



Prof. dr hab. Paweł J. Kulesza
Wydział Chemii Uniwersytetu Warszawskiego
Faculty of Chemistry, University of Warsaw
Pracownia Elektroanalizy i Elektrokatalizy Chemicznej
Laboratory of Chemical Electroanalysis and Electrocatalysis
ul. Pasteura 1, 02-093 Warszawa; Tel: (48) 22 5526344
E-mail: pkulesza@chem.uw.edu.pl

27th October 2024

**REVIEW OF THE DOCTORAL DISSERTATION SUBMITTED BY
*mgr inż. MACIEJ TOBIS (M.Sc. Eng.)***

The doctoral dissertation entitled „*Study of two-dimensional nanostructured materials for electrochemical energy storage applications*” has been prepared by *mgr inż. Maciej Tobis (M.Sc. Eng.)* at Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poland under supervision of Professor Elżbieta Frąckowiak (Poznan University of Technology) as Scientific Supervisor (thesis advisor). The dissertation has been pursued within National Science Centre (Poland) *Opus* and *Preludium* projects as well as under auspices of Polish National Agency for Academic Exchange (NAWA) - the STER programme, Towards Internationalisation of Poznan University of Technology Doctoral School (2022-2024).

The doctoral dissertation of Maciej Tobis is at the boundary of chemical sciences, particularly electrochemistry, and materials engineering, and it refers to the concepts of preparation of novel advanced electrode materials characterized by high capacitance for electrochemical capacitors. The ultimate goal of the research has been to circumvent the main problem of common capacitive materials, namely their low or moderate energy densities, which can be increased by enhancing the capacitance or potential window during operation of applicable devices. Among important issues addressed in the dissertation is the introduction of two-dimensional materials, such as transition metal dichalcogenides, to serve as electrodes in electrochemical capacitors. It is noteworthy that two-dimensional materials have been recently considered as electrode materials for application in energy storage devices because of their unique redox (faradaic) properties permitting to achieve fairly high capacitances. The justification and the feasibility of application of such two-dimensional materials, in addition to approaches to exploit their essential

electrochemical features are carefully described. Furthermore, the relationship between material morphology and electrochemical behavior is discussed in detail. The advantages and disadvantages of using transition metal dichalcogenides as electrode materials are also explained. On the whole, the dissertation significantly contributes to the development, preparation, characterization, and the charge-storage performance of materials based on transition metal dichalcogenides. On fundamental grounds, in addition to the electrochemical characteristics and the systems' potential limitations in aqueous media, the author addresses strategies to minimize these limitations, as well as considers the layered transition metal dichalcogenides as lithium-ion hosts in organic electrolytes. Special emphasis has centered on the exploration and utilization of hydrothermal route as the synthetic method leading to nanostructured transition metal dichalcogenides exhibiting properties dependent on the precursor used. For example, in a case of MoS₂, the use of an appropriate sulfur precursor, has permitted control of the structure, morphology, and microporous texture of the material, thus influencing the systems' electrochemical properties. Finally, of primary importance are also the observations concerning the influence of the morphology of carbon supports on the electrochemical performance of the respective composites, the viability of utilization of sulfur vacancies in transition metal dichalcogenides for functionalization with diazonium salts, as well as the feasibility of suppression of the systems' interfacial catalytic properties through functionalization (MoS₂) with anthraquinone leading to increase the capacity and stability of the electrode materials.

The doctoral dissertation is organized in a way that it consists of six chapters (*Literature review – electrochemical capacitors; Dissertation outline – Aim of the Dissertation, Dissertation structure; Evaluation of the electrochemical properties of two-dimensional materials; Covalent modification of two-dimensional materials by redox active species; Emergence of pseudocapacitive properties of two-dimensional materials; and Concluding remarks containing General summary, Scientific track records, References, and Co-authorship statements*). The chapters are preceded by *Acknowledgements, Table of contents, List of recurring abbreviations, Abstract* in English and in Polish – *Streszczenie*, as well as by Motivation and context of the research. The first scientific part (Chapter I) provides general literature review with crucial items of information concerning principles of operation of electrochemical capacitors, including electrical double-layer models and emergence of

psudocapacitance, as well as choice of electrolytes and electrode materials. In Chapter II of *Dissertation outline*, the author, while emphasizing that the energy density of electrochemical capacitors can be improved by enhancing the capacitance of the system and by broadening the operational potential window, mentions that materials such as transition metal dichalcogenides have been demonstrated to give high capacitance values exceeding those characteristic of carbons, and this feature is expected to improve the overall energy densities of capacitors. The results obtained are described in three parts, Chapters III, IV and V, based on the author's five original publications. In particular, Chapter III, consisting of three research articles (P1, P2, P3), introduces the concept of using two-dimensional materials as electrode materials in aqueous electrochemical capacitors. Here, details of unique hydrothermal synthetic approaches leading to various transition metal disulfides (ReS_2 , MoS_2 , NiS_2 , or FeS_2) and to their integration with conductive carbonaceous matrices to form composites are proposed and described. The relationship between material morphology and electrochemical behavior is discussed. The advantages and disadvantages of using transition metal disulfides as electrode materials are also explained. While integrating nanotextured carbons with ReS_2 or FeS_2 offers a promising approach toward the development of high-performance systems for electrochemical capacitors, special attention has to be paid to the control of catalytic properties of transition metal disulfides (hydrogen evolution, oxygen evolution) which otherwise could limit their practical application. The proposed systems have been thoroughly characterized using various analytical technique, such as scanning transmission electron microscopy, Raman spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy. In Chapter IV, which consists of one scientific article (P4), the author further pursues the issues and problems identified in Chapter III. Based on the synthetic methodology developed in Chapter III, MoS_2 has been fabricated and subjected to further functionalization with a compound exhibiting redox activity, namely anthraquinone. Consequently, the resulting electrode material has been characterized by increased capacity and stability. Systematic studies involving cyclic voltammetry and impedance spectroscopy techniques have allowed estimating the effect of the presence of functional groups on kinetics and the dominant mechanism of charge storage. Given the disadvantages observed for symmetric cells in Chapter III, an asymmetric arrangement has been proposed to avoid oxidation of MoS_2 and thus rapid loss of cell life. Preliminary electrochemical tests were also

carried out in an organic electrolyte. Among other important issues is the fact that prepared functionalized systems have exhibited improved stability and durability.

In Chapter V, the author explores promising electrochemical properties of MoS₂ in organic electrolytes, as well as utilization of distinct sulfur precursors (namely, thiourea thioacetamide, and L-cysteine) for hydrothermal syntheses. The results are consistent with the view that, depending on the precursor used, the resulting materials exhibit different structural, morphological and porosity properties. Differences in the aforementioned characteristics affect the electrochemical behavior of MoS₂. Additional operando type studies have also been performed with respect to changes in the material's crystal structure, expansion and contraction during electrochemical operation. Here, technical details of preparative procedures are provided and carefully described. Despite some complexity in preparation, by selecting appropriate precursors, it is possible to fabricate nanostructured MoS₂-based materials with the optimized pseudocapacitive properties of potential utility for high-performance energy storage devices.

Chapter VI provides general conclusions, followed by a presentation of scientific achievements and a list of literature positions cited.

The research results described in the dissertation significantly contribute to the state of the art of two-dimensional materials for applications as electrode materials in energy storage and to the development of related composite and functionalized systems. On the whole, Maciej Tobis appears as coauthor and significant contributor to seven publications, where five out of them are strictly related to his dissertation. These works have been published in very good journals of international circulation (e.g., *Small*, *Frontiers in Energy Research*, *ChemElectroChem*, *Green Chemistry*, *Electrochimica Acta*, *Journal of Power Sources*). Numerous contributions (including six oral) as a speaker or presenter to international conferences should be noted and appreciated. Maciej Tobias has also acted as principal investigator of Preludium 20 project (NCN). Furthermore, he participated as young investigator in Opus (NCN) and Team Tech (FNP) projects. He has also gained experience during short scientific internships at Karlsruhe Institute of Technology and Helmholtz Institute Ulm (Germany).

Going to the substantive evaluation of the dissertation, I would like to mention the importance of observations and achievements described therein. The main accomplishments concern synthesis, thorough characterization, as well as feasibility

of application of novel two-dimensional nanostructured materials, such as transition metal dichalcogenides, as electrodes in electrochemical capacitors. Among other important issues is detailed characterization of developed composite and functionalized materials using various techniques. Here, detailed synthetic protocols for obtaining different materials based on transition metal dichalcogenides (e.g., ReS₂, MoS₂, NiS₂, FeS₂) are provided. Furthermore, such issues as their integration with carbon nanostructures to form composite materials are addressed. Finally, critical discussion of the results obtained as well as concepts to improve the materials' performance and stability are provided and verified.

Upon reading the doctoral dissertation, my general impression is that the work is well-written. Both the literature review of electrochemical capacitors as well as the results and discussion section on preparation and evaluation of electrochemical and energy storage properties of two-dimensional materials are on high scientific level. The properties of proposed composite and functionalized materials are broadly addressed, as well as the results obtained are carefully described and interpreted. Both the results and conclusions are convincing.

I have got a few minor questions or comments that could be easily answered or explained during the doctoral defense.

(1) The section on surface redox pseudocapacitance is informative and scientifically sound. However, while discussing capacitive properties of ruthenium oxide (pages 25-26), the information about charge storage mechanism, changes of ruthenium oxidation states, propagation of charge and the limitation to only surface processes requires clarification.

(2) Equation 15 (page 30), which is commonly used to assess whether the process has a dominant capacitive or diffusion-controlled battery-type characteristics, requires attention. Here, the quantitative (reliable) approach is only correct for fast electrochemically reversible redox transitions where the Randles-Sevcik equation is applicable. Otherwise, only rough comparison of relative contributions is possible.

(3) There has been tremendous recent interest in application of transition metal (particularly molybdenum) disulfides as catalysts for electrochemical hydrogen evolution. On practical grounds, are there any realistic chances to deal with this problem when it comes to long-term operation of aqueous electrochemical capacitors?

In conclusion, I would like to express my high appreciation to the efforts of the author, emphasize high scientific value of the obtained results and evaluate very positively the doctoral dissertation. Furthermore, I would like to state that the dissertation meets the formal and customary criteria and expectations for doctoral works in the area of exact and natural sciences and chemistry discipline. Thus, I am convinced that Maciej Tobis should be readily admitted to the public doctoral defense at Poznan University of Technology.

Having in mind the importance of pursued research, the quality, the high scientific value and the application potential of results obtained (presented in valuable publications onto which the dissertation is based), I would like to recommend awarding the dissertation and conferring the Ph.D. degree to Maciej Tobis with distinction (honors).



Pawel J. Kulesza