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REPORT ON THE DISSERTATION ENTITLED "METHODS OF RECYCLING OF SOLID WASTE INTO HIERARCHICAL POROUS CARBON MATERISALS FOR ELECTROCHEMICAL ENERGY STORAGE"

The basis for issuing the opinion on the doctoral dissertation of Xiaodong Xu is the letter of Prof. Dr. Mirosława El Fray, Chairman of the Scientific Council of the Material Engineering Discipline of West Pomeranian University of Technology in Szczecin on August 16, 2023 (ZUT/RDIMat/9/2023)

A dissertation submitted by Xiaodong Xu (hereafter referred to as *the Candidate*) serves as the basis for awarding the Doctoral degree. The thesis has been conducted under the supervision of Professor Ewa Mijowska at the West Pomeranian University of Technology in Szczecin and it is a creative extension of the research topics in this team. Due to the multidisciplinary character of the research work presented in this thesis as well as considerable number of experiments performed, the report will be divided into separate sections describing the various aspects of the thesis.

1) Thesis content and contribution to the field

The *Thesis* consists of 127 pages, and it has been written using a standard layout. It begins with the Declaration, Acknowlegment, Abstract, Streszczenie, Contents, List of abbreviatons, eight Chapters, List of publications, List of patents and Participation in scientific conferences. The thesis ends with References (278 items).

This dissertation is focused on developing a novel the carbon precursors (biomass, flame retardants, polumers) as electrochemical energy storage materials prepared from through facile methods. The thesis contains very extensive research program that concerns generation of a series of materials and their full physicochemical characterization and study of their electrochemical properties. The excellent reputation of the PhD student's supervisor, Prof. Ewa Mijowska and the research team in which the work was performed let me to expect high quality

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of the results presented in the dissertation, which is indeed confirmed by a closer look at the results. Based on the fact that in recent years we have observed a steadily growing interest of chemists and representatives of material sciences in the search for the most effective energy storage systems, I believe that the scope of work presented in the dissertation is extremely important and useful not only from a purely scientific point of view, but also due to the high application potential of the presented results.

The literary essay (Chapter 1) contains a thematically relevant and concise introduction that guides the reader through the topic in a very accessible manner. *The Candidate* also provides information about the historical background, especially in the field of supercapacitors and lithium-ion batteries.

Chapter 2 contains the results of the conducted research presented in the form of general descriptions of experimental procedures. Noteworthy, *The Candidate* used various analytical techniques such as SEM, TEM, EDAX, XRD, TGA, XPS, BET method and calculation of specific surface area and pore size distribution of the carbon materials. The electrochemical measurements on LIBs, ZICs and supercapacitors were deeply discussed in experiments described in this *Thesis*.

The discussion of the research results is described in an extremely vivid language that allows the reader to engage with this part of the work with interest, without compromising its high scientific value. *The Candidate* describing the exact methodology of synthesis and characterization of the obtained systems in five chapters. I was impressed by the meticulousness of the descriptions of all the activities performed.

Chapter 3 focuses on the design and the synthesis of hierarchical porous carbons from a waste wolfberry fruits by a facile and low-cost one-pot strategy by using $SnCl_2$ as catalyst. The biowaste derived exhibited large specific surface area, hierarchical porosity with rational pore size distribution, good wettability with O-doped carbon lattice. These favorable features resulted

in outstanding electrochemical performances with high specific capacitance, good rate capability and excellent cycling stability. The high quality of the research tasks described in this Chapter was recognized by the reviewers of the *Renewable Energy* journal.

In Chapter 4 *The Candidate* reports on trials of the green $CaCO_3$ template assistant route to produce N-doped 3D porous carbon derived from milk colloid. The activator of pore formation was the release of CO_2 during the thermal decomposition process. This part of the dissertation examines the recycling of colloidal wastes and the valuable applications of these carbon-based materials for supercapacitors. *The Candidate* declares that the research results described in this chapter have been sent to a prestigious journal: *Journal of Colloid and Interface Science*.

It is with real satisfaction that I note that the results of these studies described in Chapter 5 have already been published in reputable journal: *Journal of Colloid and Interface Science*. In this part of studies N/P dual-doped three-dimensional porous carbon was synthesized via nano-$CaCO_3$ template-assistant carbonization of intumescent flame retardants precursor. It is the first example that IFRs are selected as carbon precursor to synthesize heteroatoms-doped porous carbons and possessed large specific surface area, hierarchical porous distribution and relatively high N/P contents in carbon lattice.

The Candidate declares that the research results described in Chapter 6 have been sent to a respected journal: *Journal of Power Sources*. Hierarchical porous carbon derived from in-situ amino resin N-doped (amino resin-derived hierarchical porous carbon, ARHPC) was synthesized by the catalytic carbonization method of $CuCl_2 \cdot 2H_2O$, which has advantages are: generation of abundant micropores, high heteroatom content and high efficiency. This part of dissertation describes a gentle and efficient method catalytic carbonization to produce a carbonaceous material of well-defined porous structure and doped with heteroatoms for use in advanced energy storage devices.

Chapter 7 of this *Thesis* present results and discussion on research, which was published in a distinguished journal: *Science of The Total Environment*. *The Candidate* prepared three-dimensional porous hollow carbon sphere/porous carbon flake(HCS/PCFs) from plastic wastes via a template carbonization process, followed by doping of the interconnected nano SnO_2 spheres or cubes along with the bulk SnO_2 flakes or blocks into the HCS/PCF with different loading contents. Thereafter, the fabricated SnO_2/HCS/PCF nanocomposites with built-in diverse-shaped SnO_2 nanoparticles served as anodes towards advanced LIBs.

Additionally, in the last chapter 8, *The Candidate* describes the conclusions, enumerates the elements of scientific novelty in the dissertation. An important element of the work is the high level of interpretation of the obtained results, which allows for the presentation of well-justified and significant conclusions. I would like to know which of her achievements *The Candidate* values the most? I also have a second question: have the submitted manuscripts been accepted for printing?

Publication of research results of *PhD student* in very good journals with a rigorous review process indicates both a very high substantive level of research, as well as the maturity of *The Candidate* and the responsibility of her Supervisor, who understand the meanders and threats to the contemporary publishing ecosystem.

2) Quality of the work

In the dissertation, the *Candidate* has demonstrated a solid knowledge and understanding of the fundamental principles of the nontrivial aspects of energy storage materials, as evidenced by the in-depth discussion. I am confident that the numerous, so far unpublished results presented in the work will be included in two scientific articles published in reputable journals. This confidence stems from my observation and high regard for *the Supervisor's* unprecedented scientific achievements, which are highly valued by the world scientific community.

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3) Presentation:

The presentation is excellent, especially considering that *the Candidate* is not a native speaker. The quality of figures and graphs used for the schematic representation of the obtained results is very high. The descriptions and the format of the thesis are clear. The experimental data are presented concisely and clearly. I believe that even the best and most thoroughly described activities do not illustrate the enormous work, those countless hours spent by the *Candidate* in the laboratory. Therefore, it remains for me to consider the *Candidate* as an extremely experienced chemist with a research curiosity and an open mind.

4) Originality

Undoubtedly, one of the aspects of the scientific novelty presented in this doctoral thesis is the synthesis and study of the electrochemical properties of systems from the process of recycling solid waste into hierarchical porous carbon materials. This is a beautiful example of combining the Promoter's visionary idea with practical implementation by the Candidate, resulting in stunning scientific cooperation and its effects. The acknowledgments addressed to the Supervisor and *The Candidate*'s colleagues touched me, and the belief that reading the dissertation would be a pleasure turned out to be true.

5) Summary

The Thesis presents original and valuable scientific findings in the advancement of recycling of solid wastes into porous carbon materials, precursors for electrochemical energy storage, making a significant contribution to the field of sustainable chemistry. *The Candidate's* creation of new chemical platforms exemplifies the elegant utilization of material chemistry in the exploration and design of novel multifunctional materials, showcasing bold and substantial modifications. The results are effectively presented and demonstrate a high level of scientific interpretation. I highly admire *the Candidate's* expertise in the areas of green and material chemistry. Ms. Xiaodong Xu's *Dissertation* is conceptually captivating. The work was meticulously conducted and reported with utmost care and competence, while the analysis of experimental outcomes offers valuable insights. I firmly believe that the scope of research

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presented in the *Dissertation* not only carries immense scientific significance but also harbors great potential for applications in the field of electrocatalysis, photocatalysis and gas/dye adsorption.

The exceptional scientific activity of the Candidate deserves to be emphasized. In addition to three publications included in the dissertation, she is the co-author of the article in reputable journal: *ACS Applied Energy Materials*.

Therefore, I thank the High Scientific Council of the Material Engineering Discipline of West Pomeranian University of Technology in Szczecin for the honor of being a reviewer of the work under review.

Based on the above, I firmly believe that the dissertation fulfils all the requirements, and I highly recommend awarding the candidate the PhD degree. In my opinion, the collection of articles published in very good journals in the field of material, green chemistry and electrochemistry, The large, collected experimental material and analysis of carbon-based porous systems and their properties electrochemical ones are at a very high substantive level and are clearly visible signs of scientific novelty. Both the number and substantive level of works *The Candidate* indicates her involvement and consequences in shaping her scientific career, which is why I confidently submit it to the Council for consideration Scientific Discipline of the the West Pomeranian University of Technology in Szczecin, an application for distinction of the dissertation.

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