Referee

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Referee Report

on the doctoral thesis of Mgr Yanliang Wen

submitted to West Pomeranian University of Technology in Szczecin, Faculty of Chemical Technology and Engineering, Department of Nanomaterials Physicochemistry

Title: Porous carbon materials for supercapacitor application

Author: Yanliang Wen

Supervisor: Prof. Dr. hab. Ewa Mijowska

The research work of Yanliang Wen was done in the Department of Nanomaterials Physicochemistry, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology, Szczecin. The work was supervised by Prof. Dr. hab. Ewa Mijowska, a recognized expert in the field of material science and nanotechnology. The work leads to the Ph.D. thesis of Mgr Yanliang Wen which I have the honor to review.

1. The context and the scope of the thesis

Due to fast-growing energy demands, the issue of the ever-deteriorating environment and rapid consumption of the limited fossil fuels coupled with anabatic global warming is becoming more and more urgent. Environmental sustainability requires worldwide efforts to develop environmentally friendly, low cost, and high-power energy-storage devices. Supercapacitors are one kind of the most promising energy storage systems that can harness the intermittent electricity generated from renewable and low CO_2 emission sources such as solar energy and wind power. Owing to its distinct superiorities of fast charge/discharge (in a few seconds), outstanding power density (higher than 10 kW kg^{-1}), low maintenance cost, appropriate dimension/weight, simple mode of operation, and long-cycle stability, supercapacitors have been demonstrated as the most promising candidates and the complementary alternatives for rechargeable batteries and conventional capacitors. Carbon materials have been demonstrated as the most commonly used electrode materials in supercapacitors attributing to their high conductivity, large specific surface area (SSA), excellent corrosion resistance, high thermal stability, somewhat controlled pore size distribution, satisfactory compatibility in different electrolytes, and comparatively low cost. However, the relatively low energy density and capacitance restrict the widespread application of supercapacitors. It is known that the electrode material is the most important factor determining the performance of a supercapacitor. Therefore, in order to obtain better performances in supercapacitors so that supercapacitors can show equal or surpassed importance to batteries, tremendous efforts should be made to improve the physical and chemical properties of carbon materials.

The thesis presents a comprehensive and systematic study of different porous carbon materials (PCMs) upon their application in the supercapacitor, including various materials preparation, detailed characterization, careful investigation of electrochemical performance in supercapacitors and mechanism analysis. It even extends to realize a flexible supercapacitor device. The exploration of carbon sources to synthesize PCM spans from organic molecules like pyrrole and polystyrene; various plastics waste in daily life; biomass like the tree, peanut-shell and egg white; and metal-organic frameworks, which not only realizes different heteroatom doping PCMs to engineer their electronic properties to enhance the electrochemical performance, but also offers a great way to the recycling of waste. Intensive characterizations of PCM and their electrochemical performance have been involved in lots of technical methods from the field of physics, materials, and chemistry. The application of various PCMs in supercapacitors has been systematically studied by intensive electrochemical measurements with two- and three-electrode systems.

2. Layout and the content of the Thesis

Yanliang Wen's Ph.D. thesis consists of 20 sections. The text part contains 11 chapters and 128 pages. Its structure is deliberate and transparent. The first chapter is the introduction which describes the basics associated with supercapacitors and PCMs. It also presents a brief history of the subject and a graphical description of the contents of each chapter.

The second chapter depicts the experimental details. It includes materials, chemicals, and characterization techniques as well as detailed electrochemical measurements. These are important and useful when reading this thesis.

In chapters three and four, the author focuses on the synthesis of two kinds of PCMs prepared by carbonization on the MgO template and subsequent KOH activation: hierarchical porous carbon sheets from pyrrole and porous carbon sheets from polystyrene. They show high electrochemical performances of 226 and 135 F g^{-1} with 1M H_2SO_4 electrolyte in supercapacitors.

In the subsequent fifth and sixth chapters, two porous carbon nanosheets are exhibited. They were synthesized by catalytic carbonization on organically modified montmorillonite (OMMT) followed by KOH activation from waster poly(ethylene terephthalate) and five-component "real-world" mixed waste plastics of polyethylene, poly(ethylene terephthalate), polypropylene, polystyrene, and polyvinyl chloride. Although the PCM from waste poly(ethylene terephthalate) possesses a little higher SSA (2236 m^2 g^{-1}) than the other one from mixed waste plastics (2198 m^2 g^{-1}), the latter shows higher specific capacitance (207 F g^{-1}) and carbon yield (43.3 wt.%) than those of the former (169 F g^{-1} and 31.4 wt.%). In these works, OMMT served as both catalyst and template: firstly promoted the degradation of waste plastics and then acted as a template for the in-situ growth of carbon nanosheets from the degradation products.

In chapters seven and eight, the natural abundant biomass was used as the carbon source to prepare PCMs through $ZnCl_2$ activation. Two kinds of PCMs with high SSA and reasonable porous structures from eucalyptus and peanut shells can deliver specific capacitance up to 340 F g^{-1} in 6M KOH and energy density higher than 42 Wh kg^{-1} in an organic electrolyte. The functionality of chemical blowing of NH_4Cl and catalytic graphitization of $CoCl_2$ were demonstrated in eucalyptus and peanut shells, respectively.

Chapter nine shows a kind of N/O/P co-doped 3D hierarchical porous carbon from egg white with a dual-functional nano-$CaCO_3$ as the template and activation agent. Meanwhile, Na_3PO_4 was used as the auxiliary dispersion for $CaCO_3$ and P source for the target carbon material. The as-prepared PCM displays an ultrahigh capacitance of 452 F g^{-1} (6M KOH) and energy density of 22.6 Wh kg^{-1} (1M Li_2SO_4) as well as a high capacitance of 166 F g^{-1} in a flexible symmetric solid-state supercapacitor accompanied by excellent flexibility of 86.3% (at a bending angle of 180°).

The tenth chapter presents a series of PCMs fabricated by direct carbonization of zeolitic imidazolate frameworks-8 (ZIF-8) with different particle sizes (25 to 295 nm). Through systematic characterizations and electrochemical studies of these PCMs, an optimal particle size (~70 nm) was obtained for the best supercapacitor performances in both acidic and alkaline electrolytes. It provides a significant reference to guide the future ZIF-8 related research works to achieve superior performances in supercapacitors.

The final chapter provides a summary of the thesis and presents brief directions and perspectives for further research.

3. The Main Contribution of the Thesis

Tremendous work has been involved in the synthesis and optimization of PCM from each carbon source to reach the improved performance with PCM structure from graphitic 2D to hierarchical 3D. The data clearly illustrates the improvement of the performance upon PCMs structure and electronic properties modification. The most important is that the working mechanism of the electrochemical performance of PCMs has been carefully discussed upon their structural and electronic properties engineering. The methodology used is well explored in different ways to optimize the preparation and functionalization of the materials. Furthermore, the results also point out the future direction to optimize PCMs in supercapacitors by improving the relative low capacitance and energy density.

4. Specific comments

One thing should be mentioned, as there are many things to learn from the thesis. Huge techniques have been involved in this research, like scanning/transmission electron microscope, structure analysis from x-ray diffraction, electronic properties from x-ray photoelectronic properties, optics, Raman, nitrogen adsorption/desorption measurements to estimate SSA, thermal gravimetric analysis, and so on. It will be useful for readers to get a better understanding if the thesis could present a little detailed information in the second chapter.

5. Final evaluation statement

All in all, it is a very nice and well-written scientific presentation with a systematic study of cutting-edge research to fulfill the requirement of the doctor’s degree. Such challenging work from various research fields has been very well presented in the thesis. It demonstrated the great scientific research background of the author and very skilled training during the study. It will be a significant advantage for his future research. 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 supercapacitor applications.

The research work has been rewarded with nine high-impact peer-reviewed scientific publications with three manuscripts under review. The work also has been presented in national and international conferences. It is an extraordinary achievement for a doctor's dissertation.

Therefore, I formally declare that I accept the thesis as it is. I suggest the Academic Council of West Pomeranian University of Technology in Szczecin the admission of Yanliang Wen to the next stage which is the public defense of his doctoral thesis, and admit him to become a doctor in chemical technology in the field of nanotechnology in supercapacitors.

(Assoc. Prof. (Docent) Dr. Xianjie Liu) Xianjie Liu

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