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Review

of the doctoral dissertation of Mr Maciej Tobis titled “*Study of two-dimensional nanostructured materials for electrochemical energy storage applications*”

The review was prepared on the basis of a letter from the 25th of June 2024 of the Dean of the Faculty of Chemical Technology at the Poznan University of Technology, prof. Ewa Kaczorek based on the Resolution No. RD-10/2/2024 of the Council of the Chemistry Science Discipline of the Poznan University of Technology.

The mentioned above doctoral dissertation was conducted under the supervision of Prof. Elżbieta Frąckowiak at the Institute of Chemistry and Technical Electrochemistry, Faculty of Chemical Technology of Poznan University of Technology. The main topic of the PhD thesis is focused on the utilization of layered 2D materials as electrode materials in electrochemical capacitors, including description and physicochemical and electrochemical characterization of synthesized materials as well as designing of the route in obtaining materials of desired properties.

Since its discovery by Volta, electric energy has been one of the most important factors in today’s life. The main beneficent of the electric energy is industry. As a result, global energy demand is growing very rapidly. It causes the increase in CO₂ emissions and affects climate change and pollution. It leads to global warming effect. Decarbonizing the energy sector can significantly reduce CO₂ emissions, and renewable energy sources can ensure universal access to electricity. Despite the rapid development of renewable energy, it cannot fully meet the global electricity demand. Currently, over 90% of the world's primary energy comes from fossil fuels, which necessitates an urgent reduction of this share in favour of low-emission sources. But even if we can to fully replace fossil fuels we still must find a proper method to harvest renewable energy successfully. Thus, the development of energy storage devices is in great need. Batteries, capacitors, and fuel cells are the most common devices that are able to store/convert electric energy. Batteries exhibit high specific energy but low specific power.

Contrary, capacitors show high power density but low energy density. The device that exhibits relatively high energy density and high power density is known as electrochemical capacitor. But still, electrochemical capacitors have much lower energy and power densities than capacitors and batteries, respectively. Thus, finding a proper material with improved electrochemical properties is crucial in the development of modern energy storage systems based on electrochemical capacitors.

Currently, many laboratories around the world are conducting research on the development of novel materials for electrochemical capacitors that exhibit high voltage originating from the battery, and high power capability coming from the capacitor, and Prof. Frąckowiak's team is one of the most recognizable groups in the scientific community in this field.

The doctoral dissertation of Mr Maciej Tobis is in the form of the so-called thematically coherent set of articles published in scientific journals and has 182 pages. This set of articles is consisted of 5 (after the additional results shown in Chapter 5 has been already accepted for publication) published papers. These 5 articles are devoted to three main goals: 1. development of hydrothermal synthesis protocol in obtaining novel 2D transition metal dichalcogenides (TMD) electrode materials, especially sulphide-based materials i.e. FeS_2 , ReS_2 , MoS_2 , and NiS_2 , in energy storage devices, 2. improving energy storage properties of TMDs (with MoS_2 as an example) by inhibiting their ability toward hydrogen evolution reaction (HER), and 3. the influence of different sulphur precursors on electrochemical properties of electrode material in energy storage system.

The doctoral student's hirsch index is 3 (Google Scholar and Web of Science, July 24, 2024) and the total impact factor IF of 5 publications, included in the doctoral dissertation, is 32.3 (July 24, 2024), which gives average value approx. 6.46. The average number of co-authors is 3.2, and suggests that Mr Maciej Tobis was the main investigator, especially that he was the first author in 3 out of 5 publications and was the corresponding author in one of them. The lack of values expressed in % is missing in the co-authorship statement of Mr Tobis and thus, it is hard to indicate his real contribution to the articles.

The dissertation consists of 6 chapters and is preceded by the motivation of the research. The first chapter has several subchapters and is devoted to literature review. This chapter includes characterizations of electrochemical capacitors starting from the terminology, principles of its operation, utilized electrolytes, and used electrode materials such as

carbonaceous materials and transition metal chalcogenides. This chapter is very detailed and introduces into the topic of capacitors. Although the author presents the different type of energy storage mechanism, including how to determine the type of pseudocapacitance,

1. There is a lack of information about the electrochemical techniques that are commonly used in the capacitance estimation

Additionally, in my opinion, subchapter 5.2 *Two dimensional transition metal dichalcogenides (TMD)* is too much focused on molybdenum (IV) disulphide (MoS_2). As Mr Maciej Tobis synthesized rhenium disulphide (ReS_2) he could pay more attention also to this compound in the subchapter 5.2.

2. What was the motivation to synthesize ReS_2 while the amount of Re in the Earth's crust is calculated to be $1 \cdot 10^{-7}$ wt.%?

Chapter II describes the aim and the structure of the dissertation. This chapter very well introduces the reader to the dissertation, however, the part *Dissertation structure* is more or less the doubling of the part named *Aim of the dissertation*.

Chapters from III to V familiar the reader with articles that are included in the thematically coherent set of articles. The last chapter summarizes the results obtained from the selected articles pointing the most important findings. This chapter includes all articles with Mr Maciej Tobis as co-author, attendance in conferences (6 oral presentations and 5 posters), participation in scientific projects (3), scientific internships (1), and awards (5).

The first article *Electrochemical Capacitor Performance of Nanotextured Carbon/Transition Metal Dichalcogenides Composites* is about modification of 2D transition metal dichalcogenides (ReS_2 or FeS_2) with carbon nanotubes (NT) or 3D carbon (3DG) phase to enhance electrochemical properties of such electrode material i.e. electrical conductivity, potential window, stability during polarization test etc. According to the statement, Mr Maciej Tobis synthesized ReS_2 -based composites and performed physicochemical and electrochemical characterization including data plotting and writing original draft. It was evidenced that usage of ReS_2 based electrode material led to faster capacity fading during cycling in comparison with FeS_2 electrode material. Additionally, the $\text{FeS}_2/3\text{DG}$ was able to operate at 1.5V with negligible capacity fade. Although the article is published in a very prestige article I have some questions/comments:

3. The naming of the samples is confusing. The same material is named in different ways: ReS_2/NTs and CNTs/ReS_2 (Fig. 1 and also in the text). Same with the other material.

4. Why did you not synthesize 3DG/ReS₂ for comparison with CNTs/ReS₂?
5. The comparison of different TMDs with different carbon phases is confusing. It is not so obvious to directly compare the results between CNTs/FeS₂ with 3DG/ReS₂ as these systems are different and may exhibit different electrochemical properties in EC (and they do).

The second article *Supercapacitor with Carbon/MoS₂ Composites* is devoted to usage of carbon phase with MoS₂. The presence of carbon phase was expected to enhance homogenous distribution of layered MoS₂ followed by improvement of electrochemical properties of Carbon/MoS₂ composite in terms of electrical conductivity. Conceptualization of the article, planned experiments, synthesis of the electrode materials, physicochemical and electrochemical characterization was performed by Mr Tobis. This evidences PhD student's leading role in formation of the publication. I do not fully agree with some statements in the publication:

6. Could you compare the ratio of the intensity of the signals at 33° and 58° for all 3 materials? XRD diffractogram for MoS₂ and both Carbon/MoS₂ composites do not differ much (Fig. 6). Thus, the statement "The layers are directed perpendicularly or horizontally to the NTs surface" is confusing as no differences between pristine MoS₂ and the composite were evidenced. Additionally, the crystal orientation plays important role in energy storage materials (Trzeciński K. et. al. *Sci. Rep.* (2023) 13:16668).
7. Did you perform galvanostatic charge/discharge stability tests? The capacitance of pristine MoS₂ and Carbon/MoS₂ seems to be similar, thus why to modify MoS₂ with carbon phase, unless it affects longterm cyclability?

The third article *Electrochemical Capacitor Based on Reduced Graphene Oxide/NiS₂ Composite* is about the modification of reduced graphene oxide (rGO) by NiS₂. The utilization of rGO was to increase the specific surface area of TMDs-based electrode material. Mr Tobis was responsible for characterization of the obtained material by the solid-state physic and electrochemical techniques including data plotting and writing original draft.

8. How NiS₂ was attached to rGO matrix? Was it by physisorption or by chemisorption process?
9. According to Supplementary Information there are two peaks: at ~ 500 cm⁻¹ and at ~ 1050 cm⁻¹ attributed to NiS₂. Why these maxima were not seen for composite?

10. Could you show Raman spectra of graphite with the deconvolution? I do not see the point to fit the curve with 4 peaks as for graphite it is known that there are only two maxima in the first-order region (D and G band) i.e. [Alkhouzaam A. et. al in *Nanomaterials* 2022, 12, 1240](#)
11. Could you explain why only maxima at $\sim 32^\circ$, $\sim 39^\circ$ and $\sim 59^\circ$ were seen for rGO/NiO₂ composite?
12. The result in Fig. 7B (intercept of the straight line with OX axis) do not match with results given in Table 1. Could you comment this differences?
13. Why did you take to the calculations $n=2$ and not $n=1/2$ in eq. 8?
14. Did you perform electrochemical stability test during charging/discharging for rGO, rGO/5wt%NiS₂, rGO/10wt%NiS₂, rGO/50wt%NiS₂?

The fourth article, *Nanostructured MoS₂ grafted by anthraquinone for energy storage*, is a continuation of studies on MoS₂-based electrode materials for electrochemical capacitors. According to the co-authorship statement, Mr Tobies played a crucial role in the creation of the article. He was responsible for conceptualization, planning the experiments, synthesis and characterization of the MoS₂, writing original draft and responses to reviewers. In other words: he did all. The main aim of this article was to diminish catalytic properties of MoS₂ towards hydrogen evolution reaction, This goal was reached by bonding MoS₂ to anthraquinone (AQ). Although the article was published in very good journal some questions arose:

15. The presence of carbon in pristine MoS₂ do not confirm that MoS₂ was successfully bonded to AQ (XPS).
16. I do not agree with the statement “*The very low content of MoO₂ and MoO₃ on the surface of the MoS₂ is also a proof that the hydrothermal synthesis allows for the preparation of high purity MoS₂ material.*”
 - a) According to Table S1 the at% of molybdenum ions originating from pristine MoS₂ and MoO_x is 17.3% and 6.8%, respectively. The content of MoO_x is not very low. It is only 2.5 times lower.
 - b) And the at% of molybdenum ions originating from AQ-MoS₂ and MoO_x is 5.7% and 3.8%, respectively. Any idea why the amount of MoS₂ has diminished so drastically?
17. Could you show Raman spectra in the broader region from 325 cm⁻¹ to 1000 cm⁻¹? The region 400 cm⁻¹ to 1000 cm⁻¹ is a fingerprint region to confirm or deny the presence of MoO_x.

18. Normalized intensity of absorbance or transmittance is plotted in Fig. S4?
19. What do you mean by claiming that MoS₂ exhibits a semi-crystalline pattern? The term semi-crystalline material refers to polymers.
20. Could you explain why the shape of cyclic voltammetry curve for AQ-MoS₂ electrode material is different in Fig. 5e and Fig. 7b?
21. What was the specific capacity of AQ-MoS₂ in the contact with lithium ions in organic media in mAh/g?
22. What does normalized charge mean in Fig. 10?

The last article, *Controlling Structure and Morphology of MoS₂ via Sulfur Precursor for Optimized Pseudocapacitive Lithium Intercalation Hosts*, is a result of the scientific internship in Helmholtz Institute Ulm in Germany. Mr Tobis was responsible for conceptualization, investigation, methodology, data curation, funding acquisition and writing both original draft and responses to reviewers. This article presents the influence of sulphur precursor on electrochemical properties of synthesized MoS₂ material for lithium-ion. This article, although added to the dissertation as an unpublished data, was published on the 2nd of July 2024. However, also for this article I have some questions and comments:

23. It is recommended to dry cut electrodes containing NMP at 110°C under vacuum (Wood D.L. et. al. in *Drying Technology*, 2017, 36(2), 234–244). Otherwise NMP residuals will affect the electrode performance.
24. Theoretical specific capacity of MoS₂ is 167 mAh/g. Could you comment the reason why MoS₂ TU and MoS₂ TAA showed higher values? Is it possible to reach capacity higher than theoretical? In other words, are you sure that lithium ion intercalation does not occur into the carbon phase formed during synthesis process from sulphur precursors?
25. There are 2 redox couple activities for commercial MoS₂: the first at ~ 1.9 V and the second at ~ 2.5 V. Could you propose the reactions taking place at these potentials?
26. Could you compare the long-term cycling for all materials? There is lack of any graph in the article or SI but there is a sentence in the main text: *After 1,000 cycles, two groups can be identified according to their capacity retention.*
27. What is the reason of such high electrical conductivity of MoS₂ TU electrode material?
28. Why you did not perform conductivity measurements of pure materials?

In general the dissertation is a very important contribution to the study of energy storage systems based on 2D materials modified with carbonaceous materials. The presented work is not limited to synthesis electrode materials for ECs itself but it goes beyond that including improving electrochemical properties of TMDs, especially MoS₂. Moreover, Mr Tobis demonstrated his ability to plan and conduct experimental work, to select appropriate research techniques, to discuss the results, and to conclude.

In summary, although mentioned above comments, the doctoral dissertation submitted by Mr Maciej Tobis represents very high scientific work. The PhD thesis is well written with negligible errors, and in my opinion it meets all requirements set up in Article 187 of the Act dated July 20, 2018. Law on higher education and science (Journal of Laws of 2023, item 742, as amended. d.), and I recommend to the Council of the Faculty of Chemical Technology, Poznan University of Technology for the admission of Mr Maciej Tobis to the next stages of the doctoral dissertation.

Sincerely,



Dr hab. inż. Andrzej Nowak, Profesor PG



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Application for awarding of doctoral dissertation

The doctoral dissertation of Mr Maciej Tobis is an example of very well planned and performed investigation of transition metal dichalcogenides as electrode materials for energy storage systems. The PhD thesis is about electrochemical capacitors that is very actual topic in the field of electrochemical energy storage systems. The broad research investigations are focused on 4 different transition metal dichalcogenides materials. It shows that Mr Tobis was not limited to only one electrode material. The obtained results have very high cognitive value in terms of both scientific and application approach. The most crucial achievement is optimization of the synthesis process of MoS₂ as electrode material in electrochemical capacitor in aqueous or non-aqueous electrolyte and limiting its catalytic properties towards hydrogen evolution reaction. Mr Tobis is co-author of 7 articles of the total impact factor equal to 46.3 and 840 points, in the rank given by Polish Ministry of Science and Higher Education. In 4 out of 7 PhD student is the first author. Additionally, Mr Tobis was co-investigator in 2 scientific projects and recently, principal investigator in Preludium 20. It proves his scientific maturity and is an exception at this stage of his scientific career.

Thus, I **strongly recommend awarding the doctoral dissertation of Mr Maciej Tobis by the Council of the Chemistry Science Discipline of the Poznan University of Technology.**

Andrzej Nowak

