

Poznań, 06/04/2019

Report on the dissertation entitled “Porous Carbon Nanomaterials for Energy Storage Application”

A dissertation submitted by Mr. Shuai Zhang consists a basis for awarding the Doctoral degree. The thesis has been conducted under the supervision of Prof. Ewa Mijowska at the West Pomeranian University of Technology in Szczecin, and it correlates with the research interests successfully conducted in this team in recent years. The submitted doctoral thesis has a highly multidisciplinary character with several distinct sections describing the results obtained, therefore for the sake of clarity, the report will consist of several points each of which will concern different aspect of the dissertation.

1) Thesis content and contribution to the field

The dissertation concerns the formation of a series of metal-organic framework (MOF) derived nanoporous carbon materials, investigation of their physicochemical properties and applying the most promising systems in energy storage field. The general objectives of the thesis, despite the fact that they are quite broadly formulated, include the investigations of new porous nanomaterials based on carbon featuring high stability and conductivity while maintaining a high potential as novel supercapacitor electrode material. Also, the in depth understanding of the mechanism of energy storage in such systems is foreseen to be investigated. Such a formulated research program seems to be very ambitious and certainly correlates with the currently prevailing trends in the field of nanotechnology. One cannot omit the significant role that the PhD student's supervisor, Prof. Ewa Mijowska a well-known scientist in the field of nanomaterials, in formulating the strategic directions of the research undertaken by the candidate.

The thesis contains 168 pages (including list of references). The dissertation work consist of the following parts: abstract (in Polish and English), table of abbreviations,

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table of contents and seven main chapters. Each of the seven chapters described contains thematically appropriate concisely written introduction, which in a very accessible way help the reader to become familiar with this subject as well as previously described results. Each discussed section contains objective and scope of the work. This is followed by a description of the results obtained, conclusions and references. In my opinion the thesis is very well structured with a clear division of each part of the dissertation. The background to the topic and review of the current knowledge (including literature review) is correctly described. The candidate in an elegant way highlights the gaps in the current knowledge.

The major analytical techniques employed in the presented thesis were scanning and transition electron microscopies (SEM and TEM, respectively), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy but also cyclic voltammetry (CV) electrochemical impedance spectroscopy (EIS) and X-ray diffraction (XRD). This is impressive set of analytical techniques that have been properly selected for this work. I believe that the short description included in chapter II containing main features of each of techniques employed is a very good idea and proves great scientific awareness and maturity of the PhD student.

The experimental part of the work begins with chapter III and ends with chapter VII. In chapter III the preparation of an interconnect-structured NPC material is described. The latter was derived from the direct carbonization of Al-based MOF and such constructed hybrid system was evaluated in terms of its electrochemical performances. Modulation of distinct electrolytes namely 1-Ethyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄), tetraethylammonium tetrafluoroborate (Et₄NBF₄), and lithium perchlorate (LiClO₄) was performed in order to investigate the effect of the interconnect and mesopore structures on the supercapacitor application. The CV measurements confirmed that the highest capacitance was achieved for the BMIMBF₄ presumably thanks to the good match of the sizes of both the electrolyte and pore of the NPC. At this point, I would like to ask the student about his view on the use of molecular modelling techniques for predicting of the most optimum match between the nanomaterial used and e.g. electrolyte.

The two following chapters concern the generation and analysis of two types of N-doped NPC materials. The latter were prepared by straightforward method of pyrolysis of Al-MOF-Urea complex. Large surface area with highly interconnected micro, meso- and macropores were obtained. Additionally the nitrogen content in such structures could be controlled via different annealing temperatures. Thanks to such a collection of structural properties encoded at the molecular level and well developed synthetic methodology the material presented excellent capacitance in organic and aqueous electrolytes thus showing a great potential application in energy storage field. Here I would like to ask a student to express his opinion about the potential of using a different source of nitrogen in the preparation of N-doped NPC materials than those he used in his studies so far.

In chapter VI the student prepared hybrid material based on graphene oxide and MOF complex which at the next stage of project was transformed into graphene-NPC material via carbonization process. Thanks to a such design of the constructed material much better conductivity was achieved and more importantly the NPC nanostructures deposited on graphene prevented a very undesired process of staking of the latter thus allowing an easy access of the electrolytes to its surface.

In Chapter 7, a successful attempt was made to obtain a porous carbon-based supercapacitor electrode material derived from waste PET bottle. This is certainly a very interesting direction of research because it touches on a serious problem with which the entire world is constantly trying to solve for several decades, i.e. increased pollution of plastic waste. The improve synthetic methodology that was applied leading to the generation of product in high yield and low costs certainly shows that it is the right and useful direction of research.

The last chapter consists of summary and conclusion with some outlooks on the scientific approaches mentioned above.

2) Quality of the work

In the dissertation the candidate showed to possess a good knowledge and understanding on the basic principles of material science with the focus of carbon based

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materials and their applications in variety fields of research from nanotechnology. In general, the presented results seem to be reliable and very well documented, although, as always in cutting edge research, the interpretation and discussion could be further extended and analyzed more in-depth. This is, however, the common inherent feature of essentially all young scientists. I would like to emphasize that the quality of studies shown in this dissertation is very high and concern a broad area of research and their main value consist of predominantly detailed description of the obtained results. The quality of the results is also confirmed by publications that have already been published partially based on the results included in this thesis. Journals such as *Electrochimica Acta* (x2), *Nanomaterials* or *Waste Management* are leading in the field thus further comment on the quality of presented work I believe is unnecessary.

3) Presentation:

The presentation is very good, in particular in view that the candidate is not a native speaker. The Author correctly highlights the contribution of the thesis to the field of interest's, and also notices its limitations, thus showing clearly a comprehensive understanding of the context of his work. The quality of figures and graphics used for the schematic representation of the results obtained is very high. Descriptions and the format of the thesis are clear. The experimental data are presented concisely and clearly. There is a good balance between the different parts of the dissertation. The references seem to be well adapted and up-to-date.

4) Originality

There are several aspects of the scientific novelty contained in this doctoral thesis, of which preparation of graphene@NPC material, I found particularly attractive as is led not only to generation of structure possessing improved conductivity but above all it may lead to the new method of graphene exfoliation. Of course, it would require many additional tests and analyzes, however, I consider the potential of this system as very large. The second point of work which I consider to be particularly interesting is the use of PET bottle as the raw material for MOF synthesis and ultimately an NPC material.

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5) Summary

The PhD thesis contains original and valuable scientific results of the application of porous carbon nanomaterials in energy storage, which is an important contribution to materials chemistry and nanotechnology fields. The rank of the results is highlighted by the fact that some of them were published in very good specialized journals. I would like to point out that the research undertaken by the PhD student and his supervisor concerns the most current issues in one of the most dynamically developing fields of modern science – carbon-based materials. The information at the end of the doctorate thesis shows that many more publications are under preparation. The thesis represents a great deal of work. The results are well presented and their interpretation is at the high scientific level. I really appreciate the candidate expertise in the field of materials characterization. The research it describes is ready to be defended orally and certainly meets the requirements laid down for the degree of Ph.D. specified by the Ministry of Science and Higher Education (Act on Academic Degrees and Academic Title) and I recommend the Faculty Council of Chemical Technology and Engineering of the West Pomeranian University of Technology in Szczecin awarding the candidate the degree of Doctor. At the same time, due to the high quality of experimental results included in the doctoral dissertation, reliable and systematic implementation, innovative solutions that will certainly impact on the development of the studied field, I recommend for its distinction.

Yours sincerely,

