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Doctoral thesis of Yanliang Wen

"Porous carbon materials for supercapacitor application"

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Thesis assessment

The research work of Yanliang Wen 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. dr hab. Ewa Mijowska, a recognized expert in the field of nanotechnology. The work had led to the Ph.D. thesis of Yanliang Wen which I have the honor to review.

The thesis comprises 128 pages and it is divided into eleven distinct chapters, consisting of a literature review, experimental section, results and discussion of the eight research work 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 142 important publications. Supercapacitors have been briefly described in the historical aspect, in the area of energy storage mechanism, and classification in terms of charge-storage mechanisms and the electrode materials. Based on the energy storage mechanism (electrochemical capacitors), supercapacitors can be classified into electrochemical double-layer capacitors (EDLCs), pseudocapacitors and hybrid. Compared to pseudocapacitors, 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 information about the working process of the electrochemical double-layer capacitor and to highlight significance of electrode material, which is the most important factor determining the performance of a supercapacitor. Additionally, the author also presented in the context of research strategy for this dissertation, the methods of obtaining porous carbon materials (PCM) by the direct carbonization of organic precursors in the form of organic salts and metal-organic framework, by a soft and hard templating approach, and synthesis PCM by the physical and chemical activation.

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 integrated with both high specific surface area and appropriate porosity (pore volume and pore size distribution), which is crucial for the improvement of the energy storage capabilities of the supercapacitors. The author paid special attention to this problem in Ph.D. thesis, undertaking research on obtaining expected porous carbon structures through the use of various methods and by the selection of carbon precursors. 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, experimental methods and techniques are presented. The obtained porous carbon materials, to investigate their morphological structure, thickness and number of layers, crystal composition, textural properties and thermal stability, were characterized in thesis by various techniques as SEM, TEM, AFM, XRD, Raman, XPS, BET and TGA. Additionally, during thermal gravimetric analysis (TGA) liquid products (carbonization at 700°C) and hydrocarbon gas products were analyzed by gas chromatography-mass spectrometry and gas chromatography, respectively. In the same chapter the author presented also, in cleary and detailed way, a description of the method of electrochemical measurements together with the preparation of the electrode system.

In Chapters from III to X 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 the hierarchical porous carbon sheets (HPCSs) from pyrrole through a combination of MgO template carbonization and KOH activation. To prepare carbon sheets (CSs) the pyrrole was directly carbonized on the template of porous flaked structured MgO in the autoclave by heated to 500°C at 20°C min^{-1} and holden for 1 h. Subsequently, to achieve HPCSs, CSs were activated by KOH at different temperature (600, 700, and 800°C) for 1 h in an Ar atmosphere. With increasing the temperature of activation, the specific surface area (SSA) and total pore volume (V_{total}) of HPCSs increased from 1612 to 2788 m^2g^{-1} and 1.183 to 2.427 m^3g^{-1}, respectively. The HPCS-700 (CS activated at 700°C) based electrode showed a high gravimetric specific capacitance of 226.4 F g^{-1} at a scan rate of 1 mV s^{-1} in a two-electrode configuration with an electrolyte of 1 M H_2SO_4. It also exhibited high stability of 97.3% capacitance retention after 10000 charge/discharge cycles at 10 A g^{-1}.

In Chapter IV, the porous carbon sheets (PCSs) derived from polystyrene (PS) were prepared through the MgO template coupled with KOH activation. In order to obtain carbon sheets (CSs) the PS mixed with MgO was carbonized at 700°C for 6 min. in a high-temperature muffle furnace in air. KOH activation to obtain PCSs from CSs was carried out in a nickel crucible at 800°C for 2 h in Ar. The influence of the ratio of KOH to carbon material

on morphology, SSA, and pore structure of PCSs has been studied. It was found that with increasing the mass KOH to CSs, the SSA and V_{total} increased from 710.2 to 1163.0 m^2g^{-1} and from 1.013 to 2.554 cm^3g^{-1}, respectively. According to the detailed electrochemical analysis, the best supercapacitor behavior among all samples showed the PCS-3 (activated mass ratio of KOH to CSs = 3:1). The capacitance for it was 135 and 97 F g^{-1} at the scan rate of 1 mV s^{-1} and current density of 1 A g^{-1} in a two-electrode system with 1M H_2SO_4. A high energy density of 3.4 Wh kg^{-1} was achieved at the corresponding high-power density of 250 W kg^{-1} in the aqueous electrolyte. After 10000 charge/discharge cycles at 10 A g^{-1}, the capacitance retention remained at 92.41%, demonstrating outstanding stability.

In Chapter V, the waste poly(ethylene terephthalate) (PET) beverage bottles, as a carbon precursor, were converted into porous carbon nanosheet (PCNS) by a combined process of catalytic carbonization/template and KOH activation. Waste PET was mixed with organically modified montmorillonite (OMMT) at the mass ratio of 1:5, and carbonized at 700°C for 2 h with a temperature ramp of 5°C min^{-1} under N_2 atmosphere. Obtained composite was dissolved into hydrofluoric acid and nitric acid to purify and obtain carbon nanosheet (CNS). Subsequently, to obtain PCNS the mixture of CNS and KOH was annealed at 850°C for 1 h in Ar to chemically activate CNS. From BET analysis, the specific surface area of PCNS was found to be 2236 m^2g^{-1} with a V_{total} of 3.000 cm^3g^{-1}. Produced PCNS showed high performance of 169 F g^{-1} in 6 M KOH and 135 F g^{-1} in 1 M Na_2SO_4 in supercapacitors. In an organic electrolyte, PCNS displayed a capacitance of 121 F g^{-1} and a correspondingly high energy density of 30.6 Wh kg^{-1}. Additionally, PCNS exhibits stability of 91% capacitance retention after 5000 charge/discharge cycles at 10 A g^{-1}.

In Chapter VI, PCNS was produced by catalytic carbonization of five-component mixed waste plastics on organically modified montmorillonite with the subsequent KOH activation. The mixture of plastics waste (PP 35 wt.%, PE 40 wt.%, PS 18 wt.%, PET 4 wt.% and PVC 3 wt.%) was mixed with OMMT at a mass ratio of 1/5. CNS was synthesized by carbonizing the resultant mixed waste plastics/OMMT composite at 700°C for 10 min. under N_2 atmosphere and purifying by hydrofluoric acid and nitric acid. In the next step, for preparation of PCNS, CNS was mixed with KOH at a mass ratio of 1:6 and activated at 850°C

for 1.5 h under Ar atmosphere. To study the effect of the KOH/CNS mass ratio on morphology of PCNS, different mass ratios from 2 to 6 of KOH/CNS were used. It was observed that the SSA and V_{total} increased from 1236.2 to 2198.0 m^2g^{-1} and from 0.963 to 3.026 cm^3g^{-1} respectively with increase of the KOH/CNS mass ratio from 2 to 6. Electrochemical measurements for the PCNS electrode showed high performance in supercapacitors: 207 and 120 F g^{-1} at a current density of 0.2 A g^{-1} in aqueous and organic electrolytes, respectively. Besides, PCNS can maintain capacitances of 150 and 95 F g^{-1} in the electrolytes of 6 M KOH and 1 M tetraethylammonium tetrafluoroborate/propylene carbonate (TEATFB/PC) at 10 A g^{-1}, corresponding to a good capacitance retention ratio of 72.5% and 79.2%, respectively.

In Chapter VII, the eucalyptus-derived nitrogen/oxygen doped hierarchical porous carbons (NHPCs) were prepared by reaction with NH_4Cl and activation of $ZnCl_2$. In order to obtain NHPCs, at the beginning the eucalyptus powder (EP) was dispersed into 1M NH_4Cl solution and to the homogeneously dispersed mixture the $ZnCl_2$ was added. A dried mixture at 60°C was put into a corundum boat and carbonized at 850°C for 2 h under N_2 atmosphere in a horizontal quartz tube with a flow rate of 100 mL min^{-1}. Finally, a series of NHPC-x were obtained, where the x (1, 3, 5, and 7) was the mass ratio of $ZnCl_2$ to EP. It was observed that the SSA and V_{total} for samples increased from 1052.9 to 1492.6 m^2g^{-1} and from 0.89 to 2.32 cm^3g^{-1} respectively with increase of the $ZnCl_2$ to EP mass ratio. The capacitance for synthesized carbon material (NHPC-5) was 359 and 234 F g^{-1} at 0.5 A g^{-1} in three- and two-electrode system with 6M KOH, respectively. In an organic electrolyte, NHPC-5 accomplished an energy density of 48 Wh kg^{-1} at a power density of 750 W kg^{-1}. Simultaneously, it exhibited capacitance retention on the level of 92% after 10000 charge/discharge cycles at 10 A g^{-1}.

In Chapter VIII, N/O co-doped hierarchical porous peanut-shell derived carbons (NOHPPCs) were fabricated by a combined strategy of $CoCl_2$ catalytic graphitization and $ZnCl_2$ activation. For preparation of NOHPPCs the powder of peanuts shells (PSs) was dispersed in H_2O with 10% ethanol and next $CoCl_2$ was dissolved in mixture. Thereafter, a solution with a certain mass of $ZnCl_2$ was added into the as-prepared mixture. A dry material

was placed into a corundum boat and underwent the one-pot carbonization, catalytic graphitization, and activation in a tube furnace at 850°C for 2 h with a constant flow of N_2 of 120 mL min^{-1}. The sample was named as NOHPPC-x, where x represented the weight ratio of $ZnCl_2$ to PSs. It was found that the SSA of NOHPPC-x increased from 1745 to 2257 m^2g^{-1} with increasing weight ratio of $ZnCl_2$ to PSs. Especially, the NOHPPC-2 sample possessed the highest microporous S_{BET} (S_{micro}) equal to 1507 m^2g^{-1}. The NOHPPC-2 electrode showed a capacitance of 343 F g^{-1} at 0.5 A g^{-1} in a 3-electrode system with 6M KOH and capacitance retention on the level of 90.9% after 10000 charge/discharge cycles at 10 A g^{-1}. In an organic electrolyte, NOHPPC-2 displayed an energy density of 42 Wh kg^{-1} at the power density of 375 W kg^{-1}. Additionally, it indicated stability of 89% capacitance retention after 10000 charge/discharge cycles at 10 A g^{-1}.

In Chapter IX, the N/O/P-doped hierarchical porous carbon (EW-P-T) was prepared by application of nano-$CaCO_3$ which was used as both template and activation agent, and egg white as the carbon precursor. To the distilled water with dissolved nano-$CaCO_3$, the Na_3PO_4 and egg white was added. The mixture was heated at 60°C in the air and next annealing process was performed in a horizontal quartz tube at 800°C with a heating rate of 3°C min^{-1} for 2 h under an N_2 atmosphere. From BET analysis, the specific surface area of EW-P-T was found to be 2576 m^2g^{-1} with a V_{total} of 2.90 cm^3g^{-1}. At the current density of 0.5 A g^{-1}, the EW-P-T showed the specific capacitance of 452 F g^{-1}, and cycling stability of 92.4% capacitance retention after 10000 charge/discharge cycles at 10 A g^{-1} in 6M KOH electrolyte. In the neutral electrolyte of 1M Li_2SO_4, the energy density for EW-P-T was 22.6 Wh kg^{-1} at the power density of 225.0 W kg^{-1}. After 20000 charging/discharging cycles at 10 A g^{-1} in 1M Li_2SO_4 electrolyte, the EW-P-T displayed good cycling stability with 86.1% retention.

In Chapter X, the author synthesized a porous carbon materials (CZ-x, x is the particle size of the starting ZIF-8) derived from zeolitic imidazolate frameworks-8 (ZIF-8) with different particle sizes (from 25 to 296 nm). To obtain CZ-x, the ZIF-8 was carbonized at 900°C for 2 h in the N_2 atmosphere with a heating rate of 3°C min^{-1}. CZ-72 had a hierarchical porous structure with largest S_{BET} of 1083.1 m^2g^{-1} and V_{total} of 0.8701 cm^3g^{-1}. It was found that the sample with the mean diameter of 70 nm (CZ-72) exhibits the best capacitive

performance because of the unique cross-linked porous structure, higher nitrogen doping, and the highest conductivity.

Finally, the main conclusions are summarized in the Chapter XI of the thesis. In my opinion the scope of the Ph.D. thesis was achieved since preparation porous carbon materials by different techniques 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. V_{total} is not defined in List of abbreviations.

2. The table of contents does not include the subchapter 5.4 Conclusion, page 47.

3. Why SSA (specific surface area) and S_{BET} (Brunauer-Emmett-Teller specific surface area) are used interchangeably in the text? For example: in Table 6.4 (page 54) is S_{BET}, while in the text (page 53) is SSA-in a sentence „PCNS shows a high SSA of 2198 m^2g^{-1} and a large pore volume of 3.026 cm^3g^{-1} in comparison to CNS (104.2 m^2g^{-1} and 0.400 cm^3g^{-1})".

4. How author controlled the errors of experiments in studies (error bars)? How many times was repeated each experiment?

5. In Chapter IV, on page 33 the author wrote „The D-band is associated with the disordered and defective structure of carbon material, indicating the structural defects and partially disordered structures of sp2 carbon [168]".

The D-band is associated with the sp3-type hybridized carbon.

6. In Chapter IV, on page 34 the author wrote "TGA from Figure 4.3c shows the weight loss of CSs and PCSs occurring in two stages. From ambient temperature to 300°C, the weight loss is attributed to the release of chemisorbed water, the evaporation of moisture, and the

decomposition of surface oxygen-containing functional groups of the resultant carbon materials [170]".

Have the CSs and PCSs samples been examinated on the presence and type of surface oxygen-containing functional groups (by XPS or FTIR)?

7. In Chapter VI, on page 52 the author wrote „XRD patterns display the two weak and broad diffraction peaks at $2\theta = 25.7^{o}$ and 43.9^{o}, which are assigned to the typical graphitic (002) and (101) planes, respectively, indicating the low degree of graphitization of CNS (Figure 6.4c). The absence of the characteristic peak (002) in PCNS reflects the disordered nature and irregular arrangement of graphitic layers, suggesting the exfoliation of graphitic layers".

In my opinion the peak (002) in PCNS is visible (present) although it has much lower intensity compared to the CNS.

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-X) is divided into subsections as: Introduction, Experimental section or Synthesis of carbon material, 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 13 scientific publications in international journals (as first author in the 8 publications) with a high impact factors. Additionally, he participated in 2 scientific conferences: 5th Polish Conference „Graphene and 2D materials" in September 19-21, 2019 and XXXIVth International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2020) in March 07-14, 2020.

The doctoral thesis of Yanliang Wen presents a significant amount of original and innovative work. Therefore, I suggest the Scientific Council of the Faculty of

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Chemical Technology and Engineering of West Pomeranian University of Technology the admission of Yanliang Wen to the next stage which is the public defence of his doctoral thesis. I formally declare that I accept the thesis as it is.

Wojciech Konicki