Doctoral Thesis of Zhang Shuai

"Porous Carbon Nanomaterials for Energy Storage Application"

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Referee

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Thesis assessment

The Doctoral Thesis of Zhang Shuai was finished in the Nanomaterials Physicochemistry Department, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology, Szczecin under the supervision of Prof. Dr hab. Ewa Mijowska, who is a well-known scientist in the field of material science and nanotechnology. The work had led to the Ph.D. thesis of Zhang Shuai which I have the honor to review.

The thesis comprises of a literature review, techniques for material characterizations and electrochemical properties, results and discussion for different carbon-based materials for energy storage field and conclusions. The thesis is well balanced and shows a good distribution of 168 pages for 8 chapters. The literature review, in my opinion, is well-structured and touches all the essences in the field of carbon material design and application in the energy storage field. The mechanisms of the electro-double layer capacitor and pseudocapacitor have been fully discussed, which can be used as a guide for the following researchers in this area to understand the basic concepts. In general, the design, characterization of various porous carbon materials and their applications for energy storage have been fully reviewed in Chapter I based on over 170 important publications in this field so that a research line of carbon materials for energy storage applications has been exhibited clearly, and the aims of this thesis are established on the previous research but with the novelty on the material design and the extraordinary electrochemical performance. The candidate pointed out that the short slab of the supercapacitor materials is low energy density, which limited the wide application of supercapacitor in the industrial field. In recent decades, thousands of research have focused on this problem but seldom made it. In my opinion, trying to solve this problem is a big challenge for the candidate and his research work, the progress of this research work may touch and extend the edge of the knowledge of material science.

In chapter II all the experimental techniques are described. The candidate not simply explains the technique but also has included useful information about the interpretation of the results obtained for each technique. Several techniques as SEM, TEM, XPS, Raman, BET, and electrochemical measurements, etc, have been used properly in this thesis to investigate the essence of the materials. This description was very useful when reading the thesis.

In particular, the discussion of the results and conclusions in the theoretical introduction part, Mr. Zhang shows good understanding skills and capacity to discriminate the different routes to synthesize, to purify, and functionalize of metal-organic framework (MOF) materials and the MOF-derived nanoporous carbon (NPC) materials. From Chapter III to Chapter VII, the candidate prepared different MOF precursors and functionalized via different methods. Then the MOF-derived carbon materials were prepared for supercapacitor applications.

The effect of the structure for supercapacitor behavior has been researched in Chapter

III. Highly porous and interconnected carbon materials are designed and fabricated by carbonization of nano-scale Al-based metal-organic framework (Al-MOF) and the morphology is optimized by the carbonization temperature. In this hierarchical porous structure, each building block consists of nano-scale carbonized Al-MOF. The capacitive performance of the nanoporous carbon made from carbonized Al-MOF is excellent. Several research techniques have been used to prove the interconnected structure of nanoporous carbon material can significantly increase the capacitance. This work started from the structure design and morphology study, which can be considered as bottom-up research of carbon-based supercapacitor electrode materials from the structure. The different structures affect the electrochemical performances have been first researched in this thesis, which will enlighten the other researchers from a different dimension.

In Chapter IV and V, heteroatoms-doping methods have been used in the research for increasing the capacitance. The candidate used two methods to introduce the nitrogen atoms into the MOF precursors. In ChapterIV, urea was used as the nitrogen source for the MOF modification. With the pseudocapacitance from the nitrogen groups on the NPC surface, this material exhibits an extraordinary capacitance value and energy density, which is compatible with the Li-ion battery. In Chapter V, a nitrogen-riched molecule was used as the raw material for MOF synthesize. The nitrogen-riched nanoporous carbon with interconnected structure also leads to high electrochemical performance. Furthermore, the candidate found that the broken of the interconnected structure will reduce the capacitance, which further proved the investigation in Chapter III.

Graphene oxide has also been used in the preparation of MOF-derived nanoporous carbon material for increasing the conductivity in Chapter VI. Moreover, by introducing of NPC on the graphene surface, aggregation and restacking between graphene layers were prevented and high accessible surface area with variety micro/mesopores and high conductivity are benefited from this unique structure, which ensures the efficient electron and ion transport to enable the Graphene-based NPC based supercapacitor with superior electrochemical performances. As a result, the high energy density achieved in this research is much higher than traditional capacitors and comparable with lead-acid batteries, which present opportunities to perform the wide range of applications in energy storage and industrial field.

In Chapter VII, the candidate demonstrated a highly efficient method to trans waste polyethylene terephthalate (PET) into hierarchical highly porous carbon materials with high yield. Through the hydrothermal method, waste PET bottle is converted to MOF crystals with high yield. After carbonization and purification, the carbon material is highly porous with plenty of micro- and mesopores, which is considered beneficial to the electrolyte ion storage and transfer. Based on this unique structure, the PET-derived carbon material archived a high capacitance. The remarkable electrochemical performance and environmental-friendly preparation process of this material bring a new angle of view for solving the waste plastic recycling and energy storage.

Finally, the main conclusions are summarised in the last part of the thesis. The scope of the nanoporous carbon material for energy storage application with improved energy density was obtained. The methodology used was well explored in many different ways in order to optimize the preparation and functionalization of the materials. I also believe that this work has remarkable novelty and its original input to the field will have a strong contribution to the knowledge of nanomaterials for energy storage application.

As a referee, I was obliged to find some critical point. It was very difficult, however, I have some comments and questions that I would like to discuss with a Ph.D. student:

1. Several MOF-derived nanoporous carbon materials exhibit the interconnect structure. I would like to know the self-assembly process (or mechanism) in detail.

2. The functionalization of carbon surface by heteroatoms doping increases the polarity of carbon surface which will hinder the wettability with an organic electrolyte, I would like to know why the treated carbon shows such a high power capability in this electrolytes.

3. Generally, the conductivity of nitrogen-doped carbon is lower than that of pristine carbon. With the content of nitrogen increases, the conductivity decreases. The research in the thesis showed some different conclusion, I would like to know why this phenomenon happens.

The manuscript is nicely organized, written in a good English level with a significant number of tables, graphs and illustrations which generate an enjoyable thesis to read. The thesis starts and finishes in a smooth way by having a well structured, concise but complete abstract and conclusion, which provides a nice summary of the work carried out during the preparation of the dissertation. In between those two sections the results are correctly discussed, well illustrated and nicely inserted in the thesis.

The doctoral thesis of Mr. Zhang Shuai presents a significant amount of original and innovative work. The candidate published seven research papers on scientific Journals with eight more research papers being submitted. Furthermore, the Ph.D. candidate published his papers in the journals (e.g Electrochimica Acta, Waste Management, etc..) with high impact factors.

Therefore, I suggest the Academic Council of Nanomaterials Physicochemistry Department, Faculty of Chemical Technology and Engineering of West Pomeranian University of Technology, Szczecin the admission of Zhang Shuai to the next stage which is the public defence of his doctoral thesis. I formally declare that I accept the thesis as it is.

I would like to state here that after my evaluation the Ph.D. thesis of Zhang Shuai is very high quality and I recommend to the Scientific Council of Faculty of Chemical Technology and Engineering of West Pomeranian University of Technology to proceed and let Zhang Shuai become a doctor. Additionally, due to the described outstanding scientific results, I recommend this thesis for Award for Excellence.

(Prof. Dr Xi Zhao) Xi zhao (赵熹)

Changchun, 08 April, 2019