. The carbon functional material was obtained using a low-temperature carbonization process followed by KOH activation. The interesting physicochemical properties of the studied material, including high SSA values and control over pore sizes, prompted the doctoral student to test the electrochemical properties of these materials (as electrode components). Similarly to the previously described results, this led to obtaining extremely promising key electrochemical values, thus raising hopes for the real-world application

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of these materials. The results obtained within the conducted project have already been published in the *Diamond and Related Materials* journal.

The submitted dissertation has been written in concise language, and its limited volume, in my opinion, is a significant advantage as it quickly directs the reader to the most important aspects of the conducted research. Errors, colloquial terms, or jargon appear in the text of the dissertation, but it is worth emphasizing that overall, the work has been written in correct English. The visual presentation of the dissertation has been meticulously prepared. I have read the entire dissertation with great interest.

The doctoral candidate's scientific output consists of 6 publications issued in good and very good international journals. It is worth emphasizing that the candidate is the first author in four of these papers, indicating her dominant role in their creation. Several more papers are currently being prepared. Additionally, the candidate has presented the results of her work at national and international scientific conferences, where she showcased her research findings in the form of posters.

In conclusion, I would like to state that the submitted dissertation utilizes a coherent research approach encompassing both synthetic and analytical parts. I consider such an approach extremely valuable as it develops the skills and abilities of the young researcher. In this context, I would like to highlight the very wide range of analytical techniques used by the candidate, which, in my opinion, is impressive. After careful analysis of the submitted documentation, I am convinced that Ms. Jiaxin Li is already a well-established young scientist, exploring interesting research directions and possessing all the predispositions to analyze her own research results and draw accurate scientific conclusions. I am convinced that the doctoral dissertation submitted for my review meets the requirements and conditions specified in the Act of July 20, 2018, "Law on Higher Education and Science" (Journal of Laws of 2021, item 478, as amended), and I strongly recommend the candidate's admission to further stages of the proceedings conducted by the Scientific Council of the Material Engineering Discipline at the West Pomeranian University of Technology in Szczecin.

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