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Review of Mr. Masoud Foroutan Koudahi's doctoral thesis entitled

"Study of electrode/electrolyte interface of novel layered 2D materials"

Dissertation prepared at the Faculty of Chemical Technology, Poznan University of Technology, Poland under the supervision of Prof. dr hab. Elżbieta Frąckowiak

Different energy storage devices play a vital role in our life. Thanks to their valuable properties, they have been widely applied in many areas of science, technology, industry, and typical daily human activity. For these reasons, they have also been the subject of research interest for a long time. Many papers have been published on electrochemical cells, batteries, capacitors, and supercapacitors as well as on the preparation of new electrode materials for devices of this type. The doctoral thesis of Mr. Masoud Foroutan Koudahi, entitled *"Study of electrode/electrolyte interface of novel layered 2D materials"*, fits well into the above topics.

The doctoral dissertation submitted to me for review is based on a monothematic cycle of articles. The Author declares that this cycle of papers consists of four publications. Unfortunately, the last one (Article 4) has not been published yet and that is why, in accordance with applicable regulations, it cannot be treated as a part of a doctoral dissertation. Therefore, in my review, I focused on assessing only Articles 1-3 (which, however, contain material sufficient to apply for a doctoral degree), while the unpublished work I treated as supplementary material.

The dissertation is written in English and divided into four main sections. The first section contains: Acknowledgment, Table of contents, Abstract (in Polish and English), and Abbreviations and symbols. Next, Chapter 1 provides a literature review on the fundamentals and operational principles of energy storage

devices, with particular emphasis on electrochemical capacitors. In Chapter 2, the Author discusses the investigation methods and results presented in the publications forming the basis of the PhD thesis. This section also includes copies of these publications. The last part of the dissertation contains additional information, such as lists of publications, reports, scientific conferences, and research projects as well as references and co-authorship statements.

Chapter 1 begins with a subchapter entitled *"Motivation and context of the research"*. This part contains a lot of information, but it is rather loosely related to the main topic of the dissertation, i.e., supercapacitors. The next subchapter entitled *"Introduction"* looks much better, as it well illustrates the importance of the subject of research. This well-written section provides an extensive background for subsequent parts, whereas numerous drawings facilitate understanding of the essence of the presented issues. It is also worth emphasizing that the literature on the topic has been properly selected and well discussed. Based on 165 references, the Author discusses in detail the electrode materials and electrolytes typically used for electrochemical capacitors. Moreover, he also pays much attention to the methods used for the characterization of supercapacitors. The cited references have been carefully listed at the end of the dissertation, along with the DOI number, which is rarely practiced in doctoral dissertations, but is a great convenience for the reader.

The most important part of the reviewed dissertation is Chapter 2, in which the Author presents the results published in the monothematic cycle of articles. The first paper entitled *"Electrochemical Capacitor Performance of Nanotextured Carbon/Transition Metal Dichalcogenides Composites"* was devoted to a physicochemical and electrochemical characterization of carbon composites with two dichalcogenides: rhenium and iron disulfides. Also, two carbon materials were applied in the study: multiwalled carbon nanotubes (NTs), which served as a support for ReS_2, while a 3D graphene-like network (3DG) was utilized for FeS_2 deposition. The main goal of this article was to improve the electrochemical performance of supercapacitors based on transition metal dichalcogenides by designing electrode materials with a wide working potential and fast frequency response. The hybrid electrodes with different contents of disulfides were prepared using a one-step hydrothermal method. Successful preparation of composites was confirmed using XRD analysis. It has been shown that an increase in the loading of FeS_2 to 15% results in an improvement in energy storage; however, an electrode with a 20 wt.% content of FeS_2 presented a limited charge response. On the other hand, the cell based on the latter electrode (the optimal sample) demonstrated a wide working voltage (1.5V), indicating its potential for further investigation.

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Unfortunately, it has been observed that a transition metal such as rhenium restricts the voltage range of the capacitor to 0.8 V.

This work is interesting and well written; however, I have a question (based rather on my curiosity): what was the reason for using nanotubes and 3D graphene for research? After all, there is quite a large group of other carbon materials than those mentioned above. Moreover, neither nanotubes nor three-dimensional graphene have a two-dimensional structure, so they do not fit the dissertation title.

The next article entitled *"Fast response supercapacitor based on carbon-VS_2 electrodes with a wide operating voltage range"* is an extension of the previous work. Since previous studies revealed the instability of aqueous electrolytes in ReS_2-based supercapacitors, VS_2 was selected for further research as a pseudocapacitive material. This approach turned out to be correct, as using composite electrodes based on three-dimensional graphene-like material and VS_2 decreases water decomposition. This finding is significant, suggesting that a wide working voltage (1.8V) is available for the assembled symmetric cell, enhancing its practical applicability. It is worth noting that finally, the cell reached a high energy density of 18 Wh kg^{-1} at the power density of 430 W kg^{-1} at a current density of 1 A g^{-1}.

The third paper is entitled *"$Ti_3C_2T_x$ MXene as Intriguing Material for Electrochemical Capacitor"*. This study provides meaningful insight into the charge storage in $Ti_3C_2T_x$ MXene (where: M-transition metal, X-carbon, T-Cl, F, O). The cell voltage was significantly improved by realizing an asymmetric supercapacitor based on MXenes as a negative electrode and a positive electrode in the form of activated carbon (BP2000). In this case, a very wide working voltage (2V) was obtained using a neutral electrolyte.

The next studies, presented in the manuscript submitted for publication (Article 4), reveal that MXenes are more stable in ionic liquids compared to aqueous media. Moreover, it was found that the physical and chemical properties of MXenes can be tuned to maximize their charge storage in electrochemical capacitors. So, the results obtained in this work are also very interesting, and it is a great pity that the manuscript has not been published yet, and therefore cannot be part of a doctoral dissertation.

The papers included in the above-presented monothematic cycle were published in the years 2021-2023 in high-impact factor journals from the JCR list, such as *Small* (IF=13.3) or *Energy Storage Materials* (IF=20.4). It is worth noting that Mr. Masoud Foroutan Koudahi is also a co-author of another paper, not included in the dissertation, but also published in an excellent journal, i.e., *Energy and Environmental Science* with IF=39.7. The total IF of all publications listed above is 86.7, which gives an average IF per paper of 21.7. In turn, if only works constituting a doctoral dissertation are considered, their

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total IF=47.0, while the average IF per publication is 15.7. These are excellent results not only in the context of bibliometric indicators but also in terms of the relatively short time in which the results were obtained and published.

All publications constituting the PhD thesis are multi-authored, and the analysis of co-authorship statements clearly shows that Mr. Masoud Foroutan Koudahi's participation in the creation of these works is leading and ranges from 40 to 75%. His activity mainly involved conceptualization, investigation, data curation, and manuscript writing (original draft). The Author's results were presented not only in the form of publications but also at 9 prestigious international conferences (5 oral presentations and 4 posters). It is worth emphasizing that part of the Author's research was financed by the National Science Center of Poland within the frame of two projects: Opus and Preludium. In the first grant, the Author was involved as a contractor, while in the second one, he worked as a project coordinator.

As far as the scientific achievements of Mr. Masoud Foroutan Koudahi are concerned, I have them in high opinion. The subject matter of his doctoral dissertation is interesting and of great practical importance as the electrode materials and supercapacitors he worked on can be used in many electrical and electronic applications. In addition, this topic is consistent with the current trends presented in the world literature on the subject, and the results obtained can be considered a significant element of novelty. Moreover, the doctoral thesis presents rich and interesting experimental content which (together with the data interpretation) brings an important contribution to the studies on electrochemical capacitors.

Apart from the presentation of the strengths of the doctoral dissertation, the reviewer is also obliged to point out its weaknesses. Because the papers included in the above dissertation were published in very good journals, and therefore subjected to thorough proofreading, it is difficult to find any weak points of this research. However, I have a few comments regarding the dissertation itself.

The organization of the dissertation is somewhat chaotic. Some sections of the work are numbered and some are not. This causes some confusion. For example, it is not clear where Chapter 2 ends. Apparently even the Author has some problems with this because at the beginning of the Abstract he writes "The content of this thesis can be divided into **four** main sections", while at the end we find the statement "The **third** chapter indicates the ...". By the way, there is no part titled Chapter 3 in the work.

The subchapter titled *"Abbreviations and symbols"* is very helpful for the reader; however, the Author also included in it the chemical formulas of generally known, typical compounds, such as sulfuric acid, carbon dioxide, or hydrochloric acid, which in my opinion is completely unnecessary.

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On page 13 the Author writes: "The first battery was invented by Alessandro Volta in 1800, discovering the passage of current by soaking two pieces of silver and copper into an electrolyte". If I remember correctly, Volta used zinc, not silver.

The author formulates a partial research goal before discussing each publication included in the dissertation. However, the PhD thesis does not contain a clearly defined aim specific to the entire dissertation. This aim could be expected in the subsection *"Motivation and context of the research"*, but it is not there. Similarly, the work lacks general conclusions drawn for the entire dissertation.

Although the shortcomings presented above somewhat spoil the aesthetics of the presented thesis, they do not reduce its scientific and cognitive value. In conclusion, I would like to stress that my evaluation of the contents of the dissertation submitted by Mr. Masoud Foroutan Koudahi is very high. The use of modern and advanced techniques and discussion of results make a good impression and testify to the Author's comprehensive preparation for research work. The subject of the study is ambitious, the work has important elements of novelty and the results have considerably extended the knowledge about supercapacitors. In my opinion the doctoral dissertation, I was asked to evaluate, fully satisfies the demands of a doctoral thesis included in the Act of 20 July 2018 - Law on Higher Education and Science and I would like to declare that Mr. Masoud Foroutan Koudahi can be admitted to further stages of the doctoral procedure.

Sincerely yours,

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