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REPORT

on the Ph.D. dissertation of M. Sc. **Maciej TOBIS** entitled

Study of two-dimensional nanostructured materials for electrochemical energy storage application

submitted to the Faculty of Chemical Technology of Poznań University of Technology in Poznań

For a number of decades, there has been strong interest in developing electrochemical capacitors (ECs) with high energy density which fulfill the current requirements for such devices. Higher energy values compared to the commercially available electrochemical capacitors (usually < 8-10 Wh/kg) can be achieved using modern electrode materials, electrolyte and hybrid systems. They allow to simultaneously increase the working voltage of the capacitor and achieve high electrochemical capacitance value. Therefore, new electrode materials are being developed extensively across the world to achieve high capacitance values, and appropriate electrolytes are selected to ensure operation over a wide voltage range with a long-term cycle stability of the device. The dissertation submitted by M.Sc. Maciej Tobis focuses on metal dichalcogenides (TMDs) as electrode materials for electrochemical energy storage application. TMDs are a family of 2D materials which seem to be attractive for energy storage devices due to their layered structure and high capacitance. It can be concluded that the subject of the Ph.D. dissertation is fully in line with highly important research topics.

The Ph.D. dissertation was performed in the Institute of Chemistry and Technical Electrochemistry under the supervision of Professor Elżbieta Frąckowiak. The work was financially supported by the National Science Center within two projects, i.e. the OPUS project *Study of electrode/electrolyte interface of high stability and quick charge response* and the Preludium project *Influence of redox pairs on hydrogen evolution overpotential of dichalcogenides.* It should be also added that a part of the doctoral work was completed

during the autor's scientific internship at Karlsruche Institute of Technology in Karlsruche and Helmholtz Institute Ulm in Ulm in Germany under the supervision of Dr. Simon Fleischmann. The author's three-month stay abroad was supported by the Polish National Agency for Academic Exchange (NAWA) and STER programme offered by Poznań University of Technology. The title of the research project acomplished abroad was *Investigation of energy storage mechanism of transition metal dichalcogenides (TMDs) with designed interlayer spacing.*

The Ph.D. thesis of M.Sc. Maciej Tobis has been edited in an unconventional way. As opposed to the classical form of a doctoral thesis, it is a monothematic series of five publications entitled *Study of two-dimensional nanostructured materials for electrochemical energy storage application.* Four out of the five papers were published over a three-year period in 2021-2024 in high-impact journals such as *Small* (P1: IF=13.3, 2021), *Frontiers in Energy Research* (P2: IF=3.4, 2021), *ChemElectroChem* (P3: IF=4.0, 2022) and *Journal of Power Sources* (P4: IF=9.2, 2024). The fifth publication included a paper (P5) that is currently under review by *Batteries & Supercaps* (IF=5.7). In three out of the five papers, Maciej Tobis is the first author. Moreover, he is a corresponding co-author in the paper published in the *Journal of Power Sources*. His contribution in the aforementioned papers has been provided. In addition to the publications included in the dissertation, M.Sc. Maciej Tobis has co-authored two other papers which were published in *Green Chemistry* (IF=9.8) and *Electrochimica Acta* (IF=6.6).

The dissertation of M.Sc. Maciej Tobis has 182 pages, including the list of references (231 items), abstracts in Polish and English, a list of abbreviations, the author's scientific track records and co-authorship statements of publications related to the dissertation. The dissertation opens with a short paragraph which presents the *Motivation and context of the research*, highlighting the importance of electrochemical energy storage devices. The author explains the reason and motivation for undertaking the study on the development of active electrode materials for electrochemical capacitors (ECs). The main part of the dissertation is divided into five chapters. **Chapter I** is the literature section focused on the electrochemical capacitors. First, the principle of ECs operation and the mechanisms of energy storage in ECs are described. Several electrical double-layer models describing energy storage mechanism in EC are discussed. Further, a special focus is put on the pseudocapacitance in electrode materials. The author presents the classification of pseudocapacitance phenomena into three different types proposed by Conway, i.e. adsorption pseudocapacitance, redox pseudocapacitance and intercalation pseudocapacitance. Electrochemical behavior of intrinsic and extrinsic pseudocapacaitance materials is graphically demonstrated and discussed, indicating a battery-like nature of the latter materials. Finally, different electrochemical responses based on EDL, pseudocapacitance and battery-like are compared.

Moreover, a brief overview of electrolytes (aqueous, organic, ionic liquids) and electrode materials for EC is presented in Chapter I. Advantages and disadvantages of different types of electrolytes in terms of their application in ECs are explained. In the last subsection of Chapter I, various energy storage materials are described, including ACs, CNTs and graphene only

briefly and TMDs thoroughly. TMDs seem to be very promising electrode material for energy storage devices due to high capacitance/capacity, however, their conductivity is not high. The review part of the dissertation focuses mainly on most reported molybdenum disulfide MoS_2, methods of its synthesis, structure, functionalization and electrochemical properties.

Chapter II presents the aim and structure of the dissertation. As follows from the literature, TMDs may have great potential for advancing electrochemical energy storage technologies, especially in ECs and batteries. The author emphasizes that available existing reports do not provide a full and reliable evaluation of TMDs as electrode materials for these devices, since most studies were conducted in a three-electrode system characterizing the electrochemical behavior of a single electrode, rather than an entire two-electrode system. Moreover, in some works the electrode masses used were very small (~1 mg), which has no practical application. Therefore, the author is going to verify the hypothesis whether such 2D materials as TMDs can increase effectively the EC capacitance. Taking into account the moderate conductivity of TDMs, the introduction of carbon material of high conductivity into TMD electrode material is one of the strategies to enhance electrochemical performance of the ECs (Chapter III, three publications P1, P2 and P3). Another way to improve the performance of the TMD-based device proposed by the author is functionalization of TMDs (Chapter IV, one publication P4). Chapter V (one publication under review P5) describes the results of the study on the influence of sulfur precursor on the morphology, structure and porous texture of the synthesized TMDs and their electrochemical lithium intercalation behavior. It should be added that the copy of each publication enclosed in the dissertation was preceded by a short description (two-three pages) of the context of the research and a summary followed by a graphical abstract. Concluding remarks are presented in the form of a general summary in Chapter VI.

In this work, a series of TMDs, including ruthenium disulfide (ReS_2), iron disulfide (FeS_2), molybdenum disulfide (MoS_2) and nickel disulfide (NiS_2) and their composites with conductive carbon materials were successfully obtained by hydrothermal treatment using different precursors depending on the synthesized material. They were thoroughly characterized by means of several advanced techniques in terms of morphology, structure and porous structure (SEM, SEM-EDX, HRTEM, elemental analysis, XPS, Raman spectroscopy, FTIR, sorption of N_2 at 77 K), and electrochemical properties (cyclic voltammetry, galvanostatic charge-discharge, electrochemical impedance spectroscopy, conductivity measurements). The materials synthesized in this work were evaluated in a three-electrode cell and symmetric and asymmetric two-electrode systems to have a full overview of their potential for electrochemical energy storage application.

Chapter III presents the results of the studies (P1, P2, P3) on the hydrothermal synthesis of layered ReS_2, FeS_2, MoS_2 and non-layered NiS_2 and their composites with carbon nanotubes (ReS_2/NTs, MoS_2/NTs), carbon black (carbon/MoS_2), and graphene materials (FeS_2/3DG, Ni/rGO). The contribution of carbon materials ensures higher conductivity and surface area of the TMD-based electrode material enhancing electrochemical performance. A comparison of symmetrical cells with the ReS_2/NTs-based electrodes (1 M Na_2SO_4 as electrolyte) and the

FeS_2/3DG-based electrodes (1M Na_2SO_4 as electrolyte) revealed much better performance of the device containing the latter composite electrode material (110 vs. 240 F/g). The ReS_2-based composite exhibited a much lower voltage limit compared to FeS_2/3DG composite (0.8 *vs.* 1.5 V) due to strong catalytic activity towards aqueous electrolyte decomposition (P1). In case of MoS_2-based composites with carbon black BP2000 and CNTs, the electrochemical voltage window of the cells was limited to below 1 V again due to catalytic activity towards hydrogen evolution (HER). CNTs proved to enhance capacitance to a higher extent than BP2000 (P2). Hydrothermal synthesis of NiS_2/rGO composite and its evaluation as a positive electrode in asymmetric EC with rGO as a negative electrode was the subject of investigation presented in the publication P3. The superior capacitance (165 F/g at 0.2 A/g) of such device operated in 6M KOH was achieved for a composite with a weight ratio of 5 (NiS_2): 95 (rGO) at a voltage cell of 1 V. It can be concluded, that one of the reasons for the low potential window of EC is the catalytic activity of TMDs toward HER.

To overcome this drawback, the author proposed blocking active sites by covalent functionalization and successfully carried out this idea using MoS_2 as an example. The obtained results are presented in P4 (**Chapter IV**). In my opinion, this is a very valuable part of the dissertation with essential novelty. Layered nanostructured MoS_2 was modified with anthraquinone (AQ) using diazonium salt. The modified MoS_2 was thoroughly studied to follow the mechanism of functionalization and to determine the structure of the obtained products. XPS, XRD and TEM results confirmed covalent bonding between AQ molecules and the MoS_2 surface. As a result of AQ redox reactions, the capacitance of MoS_2 significantly increased reaching 263 F/g in 1M H_2SO_4. Moreover, the blockage of active sites in the structure of MoS_2 by AQ resulted in a decrease in the catalytic activity towards HER. The use of carbon black as a positive electrode in a hybrid system with a modified MoS_2 as a negative electrode allows for the extension of the cell potential window to 1.2 V.

Chapter V consist of the recent publication (P5) in which the author demonstrates how, by selecting a sulfur precursor, the structure and morphology of layered MoS_2 can be tailored affecting lithium pseudocapacitive intercalation properties. Lithium intercalation experiments were performed in the 1 to 3 vs. Li/Li^+ potential range. Various sulfur precursors were used in this study such as thiourea (TU), thioacetamide (TAA) and L-cysteine (LC). Commercial bulk MoS_2 was used for comparison. The synthesized MoS_2 materials using TAA and LC appeared to be the most effective in improving capacity at superior capacity (100 mAh/g at 10 A/g) due to their nanostructure nature in the form of nanosized flakes, higher surface area and increased porosity. The charge storage mechanism was determined thanks to the application of modern tools such as operando X-ray diffraction, operando dilatometric height change and 3D Bode plot analyses.

The main achievements of the dissertation are the following:

1. The mechanisms of charge storage in layered and non-layered TMC-based ECs in aqueous electrolytes were determined based on the results obtained by advanced

analytical techniques used for the characterization of the synthesized TMDs and their composites with carbon materials. Advanced interpretation of the electrochemical results should be also emphasized.

2. Successful reduction of the catalytic activity of MoS_2 towards HER by functionalization with anthraquinone leading to improved performance of EC.
3. It was revealed that the structure, morphology and porous texture of MoS_2 obtained by hydrothermal method is highly dependent on the sulfur precursor used in the synthesis, affecting its electrochemical behavior during lithium intercalation in organic electrolyte.

Summarizing, the Ph.D. dissertation prepared by M.Sc. Maciej Tobis presents a high scientific level in terms of synthesis of TMCs and their composites with carbon/graphene materials, physiochemical and structural characterization of the synthesized nanomaterials and their electrochemical evaluation as electrode active materials for supercapacitors and hybrid capacitors. A wide spectrum of the advanced analytical techniques and the in-depth interpretation of the obtained results makes the dissertation highly valuable. The obtained results are well presented and thoroughly discussed, confirming the author's extensive knowledge of chemistry and physics of TMDs and carbon materials, electrochemical charge storage mechanisms and systems. It should be added that most of the research results presented in the dissertation were reviewed and positively approved by reviewers of high impact journals from the JCR list.

The following questions and comments should be considered during the PhD defense.

1. **P1.** Fig. 8. For 3DG-20wt%FeS_2 a broad peak at 2Θ~24^o can be observed, which corresponds to the 002 plane in graphite. The intensity decreases with a higher contribution of graphene material, despite an increasing contribution of graphene material in the composite. How to explain this observation ?
2. **P1**. The question concerns the purity of MWCNTs used in this study. Was it checked after MWCNTs were delivered ?
3. **P1**. Why were the electrode masses of ReS_2/7wt% CNT and 3DG/15wt% FeS_2 different (8-10 mg vs. 2.5-3 mg, respectively)?
4. **P2.** What is the porous structure parameters of carbon black BP2000 on which MoS_2 was deposited?
5. **P3**. How to explain the observed impact of pH value on the porous texture of the obtained rGO (Fig. 2, Table S3) ?
6. **P3**. The equation (7) describing the number of graphene layers in the crystallite is incorrect. It should be $N_c=L_c/d_{002} + 1$.
7. Generally, metal sulfides are prone to oxidation. How do they behave during storage ?
8. Have you studied the morphology of TMDs after long-term galvanostatic charge-dicharge cycling ?

9. **P4.** Table S2. The values of $L_{0\ MICRO}$ and $L_{0\ MESO}$ have too many significant places. What method was used for determination of the micropore volume, the mean size of micropores and mesopores ?
10. Having gained at least four years of experience working with TMDs, what is your opinion on using TMCs as electrode material for ECs of high energy density? Could you take into account narrow safe operating voltage, oxidation of sulfide at positive polarization, relative low cyclic stability, strong catalytic activity towards HER, moderate conductivity, low surface area and other factors.

Concluding, the thesis prepared by M.Sc. Maciej Tobis under the scientific supervision of Professor Elżbieta Frąckowiak fully meets the requirements for receiving the PhD degree in Chemical Sciences. I recommend the submitted thesis for public defense. Moreover, I propose to nominate the Ph.D. dissertation of Maciej Tobis for an award due to high scientific level and novelty of the obtained results which were published in high-rank journals.

Request for distinction

The doctoral dissertation of M. Sc. Maciej Tobis submitted for review presents a high scientific level. It contains very interesting research material with in-depth interpretation of the obtained results, much of it verified by foreign reviewers in JCR-listed journals. Publication of the results of the dissertation in reputable scientific journals proves the novelty of the research.

It is also important to point out the author's overall achievements, including six publications in high-impact journals, one paper under review, six oral presentations and five poster presentations at conferences, leadership at the research projects and participation as a contractor in other projects.

Therefore, I propose to nominate the Ph.D. dissertation of M.Sc. Maciej Tobis for an award.