REVIEW

on PhD Thesis for obtaining the educational and scientific degree "Doctor"
in the field of higher education 5. Technical sciences,
professional field 5.10 Chemical technologies,
scientific specialty 02.10.12 "Technology of silicates, binders and refractory non-metallic materials"

Author: Mag. Eng. Dimitar Vassilev Georgiev
Title: Research on the production of electrodes and dielectrics for supercapacitors using high-porosity silicate and carbon materials
Reviewer: Assoc. Prof. PhD. Tsvetan Ivanov Dimitrov, University of Ruse "A. Kanchev", Razgrad branch, department Chemical, Food and Biotechnology

I have been appointed a reviewer in the scientific jury for the dissertation on "Research on the production of electrodes and dielectrics for supercapacitors using high-porosity silicate and carbon materials", presented for the educational and scientific degree "Doctor" in higher education 5. Technical sciences from professional field 5.10 Chemical technologies in scientific specialty "Technology of silicates, binders and refractory non-metallic materials".

The author of the dissertation is Mag. Eng. Dimitar Vassilev Georgiev - PhD student at the Faculty of FTN with supervisors Prof. Dr. Irena Markovska and Assoc. Prof. Dr. Dimitar Rusev

Presented by Mag. Eng. Dimitar Vassilev Georgiev materials are in accordance with the Regulations for the acquisition of scientific degrees and holding academic positions at the University "Prof. Dr. Asen Zlatarov", Burgas. The dissertation corresponds to the requirements for the investigation of research problems. The materials are well designed, carefully arranged and logically connected.

The dissertation includes: introduction, theoretical part, experimental part, conclusions, scientific and scientific-applied contributions, publications and patents, literature and applications. The text is 144 pages, which includes 69 figures and 15 tables. 218 literature sources were used.

1. Topic and relevance of the dissertation

Growing fuel problems in recent years require urgent development of new technologies. The European Commission has announced new carbon targets to be reached by 2030. This is only possible by reformatting the automotive industry in the direction of hybrid and electric cars.

Against the background of the many advantages of electric cars in terms of air protection, car companies are facing another challenge related to the rapid construction of additional capacity for battery production, and in the near future new generation capacitors will be used everywhere. This will be possible by actively increasing the specific capacity of the devices. The use of new materials such as graphene, electrically conductive polymers, carbon nanotubes and fullerenes will meet the

requirements for a larger active surface of the electrodes, respectively higher capacity, combined with low weight.

The aim of this dissertation is to obtain innovative and effective coatings for electrodes, using silicate and carbon materials, in order to develop an experimental supercapacitor.

To achieve this goal, systematic research has been conducted, which covers the solution of the following main tasks:

- graphene preparation and deposition on the surface of the electrodes;
- obtaining electrically conductive paint, through which to attach the graphene to the electrode of the supercapacitor;
- synthesis of barium titanate and its introduction into the composition of the electrode coatings;
- construction of an experimental capacitor based on all developed components and measurement of its capacity.

These studies are a prerequisite for the development and improvement of methods for obtaining innovative and effective coatings for electrodes. On the other hand, in the literature the data in this field are scarce, which makes the research on the dissertation relevant and necessary.

2. Review of the cited literature

The review of the literature cited in the dissertation includes 218 titles, almost all of which are in international journals. This shows a good knowledge of research in the field of dissertation. Literary titles correspond to the topic of the dissertation. The literary sources published after 2010 is about 50%. As a result of the reviewed sources used and presented in the dissertation, I believe that the doctoral student is very well acquainted with the topic.

3. Research methodology

Graphene (chapter 2) from 1 to 5 layers was obtained using ultrasound, which was proven by Raman spectroscopy, SEM, TEM and infrared spectroscopy. As a precursor for the synthesis of graphene, finely dispersed graphite was used, which was placed in a solution of dilute sulfuric acid with different concentrations.

The production of graphene by the combined application of electrolysis and ultrasound is described in Chapter 3. It was found that the combination of dilute sulfuric acid and simultaneous treatment with ultrasound and electrolysis in an ultrasonic bath loosens the Van der Waals forces that bind graphene layers in graphite.

Chapter 4 presents the preparation of graphene coating on substrates. The possibility of applying a layer of graphene coating on an aluminum substrate using a high voltage generator has been proven. The SEM images of the carbon-coated aluminum substrate show that the resulting graphene coating is homogeneous.

Chapter 5 of the experimental part deals with the production of electrically conductive graphite paint for electrode coatings. Electrically conductive paint has been developed using liquid silicate $Na_2O.nSiO_2$ filled with fine graphite particles and NaOH additive. The suspension can be applied on ceramic, glass, paper, metal and other types of substrates. It has been proven that the resulting paint can be used to

create an electrically conductive coating with good adhesion and resistance, in order to improve the electrical and capacitive characteristics of capacitor electrodes.

Chapter 6 of the experimental part presents the preparation of a dielectric from barium titanate, by solid-phase synthesis and by sol-gel method. The solid-phase synthesis was carried out at relatively low temperatures in the range of 900 ° C-1100 °C, and the powdered raw materials were activated by sonication in various liquid media. It has been found that the powders obtained by the sol-gel method are finer in size, thus providing a high active surface on the electrode of the supercapacitor. The molar concentration of barium and titanium chloride solutions affects the particle size obtained by the sol-gel method.

At the end of the experimental part, in chapter 7 the development and construction of experimental models of supercapacitors and measurement of their capacities are considered. Two experimental capacitor cells - K1 and K2 - were constructed. From the measurements made it was found that K1 has a larger capacity than K2. The obtained values for the specific capacity of the capacitors give good results, which can fully confirm the idea of a working supercapacitor based on electrodes, paint and barium titanate.

In my opinion, the chosen methodology corresponds to the goals and objectives of the dissertation.

4. Scientific and applied contributions of the dissertation

The achieved most important scientific and applied results obtained in the dissertation of the mag. Eng. Dimitar Vassilev Georgiev can be summarized as follows:

□ Cheap and environmentally friendly technology for graphene production is proposed, through combined application of electrolysis and ultrasound;

□ A technology for graphene coating on a metal aluminum base using a high voltage generator has been developed;

□ An innovative electrically conductive solder is obtained, necessary for laying and attaching the active ingredients on the surface of the electrodes;

□ On the basis of the developed innovative coatings and the used electrolytes, a construction has been proposed and experimental capacitor cells have been made, and their specific capacity has been determined;

□ A software product has been developed for processing the experimental data obtained from the research and for optimizing the construction of the capacitor plates.

I accept and agree with the scientific and applied contributions determined by the doctoral student.

5. Publications and citations of publications on the dissertation

The main results of the dissertation are published in 2 articles in the Journal of the Balkan Tribological Association in 2020 (Imp. Factor 0.737, Q3) and 2022 (Imp. Factor 0.544, Q3), 1 article in the Journal of Chemical Technology and Metallurgy in 2021. (SJR 0.220), 2 articles in the Scientific Papers of the University of Ruse "Angel Kanchev", 1 article in the Scientific Papers of the University "Prof. Dr. Assen Zlatarov" in Burgas, as well as in 2 abstracts of the Scientific Conference for students, PhD students and young researchers in the section "Natural and Technical Sciences" of

the University "Prof. Dr. Asen Zlatarov" Burgas has a patent issued in 2019 on the topic of the dissertation.

6. Authorship of the obtained results

I have no doubt that Dimitar Vassilev Georgiev has a personal participation both in the publications, 2 of which he is the first author, and in the overall research and writing of the dissertation. In addition, the doctoral student participates in 1 project under the National Research Program and in 2 contracts № NIH 415/2018, № NIH 445/2020, which is also an indication of his qualifications and participation in research projects.

The doctoral student has an excellent style of presenting the results, formulating the conclusions and contributions. I think that the dissertation and the results obtained are the personal work of Dimitar Vassilev Georgiev.

7. Abstract and author's reference

The dissertation is synthesized and presented in an abstract of 50 pages. A general description of the dissertation is made, after which the main material is presented in five chapters. The conclusions from the dissertation work on the different sections, the scientific and scientific-applied contributions, as well as the list of publications and participations in scientific sessions, the issued patent and participation in scientific projects are presented. The content of the abstract corresponds to the content of the dissertation. My assessment is that the abstract meets the generally accepted requirements and accurately reflects the content and contributions of the dissertation.

8. Remarks on the dissertation and questions to the doctoral student:

- There is no uniform edition of all cited literature sources, which may make it difficult to find the cited literature sources. Information on some literature sources is incomplete: there is no year of publication of some sources (168, 172, 175, 215);
- The designations of the SI units of measurement are not uniform in different parts of the dissertation - for example cm, sm and cm; г, g and гр ; ml and мл, etc .;
- There is an error in writing formula (2) from page 10 - the magnitude of the current is equal to the charge passed per unit time through the cross section of the conductor - $I = dQ / dt$;
- Some pages of the dissertation, where there are formulas are not formatted properly and there is a large distance between the formulas, thus a large part of the page remains blank - pages 23, 103, 104;
- Some formulas are not numbered - pp. 104, 117-119;
- There is no indication of the dimension according to the ordinate of the powder diffraction patterns - Fig. 48 - 50.

The remarks made do not change in any way my overall positive assessment of the content and the presence of significant contributions to the doctoral thesis. They make sense of a proposal to improve its qualities.

9. Conclusion

The results obtained in the dissertation represent an original contribution and meet all requirements of the current legislation.

The dissertation shows that Dimitar Vassilev Georgiev has in-depth theoretical knowledge and professional skills in PhD program "Technology of silicates, binders and refractory non-metallic materials" demonstrating qualities and skills for independent research. Based on the above, I confidently give my positive assessment and recommend to the scientific jury to award the educational and academic degree "Doctor" in the field of higher education 5. Technical sciences, professional field 5.10. Chemical technologies and PhD program "Technology of silicates, binders and refractory non-metallic materials" to Dimitar Vassilev Georgiev.

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April 27, 2022.
Razgrad

Reviewer:
/ Assoc. PhD Tsvetan Dimitrov /