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Doctoral thesis of Xiaoguang Liu

"Biomass derived porous carbon materials for electrochemical energy storage"

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Thesis assessment

The research work of Xiaoguang Liu was done in the Department of Nanomaterials Physicochemistry of Faculty of Chemical Technology and Engineering, at West Pomeranian University of Technology in Szczecin, Poland. His work was supervised by Prof. Xuecheng Chen, a recognized expert in the field of nanotechnology. The work had led to the Ph.D. thesis of Xiaoguang Liu which I have the honor to review.

The thesis comprises 112 pages and it is divided into nine distinct chapters, consisting of a literature review, experimental section, results and discussion of the six research works and conclusions. The thesis is well balanced and shows a good distribution of pages for each chapter. The literature review is well-structured and touches all the main issues in the field.

At the beginning of the Ph.D. thesis, the author included the abstracts of the research with graphical presentation in English and Polish. This is a very valuable and worth continuing idea, because the every reader can get essential informations about the scope of research, right at the beginning.

An introduction to the subject of the Ph.D. thesis is in the Chapter I, which includes information on supercapacitors, electrochemical double-layer capacitors and porous carbon materials, and is based on 125 important publications. Supercapacitors have been briefly described in the development of commercial aspect, in the area of energy storage mechanism, and the electrode materials. According to the different energy storage mechanisms, supercapacitors can be classified into electrochemical double-layer capacitors (EDLCs), redox-based pseudocapacitors and hybrid capacitors. The energy storage/release process of electrochemical double-layer capacitors (EDLCs) is reversible physical adsorption-desorption process without any the electrochemical reactions. Simultaneously, EDLCs feature the high power density and long cycle life, which is very favorable in case of many electric an electronic systems. Therefore, it is very valuable to include in Ph.D. thesis informations about the charge storage mechanism in electrochemical double-layer capacitor and to highlight significance of electrode material, and electrolyte in the performance of EDLC. Additionally, the author also presented in the context of research strategy for this dissertation, the possibility of obtaining porous carbons depending on the type of carbon precursors (organic molecule, metal-organic frameworks (MOFs)/covalent organic frameworks (COFs), biomass, and polymers), template method (hard-template method, soft-template method), and carbonization and activation process.

Supercapacitors, as promising candidates for energy-storage devices, are particularly attractive because of their ultrahigh power density, fast charge and discharge response and long cycling life. The dominant electrode materials for supercapacitors are carbon-based materials due to their high chemical/thermal stability, and excellent electrical conductivity. Unfortunately, the relatively low capacitance and energy storage of carbon-based supercapacitors are their weaknesses and hinder their further practical application. Therefore, it is still a big challenge to prepare porous carbon materials with optimized physicochemical properties enabling to obtain next-generation supercapacitor. The crucial for the improvement of the energy storage capabilities of the supercapacitors are the physicochemical properties of porous carbons, described by morphology, pores architecture (pore volume and pore size distribution), ion-accessible specific surface area and surface functional groups.

The author paid special attention to this problem in Ph.D. thesis, undertaking research on obtaining expected porous carbon structures derived from different carbon precursors (biomass, organic molecule, and polymer) and through the use of various synthesis methods. Therefore, in my opinion, the adopted direction and scope of research presented in the thesis completely fits into its subject matter and constitutes a significant contribution to the development and extension of knowledge in this field.

In Chapter II, a description of the all materials used in work, techniques for characterization of obtained porous carbons and also, in cleary and detailed way, a description of the method of electrochemical measurements together with the preparation of the three-electrode and two-electrode system are presented. The obtained porous carbon materials, to investigate their morphological structure, thickness, crystal composition, textural properties and thermal stability, were characterized in thesis by various techniques as SEM, TEM, AFM, XRD, Raman, XPS, BET and TGA.

In Chapters from III to VIII are presented individual studies for the synthesis of porous carbon materials, their characteristics, and electrochemical properties as electrode materials in supercapacitors.

In Chapter III, the author synthesized, using the low-cost biomass in form of jujube as the carbon precursor, a robust 3D porous high-temperature carbons (PHCs) via high-temperature carbonization (800°C for 2h with a heating rate of 5°C min^{-1} under an inert atmosphere N_2) and subsequent, for different mass KOH, activation (800°C for 1h). Additionally, the porous low-temperature carbons (PLCs) were prepared by carbonization of freeze-dried jujube sheets at 500°C for 2h under a N_2 atmosphere. The influence of the ratio of KOH to carbon material on morphology, SSA, and pore structure of PHCs and PLCs has been studied. It was found, that for the PHCs samples, with increasing the m_{KOH}/m_{HC} mass ratio from 2 to 6, the SSA increased from 656 $m^2 g^{-1}$ for PHC-2 to 829 $m^2 g^{-1}$ for PHC-4 and then decreased to 783 $m^2 g^{-1}$ for PHC-6. While, for the PLCs samples, with increasing the m_{KOH}/m_{HC} mass ratio from 2 to 6, the SSA increased from 2499 $m^2 g^{-1}$ for PLC-2 to 3818 $m^2 g^{-1}$ for PLC-6. The electrochemical performance of carbon samples was evaluated in a two-electrode system using 1M H_2SO_4 electrolyte. For PHC-4 based electrode a specific

capacitance at 1 A g^{-1} was equal 158 F g^{-1}. Additionally, PHC-4 exhibited stability of 91% capacitance retention after 10000 charge/discharge cycles at 10 A g^{-1}. Research conducted for the PHC-4 based symmetric supercapacitor showed a high volumetric energy density of 13 Wh L^{-1} at a volumetric power density of 477 W L^{-1} in 1M Li_2SO_4 electrolyte.

In Chapter IV, the biomass in form of leek was used to produce a 3D hierarchical porous carbon (HPCs). The leek was freeze-dried for two days followed by carbonization at 500°C (5°C min^{-1} for 1 h under an inert atmosphere N_2). After carbonization the leek derived carbon was mixed with KOH, using different mass ratios, and was activated at 800°C for 1 h. The influence of the ratio of KOH to carbon material on morphology, specific surface area, and pore structure of 3D hierarchical porous carbon has been studied. It was observed that the SSA and V_t increased from 132 to 2512 m^2g^{-1} and from 0.13 to 1.62 cm^3g^{-1} respectively with increase of the KOH/leek derived carbon mass ratio from 2 to 6. The carbon samples were tested in a three-electrode system using 6M KOH electrolyte. Electrochemical measurements showed high specific capacitance equal to 349 F g^{-1} at 0.5 A g^{-1}. The cycling test showed no capacitance decay after 10000 cycles at 20 A g^{-1}. In a two-electrode system, the symmetric supercapacitor showed the specific capacitance of 191 F g^{-1} at a low current density of 0.5 A g^{-1}. Additionally, synthesized supercapacitor manifested a high energy density of 86 Wh kg^{-1} at a power density of 450 W kg^{-1}.

In Chapter V, the hierarchical porous carbon was synthesized from waste coffee grounds (biowastes) via catalytic-carbonization and alkali activation. A waste coffee grounds (CGs) were mixed with $FeCl_3$ using a mass ratio of $m_{CGs}/m_{FeCl3}=5$ in distilled water followed by sonication. Then the mixture was freeze-dried for three days to obtain a fluffy solid. Carbonization process was conducted in a tube furnace at a high temperature of 700°C for 2h with a ramping rate of 10°C min^{-1} under an argon atmosphere. Subsequently, obtained biochar was mixed with different mass of KOH, and the mixture was activated at 800°C (5°C min^{-1}) for 2 h. The influence of the ratio of KOH to carbon material on morphology, specific surface area, and pore structure of hierarchical porous carbons derived from biowaste coffee grounds has been studied. From BET analysis, the specific surface area of hierarchical porous carbon (HPC-4) was found to be 3549 m^2g^{-1} with a V_t of 2.41 cm^3g^{-1}. According to the detailed

electrochemical analysis, in a three-electrode system, the HPC-4 based electrode exhibited a high specific capacitance of 440 F g^{-1} in 6M KOH aqueous electrolyte. After 10000 charge/discharge cycles at 10 A g^{-1}, the capacitance retention remained at 94% for HPC-4 based supercapacitor, demonstrating outstanding stability. In a two-electrode system, in ionic liquid $EMIMBF_4$, a maximum energy density of 101 Wh kg^{-1} was achieved at a power density of 900 W kg^{-1}. Additionally, it indicated stability of 92% capacitance retention after 10000 charge/discharge cycles at 10 A g^{-1}.

In Chapter VI, two-dimensional nitrogen-doped hierarchical porous carbon nanosheets (2D-NPC) were prepared by a one-step pyrolysis-activation process under the synergistic effect of melamine/potassium oxalate. The mixture of glucose, potassium oxalate monohydrate (activation agent) and melamine (nitrogen source) was heated at 800°C (3°C min^{-1}) for 1 h under an inert atmosphere N_2. Subsequently, the obtained material was refluxed with diluted HCl acid and purified with distilled water. Additionally, obtained 2D porous carbons without adding potassium oxalate monohydrate (G-NC) or melamine (G-PC). The SSA and V_t for 2D nitrogen-doped hierarchical porous carbon nanosheets (2D-NPC) were 1730 m^2 g^{-1} and 1.51 cm^3 g^{-1}, respectively. Simultaneously, the SSA of G-PC was 1649 m^2 g^{-1}, much higher than 177 m^2 g^{-1} of G-NC. The electrodes were tested in a three-electrode system using 6M KOH electrolyte. It was reported that the specific capacitances were 49, 294, and 523 F g^{-1} at 0.5 A g^{-1} for G-NC, G-PC, and 2D-NPC, respectively. The cycling test of 2D-NPC based electrode showed a 100% capacitance retention over 10000 charge-discharge cycles at 10 A g^{-1}. The electrochemical performance of 2D-NPC was also studied using the EMIMBF4 electrolyte. At the current density under 20 A g^{-1}, the 2D-NPC based electrode retained a capacitance of 160 F g^{-1}. Simultaneously, it was observed that for the 2D-NPC based supercapacitor, energy density of 108 Wh kg^{-1} at a power density of 900 W kg^{-1}. A flexible supercapacitor assembled using two 2D-NPC based flexible electrodes, showed a an areal energy density of 83 μWh cm^{-2} at an areal power density of 625 μW cm^{-2}.

In Chapter VII, the waste poly(ethylene terephthalate) (PET) bottles, as a carbon precursor, were applied to produce the hierarchical porous carbons (HPCs) by low-temperature carbonization followed by high temperature activation. The PET pieces were

carbonized at a low temperature of 500°C with a ramping rate of 5°C min^{-1} for 1h under an inert atmosphere N_2. Subsequently, the obtained carbon was mixed with KOH with different mass ratios, and the mixture was activated in a tube furnace at 700°C for 1h. Additionally, to study the impact of carbonization temperature on electrochemical performance, the waste PET pieces were carbonized at a high temperature of 700°C for 1h in a tube furnace under N_2 atmosphere. From BET analysis, the SSA of prepared hierarchical porous carbon (HPC-6) was found to be 2644 m^2g^{-1} with a V_t of 1.52 cm^3g^{-1}. In a three-electrode system, using 6M KOH electrolyte, the hierarchical porous carbon (HPC-4) exhibited a capacitance of 413 F g^{-1} at 0.5 A g^{-1}, while the microporous carbon (C-700-700) showed a maximum capacitance of 142 F g^{-1} at 0.5 A g^{-1}. The capacitance for HPC-4 was 301 F g^{-1} in two-electrode system, and it was higher compared to the other samples. While the microporous carbon C-700-700 showed a low capacitance of 102 F g^{-1} at 0.5 A g^{-1}.

In Chapter VIII, a combined catalyst of ferrocene and sulfur was applied to convert the waste polypropylene into 2D carbon nanosheets. The mixture of ferrocene, sulfur, and waste polypropylene pieces heated to 700°C for 1.5 h in a furnace. Subsequently, obtained black composite in form of carbon nanosheets (CNS) was mixed with KOH with different mass ratios, and was activated at 800°C (10°C min^{-1}) for 1 h under N_2 atmosphere. After activation, the activated carbon nanosheets (ACNS) possessed a well-defined hierarchical porous structure with a large specific surface area. Obtained 2D carbon nanosheets (ACNS-4) possessed a SSA of 3200 m^2 g^{-1} with a V_t of 3.71 cm^3 g^{-1}. Electrochemical measurements for the ACNS-4 electrode, in a three-electrode system using 6M KOH electrolyte, showed its highest capacitance of 349 F g^{-1} at a current density of 0.5 A g^{-1} compared to ACNS-2 and ACNS-6. Additionally, a ACNS-4 based electrode exhibits stability of 99% capacitance retention over 10000 charge/discharge cycles at 5 A g^{-1}. Examined were also electrochemical properties the ACNS-4 based symmetric supercapacitor fabricated using neutral 1 M Li_2SO_4 aqueous electrolyte. The symmetric supercapacitor manifested a high energy density of 23 Wh kg^{-1} at a power density 225 W kg^{-1}. Simultaneously, the cycling test of the symmetric supercapacitor revealed cycling stability at the level of 92% capacitance retention at 10 A g^{-1} after 10000 cycles.

Finally, the main conclusions are summarized in the Chapter IX of the thesis. In my opinion the scope of the Ph.D. thesis was achieved since preparation porous carbon materials by different techniques using also different carbon precursors, and their good performance as materials for supercapacitors were obtained. The methodology used was well explored in many different ways in order to preparation of the materials by different methods and obtaining with expected physicochemical and structural properties of porous carbon 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 carbon nanomaterials for application in supercapacitors.

However, as a Referee I have a number of comments and questions that I would like to discuss with the candidate as follows:

1. Incorrect page numbering in Contents for Declaration-II and Acknowledgment-I
2. In Chapter IV, on page 38 the author wrote „The decreased sp^2-carbon content and the increased sp^3-carbon content in HPC-4 were detected, suggesting the introduction of many defects during activation".

   Why the author not referring, for example, to the HPC-6 sample, whose I_G/I_D ratio (0.50) is lower in comparsion to HPC-4 (0.51)?

   With increasing concentration of KOH in the LC+KOH mixture (increase of mass ratio m_{KOH}/m_{LC}), a decrease the ratio value of I_G/I_D after the activation process, and thus an increase the number of defects from the LC sample (without KOH activation) to HPC-6. In my opinion, the author should refer, taking into account the I_G/I_D ratio and number of defects during activation, to all samples (from LC to HPC-6).
3. Redundant description of the symbols that are listed in List of abbreviations for the Table 3.1, Table 3.3, Table 4.2, Table 6.1, Table 7.2 and Table 8.2.
4. Differences in marking of total pore volume. In List of abbreviations is V_{total}, while in text is V_t (e.g. in description of table 3.1).

5. In Chapter IV, on page 41 the author wrote „The electrochemical impedance spectroscopy (EIS) measurements from 100 kHz to 10 mHz were further conducted".

   The range for electrochemical impedance spectroscopy (EIS) measurements should be presented in the range from 10 mHz to 100 kHz.

6. Have the hierarchical porous carbon samples for Chapter 5 been examinated by X-ray diffraction (XRD) and Raman spectroscopy?

To sum up, the manuscript is nicely organized, written in a good English level with a significant number of well-built 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 and perspectives, which provides a nice summary of the work carried out during the preparation of dissertation. In between those two sections are individual chapters with the well-illustrated and correctly discussed the results. Simultaneously, each chapter related to research (III-VIII) is divided into subsections as: Introduction, Experimental section, Results and discussion, and Conclusion. Thanks this the manuscript is functional. I would like also to highlight the list of publications of author. He is an co-author of 11 scientific publications in international journals (as first author in the 6 publications) with a high impact factors. Additionally, he participated in 2 scientific conferences: Global Conference on Carbon Nanotubes and Graphene Technologies, March 28-29, 2019 at Milan, Italy and the 5th Polish Conference „Graphene and 2D materials", September 19-21, 2019 at Szczecin, Poland.

The doctoral thesis of Xiaoguang Liu presents a significant amount of original and innovative work. Therefore, I suggest the admission of Xiaoguang Liu to the next stage which is the public defence of his doctoral thesis. I formally declare that I accept the thesis as it is.