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Dr hab. inż. Miroslawa Pawlyta, prof. PŚ.
Laboratorium Badania Materiałów
Wydział Mechaniczny Technologiczny
Politechnika Śląska
ul. Konarskiego 18a, 44-100 Gliwice
E-mail: miroslawa.pawlyta@polsl.pl

Review of the doctoral thesis of M.Sc. Eng. Klaudia Kurtyka „Hollow 3D Graphene structures as active material for Li-ion batteries”

The doctoral dissertation presented for review was prepared at the Center of Polymer and Carbon Materials of the Polish Academy of Sciences in Zabrze under the supervision of Prof. Dr. Mark H. Rümmeli. The formal basis for the review was the resolution of the Scientific Council of the Center for Polymer and Carbon Materials of the Polish Academy of Sciences, adopted on 10 April 2024.

A critical examination of the research issues

Rechargeable batteries are a fundamental component of contemporary society, providing a reliable source of electricity in a multitude of applications. Lithium-ion batteries were first introduced to the consumer electronics market in the early 1990s and have since become the dominant technology, largely due to their high energy density. The principal applications of lithium-ion batteries are in portable consumer electronics. However, there is also growing interest in the use of batteries in electric vehicles and stationary grid storage, which enables the storage of excess electricity provided by wind and solar power on a very large scale at low cost. Consequently, the demand for these batteries is high and constantly growing, which justifies the effort put into searching for better

solutions. In essence, the search for "better batteries" is about increasing energy density or reducing cost compared to the most modern technology available. In a broader perspective, other parameters are also taken into account, including safety, cycle and calendar time, temperature range, and so forth. The chemistry of lithium-ion cells is based on the insertion of lithium ions into various host structures. The most commonly used positive electrode materials are various layered oxides, spinel and olivine oxides, while the most common negative electrode material is commercially available highly crystalline graphite. Research on systems with low working potential, high reversible capacity and high structural stability is important.

Although lithium-ion batteries are an example of a real success story, their production technology also has its barriers. In the coming years, the limit value of the capacity of graphite anodes currently used in lithium-ion batteries will be reached. It is therefore necessary to replace graphite with other materials. The author of a doctoral thesis documented (Table 2.2) that three-dimensional graphene structures have the potential to obtain high reversible capacity in the range of 365 - 935 mAh/g and stable cyclic operation during 100 cycles at 100 mA/g. At the same time, she pointed to an interesting and important research problem regarding the potential impact of the morphology and size of three-dimensional graphene structures on the capacity and ability to store lithium ions during the process of charging and discharging lithium-ion batteries. The topic of the presented work "3D hollow graphene structures as an active material for lithium-ion batteries" is therefore a current and important research issue, and at the same time opens new possibilities for improving the application properties of lithium-ion batteries. It is worth emphasizing the courage necessary to face a problem that requires the acquisition of a number of very diverse skills and the use of advanced research techniques that enable the synthesis and modification of the analyzed material, its comprehensive characterization and difficult application research.

Formal assessment of the dissertation

The dissertation is written in English and follows the traditional format of a scientific monograph. It comprises seven chapters, an appendix, an abstract (in Polish and English), a list of abbreviations, an extensive list of references (315 items), a list of figures and tables and a presentation of the PhD student's scientific achievements (publications, participation in projects). The entire dissertation is contained on 188 typescript pages, forming two separate parts. The first part is a literature review that presents the current state of knowledge regarding the subject of the work. The conclusions from the literature review were the basis for formulating the aim and hypothesis of the work. The second part presents the course and results of experimental research obtained as part of the doctoral thesis and their discussion. The order of the chapters is correct, and the arrangement of content in individual subchapters is logical and interconnected. The cited literature is selected appropriately for the topic of the dissertation and is up-to-date. The author refers mostly to English-language articles from the last ten years. However, there is a lack of references to classic works on the interpretation of the results of research on the structure of carbon materials. For example, in the case of XRD research, articles that explain the method of phase identification of carbon materials with a poorly ordered structure are not cited. Additionally, there is no reference to the turbostratic structure of these materials. Instead, articles are cited in which XRD tests of similar materials were also performed, but this is not their main topic.

A significant advantage, particularly from the reviewer's perspective, is the transparency of the reviewed work and the presentation of all information necessary for evaluation. The author's considerable effort to maintain a logical and transparent layout of the dissertation is evident, particularly in the presented table of contents. From the reader's perspective, this task has been accomplished successfully, as locating the necessary information in the extensive manuscript is relatively straightforward. The price paid for this is minor repetitions (section 4.4 and section 5.1) and inevitable simplifications. The chapter titles unnecessarily link the research technique to the type of information obtained, for example limiting TEM to morphology studies and suggesting that Raman spectroscopy is the main source of information about structure. These reservations apply only to the table of contents.

The doctoral thesis is prepared with great care in terms of language and editing. It is the reviewer's duty to point out errors, but I must admit that I practically did not notice them while reading. There are only a few comments that could be treated as a guide:

- Objections may concern the classification and terminology used to describe carbon materials. According to the reviewer, a division into graphitic carbon, soft carbons, hard carbons and nanostructured carbons would be more justified. This division better reflects the proportions in the current practical use of carbon materials in lithium-ion batteries. It also makes it easier to explain phenomena and processes that, in the case of hard carbon, were often explained many years earlier and, if this group of materials is omitted, must be rediscovered.
- The doctoral student adopted a convention of linking the described feature of the carbon material with the method or methods of its determination. For example, chemical composition – EDS, WDS; carbon structure – Raman spectroscopy, chemical structure – IR, XPS. However, according to the reviewer, this is too much of a simplification. Answers to the question: What information about carbon can be obtained by electron microscopy? cannot fit into one sentence.
- The terminology used to describe carbon materials is always problematic. Unfortunately, we have to come to terms with this, because it is an issue that could be the subject of a separate PhD thesis. Nevertheless, it is advisable to avoid the use of multiple terms in lieu of a single one (e.g. degree of structure order, degree of graphitization, degree of disorder in carbon materials; EDS and EDX) and to provide an explanation of the terms employed (What is the distinction between carbon structure, chemical structure, phase composition, chemical composition?).
- Measurement results should be provided along with measurement uncertainties. The method of notation should be uniform and unambiguous throughout the entire doctoral thesis. The notation used in this work ($1361 (\pm 368)$) does not indicate whether standard or extended uncertainties are given. The uncertainty should be recorded to two significant digits, and the result should be rounded to the same place as the uncertainty (1360 ± 370).

Substantive evaluation of the thesis

The aim of the research planned in the dissertation was to determine the influence of the dimensions of empty three-dimensional graphene structures on their structural and electrochemical properties

during the charging and discharging processes of a lithium-ion half-cell. The scope of the work included the synthesis and characterisation of the prepared materials using microscopic, spectroscopic and diffraction techniques, the preparation and assembly of electrodes containing the prepared material, the electrochemical analysis of the prepared electrodes and the post-mortem analysis of aged electrodes.

The PhD student's achievement is the synthesis of three three-dimensional graphene structures with the same number of carbon layers and different sizes of internal voids. Although the produced particles vary in size (they are not perfectly uniform), the individual size ranges are separated (they do not overlap).

The PhD student used a range of research methods in the analyses, including optical microscopy, scanning electron microscopy SEM, transmission electron microscopy TEM, energy dispersive X-ray spectroscopy EDS, wavelength dispersive X-ray spectroscopy WDS, X-ray powder diffraction XRD, Raman spectroscopy, Fourier transform infrared spectroscopy FTIR, X-ray photoelectron spectroscopy XPS and specific surface area BET measurements. The lack of spectacular results from these analyses is not due to incorrect measurements or incompetent interpretation, but is a consequence of the three-dimensional structure of poorly ordered carbon materials.

Electrochemical studies are an important part of the thesis. The part on theoretical calculations of specific capacitance for three-dimensional hollow graphene structures is interesting. The research material produced, with the necessary simplifications, encourages computer simulations. Even if one has some reservations about the reliability of the experimentally determined parameters, the consistency of the results obtained for the assumed (ideal) and actual (experimental) values is convincing. The achievement of higher capacitance values for the disordered carbon structure compared to the ordered graphite structure is also in line with expectations.

Cyclic galvanostatic measurements indicate that hollow 3D graphene structures offer higher specific capacitances than commercially available graphite anodes. Cyclic tests suggest a gradual increase in efficiency as a result of a gradual deterioration in the order of the carbon structure. The research has been carried out and described very carefully and professionally. The interpretation is interesting and convincing, although the final conclusion is that the performance of the samples tested is similar and that the differences observed are within the limits of measurement error.

The third part of experimental research is post-mortem research. The usefulness of these tests is beyond question. The main result is a significant increase in electrode volume for all materials tested. The materials compared also proved to be mechanically unstable - the degradation is lowest for electrodes containing particles of 100 nm diameter as active material. The degradation process may be related to the particle size of the 3D graphene structures used as the active material in the working electrode, but the unfavourable effect of the heterogeneity of the slurry containing the compared carbon materials, the conductive agent and the binder cannot be ruled out.

The extensive research carried out by the PhD student has produced important and interesting results in the field of the properties of the materials produced and their application properties. These were experiments with a high risk of failure, which deserves recognition in view of the current emphasis on rapid completion of doctoral theses and effective publication. The results obtained confirm the potential of the tested carbon materials - three-dimensional graphene structures - for use in lithium-ion cells, while at the same time pointing to ways of improving them and to significant threats. It should also be noted that the author is aware of the need to continue and complement the research carried out.

The results of the research conducted as part of the doctoral thesis are scientific material that stimulates discussion. Having read the thesis, I would like to know the doctoral student's opinion on a number of questions relating to both the literature and the experimental part:

- Can she indicate what the optimal (desirable) parameters (specific surface area, porosity, degree of order in the crystal structure) should be for a carbon material used as an active anode material in lithium-ion cells? Which of these parameters could be achieved with hollow three-dimensional graphene structures?
- Can the conclusions and observations presented in the thesis be extended to sodium-ion batteries? In the case of sodium-ion batteries, graphite cannot be used because the interplanar distances for sodium atoms are too small. However, the use of hard carbon is being investigated. What are the arguments for or against the use of empty three-dimensional graphene structures in sodium-ion batteries?
- Does the significant increase in volume of the electrode material containing 3D graphene structures observed during the research exclude its use as an active element in lithium-ion batteries?
- The post mortem analysis shows the importance of the preparation of the slurry (homogeneous mixing of the active component, binder and carbon black). Assessing the dispersion of the components of this mixture would be very valuable, but at the same time very difficult. Do you think it is possible?
- There is no basis for identifying the hexagonal phase in the carbon material analysed. It should be replaced by a turbostratic phase. This is a common simplification in scientific publications, also because crystallographic databases usually do not contain files for this phase (allotropy). However, in the case of a PhD thesis devoted to coal research, the description should be more precise. It is also incorrect to identify the sharp peak for which the interplanar spacings are 3.27 Å as an effect of local graphite formation. The minimum value of interplanar spacings for graphite is 3.35 Å and cannot be lower. The peak is probably due to some contamination. The statement "The produced material is a layered structure with a spacing of 0.3 - 0.4 nm, which is typical for graphite materials" is not correct. The range should start from a value of 3.35 Å. This also confirms the low accuracy of distance determination from TEM images.

Final grade

I believe that the reviewed doctoral dissertation by Ms. M.Sc. Eng. In accordance with the Act on Academic Degrees and Scientific Titles and on Degrees and Titles in the Field of Art, Klaudia Kurtyka's dissertation, "Hollow 3D Graphene Structures as Active Material for Li-ion Batteries," meets the requisite standards. In accordance with the regulations set out in the Act on Academic Degrees and Scientific Titles and on Degrees and Titles in the Field of Art, as amended on 18 March 2011, and in particular the conditions for doctoral dissertations, I request that the aforementioned doctoral dissertation be publicly defended once all other formal conditions have been met.

In my opinion, the reviewed work, due to its ambitious and current topic, the high level and diversity of advanced research techniques used and the groundbreaking nature of the results obtained, also deserves recognition if the formal conditions defined by the Scientific Council of the Center for Polymer and Carbon Materials of the Polish Academy of Sciences are met. The outstanding scientific achievements of the PhD student constitute an additional justification for my application.

