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REVIEW OF THE DOCTORAL DISSERTATION

MSc Eng. Klaudia Kurtyka

Titled: HOLLOW 3D GRAPHENE STRUCTURES AS ACTIVE ANODE MATERIAL FOR LI-ION BATTERIES

Supervisor: prof. dr Mark H. Rümmeli
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This doctoral dissertation, titled: HOLLOW 3D GRAPHENE STRUCTURES AS ACTIVE ANODE MATERIAL FOR LI-ION BATTERIES, investigates the potential usage of three-dimensional (3D) graphene as a new anode material due to its unique properties. The author's hypothesis is well-formulated: "The dimensions of hollow three-dimensional graphene structures and the parameters of the CVD process will affect their structural properties and their ability to efficiently store lithium ions during lithium-ion semi-cell operation." It is clearly written, logical and is testable through experimental work, making it a valid scientific hypothesis.

The main research objectives are structured in well planned distinctive work packages. This included investigating how the size of hollow three-dimensional graphene structures influences their structural and electrochemical properties during the charging and discharging processes of lithium-ion cells. The study included the synthesis of three different sizes of 3D graphene structures (300 nm, 100 nm, 10 nm) using the CVD process, with magnesium oxide powders serving as templates to achieve the target sizes. The synthesis was optimized to ensure a controlled and repeatable number of graphene layers by adjusting the heating time for each size.

The advanced measurement techniques, such as TEM, XPS, FTIR, and BET were used for full microscopic and spectroscopic characterization of the 3D graphene spheres. Over 600 CR2032 cell batteries were assembled for application research, including electrochemical tests like cycling tests, cyclic voltammetry, and electrochemical impedance spectroscopy to ensure statistical power. Battery

usability tests for the proposed active anode materials lasted over 720 days, concluding with post-mortem analyses to examine the aging process of the electrodes, to understand the reasons for the enhanced electrochemical properties of the 3D graphene structures, and to investigate their structural stability during the lithiation-delithiation process.

Conclusively, based on the evidence of the conducted research, the work proves that 3D graphene structures of different sizes, produced by CVD synthesis and etching, have similar chemical and phase compositions but differ in morphology, defects, porosity, and surface area. The hollow 100 nm 3D-GS, produced by CVD at 800°C with a 60-minute annealing time, exhibits the best electrochemical properties, including the highest average capacity and mechanical integrity after 100 charge/discharge cycles. Thus, both the size and annealing time, affecting the carbon structure and layer deposition, influence the electrochemical properties.

The result of this research work finally indicate the potential of 3D graphene structures for use in lithium-ion batteries, particularly in relation to process parameters and matrix sizes. Well defined conclusions are clearly listed in 10 separate points. The candidate recognises some limitations of the research due to the complexity of boundary processes during charging and discharging, and the numerous variables involved, and recognises that further research and observations are required.

The doctoral dissertation submitted for review has been prepared in the form of a monograph, as permitted by the current law on academic degrees and titles, as well as degrees and titles in the field of arts. The thesis comprises 188 pages, including the following sections: Introduction and 'State of the Art' literature review section presenting the current state of knowledge in the field; clearly stated hypothesis and objectives; Experimental section with research methodology, material characterization, and experimental electrochemical studies; Results and Discussion; Summary of the most significant findings; Conclusions; Appendices; and Bibliography.

The work is complemented by 55 figures, covering topics such as the publication trends related to Li-ion batteries, the construction principles of lithium-ion cells, different cell configurations, electrode materials, SEM observations, overview photographs of the working electrode surfaces, battery production processes, and graphene structures. Additionally, the figures illustrate experimental methodologies, materials characterization, performance evaluations, and morphological analyses of the developed 3D graphene-based electrodes, providing a detailed overview of the research conducted.

The work is also complemented by 19 Tables, providing valuable data on electrochemical characteristics of insertion compounds, synthesis methods and electrochemical performance of 3D graphene structures in Li-ion batteries, experimental materials, statistical parameters describing particle and graphene layer distributions, structural parameters of nanoparticles, composition of

surface structures, physical properties of graphene structures, theoretical capacity calculations, impedance parameters, thickness variations of electrodes, and densities of hollow 3D graphene structures. The dissertation is accompanied by an extensive bibliography comprising 315 carefully selected cited references. These references provide a good overview of the field and support for the research findings and conclusions presented in the document.

The thesis under review is very well prepared and organized. Results are presented in very clear manner, the structure of the document in very consequent way is leading from hypothesis and state of the art, showing importance of the studies, till well concluded discussion and summary.

Considering the substantial amount of effort invested, I would like to inquire what the doctoral candidate perceives as the greatest challenge She had to overcome while conducting the research covered in the dissertation?

What would you say is the most important conclusion from your research?

The dissertation is also complemented by an introductory summary in Polish, providing an overview of the doctoral work as well as the candidate's scientific portfolio. Ms. Kurtyka, M.Sc. with an H-index of 7, has co-authored a total of 17 publications (2 as a first author) in top scientific journals, focusing on advanced materials for energy storage and wearable electronics. Her research includes work on 3D graphene anodes for lithium-ion batteries, piezoelectric nanogenerators, and sustainable composite materials. The Doctoral Candidate has participated in international research projects. She was also – Principal Investigator in “3D graphene materials as active anode platforms for Li-ion batteries” PRELUDIUM-20 grant. Ms. Kurtyka, M.Sc. has contributed substantial work to the field of nanotechnology and material science and demonstrates strong proficiency in executing assigned research tasks. Her scientific achievements are really outstanding as for PhD Student.

In conclusion, after reviewing the doctoral dissertation of Ms. Kurtyka, M.Sc., entitled " HOLLOW 3D GRAPHENE STRUCTURES AS ACTIVE ANODE MATERIAL FOR LI-ION BATTERIES" I affirm that, doctoral dissertation prepared under the supervision of a prof. dr Mark H. Rümmeli meets the statutory requirements and may be presented for public defines. If the doctoral dissertation meets the requirements for outstanding works at the Centre of Polymer and Carbon Materials Polish Academy of Sciences, I would like to propose it for distinction.