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Doctoral thesis of Xiaoguang Liu
"Biomass derived porous carbon materials for electrochemical energy storage"
Supervised by dr hab. Xuecheng Chen, prof. ZUT

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Referee

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Thesis assessment

This is the assessment on the doctoral thesis entitled "Biomass derived porous carbon materials for electrochemical energy storage", submitted by Mr. Xiaoguang Liu, under the supervision of prof. dr hab. Xuecheng Chen at the Department of Nanomaterials Physicochemistry, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology in Szczecin, Poland.

The thesis is divided into nine chapters, in total 130 pages, which consists of a literature review, general experimental description and methodologies employed in the thesis work, followed by six concrete research works all focusing on the theme of this thesis, and a conclusion and perspective section.

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The thesis begins with a very nice graphical abstract, which comprehensively summarizes the research works being carried out. The six beautiful graphics vividly illustrate the ideas of materials design, materials synthesis process and/or electrochemical performance (in some graphics), which provide readers with essential information about the scope of research and key performance achieved by the supercapacitors fabricated.

Chapter 1 presents an overview about supercapacitors (SCs), which covers a variety of aspects including the historical development of SCs and their classification. The focus is then placed on EDLC, the type of SCs of interest in this thesis work. The charge storage mechanisms and charge storage processes are explained, and the principal components of SCs including electrolytes and electrode materials are reviewed. Afterwards, carbon materials of different types and their preparation methods are highlighted, which are closely linked to the theme of this thesis. At the end of Chapter 1, the scope of research of this thesis is introduced. Overall, Chapter 1 is very well structured and focused, and also provides a broader view about the development of this research field.

Chapter 2 describes the general experimental conditions used in the candidate's research, including materials and chemicals employed, methods used to characterize physicochemical properties of the prepared electrode materials, and how the supercapacitors are assembled and electrochemical performance assessed. All materials characterization methods chosen are justified and the calculations of specific capacitance, energy and power densities are presented in detail.

In Chapter 3, the candidate presents an example of 3D porous carbon derived from pyrolysis of jujube. The influence of carbonization temperatures and subsequent chemical activation parameters on the graphitization degree, pore structure, particle density, morphology, and electrochemical performance has been systematically investigated. It is demonstrated that the supercapacitor fabricated using the high-temperature derived carbon shows a good rate capability and superior cycling stability (91% capacitance retention after 10000 cycles) in 1 M H_2SO_4 electrolyte. Moreover, given the high particle density, the candidate demonstrated that a volumetric energy density as high as 13 Wh L^{-1} can be achieved in 1M Li_2SO_4 neutral electrolyte.

Chapter 4 shows another case study of biomass-derived 3D porous carbon electrode materials, with big cavities and hierarchical pores, which can help address the slow diffusion kinetics of organic and ionic electrolytes. As a result, the supercapacitor prepared using this kind of carbon materials manifests a high capacitance of 191 F g^{-1} at 0.5 A g^{-1} and high rate capability with 64% capacitance retention at 20 A g^{-1}, even if the viscous ionic liquid $EMIMBF_4$ is used as electrolyte. The candidate also compares the performance of the supercapacitor he prepared to that of others reported in the literature and verifies the good electrochemical performance dictated by the 3D porous carbon materials he prepared.

In Chapter 5, waste coffee grounds are used as precursors to prepare porous carbon materials. Interestingly, a $FeCl_3$ enabled catalytic carbonization process is introduced, which allows for the formation of a well-defined mesoporous structure with a high carbon yield of 42.5%. Upon alkali activation, abundant micropores are introduced, which in conjunction with the mesopores form a hierarchical pore structure. Consequently, a very high specific capacitance of 440 F g^{-1} has been obtained. Moreover, the symmetric supercapacitor fabricated exhibits a good capacitance retention of 81% at 20 A g^{-1}. The candidate also further demonstrates the supercapacitive performance in ionic liquid electrolyte, and comprehensively compares their SCs with those reported in the literature.

Chapter 6 presents an interesting 2D N-doped hierarchical porous nanosheet (2D-NPC) structure that is synthesized in a one-step synthesis process. How the morphology, pore structure, specific surface area, degree of graphitization, and surface chemistry can be affected by the addition of melamine and potassium oxalate has been systematically studied using a number of materials characterization techniques, and a rational formation mechanism of the 2D porous nanosheet structure is proposed. When tested in a three-electrode configuration, the 2D-NPC electrode shows a high capacitance of 523 F g^{-1}. Moreover, 2D-NPC is also tested in a symmetric supercapacitor using ionic liquid as the electrolyte, which can deliver 108 Wh kg^{-1} at 900 W kg^{-1}. Furthermore, a flexible supercapacitor based on 2D-NPC is demonstrated, showing a reasonably high energy density of 83 μWh cm^{-2} at an areal power density of 625 μW cm^{-2}.

In Chapter 7, the candidate deals with waste polymer (PET) derived carbon materials. A brief overview about the current state-of-the-art on this specific topic is firstly given, justifying the motivation of this work. Thus-obtained carbon demonstrates a surface area of 2238 cm^2 g^{-1}, much higher than that of other carbonaceous materials reported in the literature derived using a similar method. The mechanism proposed rationally explains why the hierarchical porous structure is obtained. As done in the other works, the electrochemical performance of the derived porous carbon is investigated in both three-electrode and two-electrode configurations, and

Swagelok-type supercapacitors as well as flexible supercapacitors are demonstrated.

Chapter 8 is also concerned about the conversion of waste polymer (polypropylene) into porous carbon nanostructures (2D carbon nanosheets). In this case, a combined catalyst of ferrocene and sulfur is used. A high yield of 62.8% is achieved. The role of the combined catalyst is comprehensively investigated. The carbon nanosheets exhibit a specific surface area as large as 3200 m^2 g^{-1} after KOH activation. The supercapacitive properties of the carbon nanosheets are also studied in a three-electrode configuration and a Swagelok-type cell. Overall, the works in both Chapters 7 and 8 provide a new avenue to convert water plastic into high value-added carbon products, which is additionally beneficial to environmental protection.

The main conclusions of the thesis are summarized in Chapter 9 together with a short discussion about the synergistic effect.

As a Referee of this thesis, I have a number of comments and questions that I would like to discuss with the candidate and the thesis is perhaps able to be further improved, if possible:

- The title of the thesis is “Biomass derived porous carbon materials for electrochemical energy storage”, but the contents of the thesis cover carbon materials derived not only from biomass but also from waste polymers. Maybe the candidate may consider rephrasing the title.
- The page numbers of “declaration” and “acknowledgement” sections in Table of Contents are confusing. Maybe these sections can be re-numbered or deleted from the ToC.
- Paragraph 1, Chapter 1: “fuel cells” cannot store energy and they are just energy conversion devices that transform chemical energy into electrical energy. Looking into the context, “regenerative fuel cells” is more appropriate to be used here, since they comprise a water electrolysis cell that can convert renewable energy into hydrogen and a hydrogen fuel cell that will convert hydrogen back to electricity, which can be used to balance the grid.
- Page 6, chapter 1: The sentence “The capacitance of the two electrodes was half of the capacitance of the supercapacitor” is confusing. The specific capacitance of a symmetric supercapacitor is usually the half of the specific capacitance of the electrode measured

in the three-electrode configuration. The above statement looks like the opposite.

- Section 1.2.3: since this section provides an overview about electrolytes used in EDLC, it will be better to briefly mention the polymer gel electrolyte that can be used in solid state supercapacitors as well, because this is also used in some works in this thesis, as mentioned in Chapter 2.
- Section 1.4: It would be better to highlight why biomass- and polymer-derived carbons are of interest from economic perspectives. This is an important aspect particularly in consideration of practical applications.
- Chapter 2: it would be better to provide more detail about the some materials characterization methods used. For instance, the BET measurements, which curve was selected to calculate surface area, etc.
- In Chapter 9, the candidate is encouraged to provide more perspectives about his future work to be done. This is a part that can reflect the independent thinking about his research topics and future plans.
- The thesis is written in a good level of English. However, there are still some improvements that can be made. For instance, when describing models and basic principles/theories, the present tense, rather than the past tense, should be used; “singular” and “plural” forms are used incorrectly in some places. In addition, there are also some typos, e.g. “powder” is incorrectly typed as “power” in several places.

Overall, I think that the thesis is nicely organized and clearly structured, with a significant number of informative figures, illustrations and tables included, which is enjoyable to read. In-depth data analyses and comprehensive performance assessments are given throughout the thesis, which reflect that the candidate has broad knowledge and a very good command of a variety of materials characterization techniques and electrochemical testing protocols. This justifies the qualification of the candidate as a Ph.D. Furthermore, I would like to highlight that the candidate published 11 SCI-indexed papers in high-profile journals during his PhD, in 6 of which he acts as the first author. In addition, he made two poster presentations at international conferences. I think this is an impressive achievement for a PhD student.

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In summary, the doctoral thesis of Xiaoguang Liu presents a significant amount of original and innovation work. The dissertation deserves to be distinguished as OUTSTANDING. Therefore, I would suggest that the West Pomeranian University of Technology in Szczecin admit Xiaoguang Liu to the next stage which is the public defense of his doctoral thesis. I formally declare that I accept the thesis as it is.

Yours faithfully,

Lifeng Liu

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