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Review

of the doctoral dissertation of Mr. Masoud Foroutan Koudahi titled "*Study of electrode/electrolyte interface of novel layered 2D materials*"

The review was prepared on the basis of a letter from the 16th of April 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-7/2/2024 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.

Electric energy is one of the most important factors in today live. It is a heart of modern economies. Global energy demand is growing very rapidly and is one of the key reasons why CO_2 emissions is also very high. It affects climate change and pollution. Decarbonisation of electricity could provide a platform for reducing carbon dioxide emissions. Moreover, renewable energy may provide the access to electricity for all. Renewables are expanding quickly, but not enough to fulfil requirements of the global electricity demand. It is known that over 90% of global primary energy comes from fossil fuels. As a result we must rapidly reduce this share by displacing them with low-carbon energy sources.

Among renewable energy sources the most common are solar, hydro, wind, biomass, geothermal and tidal. The utilization of them is mainly in stationary large-scale energy storage. However, in our daily activity there is a need for some other system that could be easily applied in mobile systems. The batteries and capacitors are the most suitable for such application. The

former exhibit high specific energy, while the latter show high specific power. The problem with capacitors is that they operate usually in aqueous environment, and are limited to up 1.2 V. It affects the power end energy density of capacitor. Thus, finding a material working in a broader potential range is crucial in development 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 the high voltage originating from battery, and high power capability.

The doctoral dissertation of Mr. Masoud Foroutan Koudahi is in the form of the so-called thematically coherent set of articles published in scientific journals and has 151 pages. This set of articles is consisted of 3 published papers and one manuscript. These 3 articles are devoted to three main issues: 1. finding a suitable electrode material for electrochemical capacitor based on carbon phase and transition metal dichalcogenide (TMDs), 2. finding a synergistic effect between carbon and TMDs, 3. utilization of MXene as electrode material in electrochemical capacitor. According to the requirements (Dz.U. 2023 r. poz. 742 z późn. zm.) articles must be published to be taken into account to the mentioned set, thus I have not included Article 4 in the Review.

The doctoral student's hirsch index is 5 (Google Schoolar, May 22, 2024) and the impact factor IF of 3 publications, included in the doctoral dissertation, is 47 (May 22, 2024), which gives average value approx. 15.66(7). The number of co-authors is only 2-3, which is very low, and evidences that Mr Foroutan Koudahi was the main investigator, especially that he was the first author in 2 out of 3 publications. It is however confusing why the PhD Student was not the correspondence author in articles where his contribution was over 70% according to the statements. It is very important for a young scientist to take an active part in the submitting manuscript process.

The dissertation is split into two main chapters. Each chapter has several subchapters. The first chapter is devoted to literature review including motivation of the Author's research, listing the types of energy storage systems with the focus on electrochemical capacitors. The subchapter about electrochemical capacitor is very detailed and introduces into the topic of capacitors. It describes materials utilized electrodes, carbons and transition metal based compounds, mainly dichalcogenides and carbides/nitrides, electrolytes (aqueous, organic, ionic liquids) and electrochemical cell. The short description of the used electrochemical techniques

i.e. cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge-discharge. This part is as a whole is clear and explain the scope of the thesis. However,

1) I have doubts regarding naming "galvanostatic charge-discharge" as a technique. In my personal opinion it is rather method. I think that more proper name is chronopotentiometry.

The second chapter familiars the reader with articles that are included in the thematically coherent set of articles. At the end of this chapter there is an information about publications that were not included to the dissertation, attendance in the conferences (9), participation in the international research projects (2), and the contribution of Mr. Foroutan Koudahi in each article.

The first article *Electrochemical Capacitor Performance of Nanotextured Carbon/Transition Metal Dichalcogenides Composites* deals with 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. 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 3DG/FeS_2 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:

2) Why you did not synthesize NT/FeS_2 nor 3DG/ReS_2?
3) The comparison of different TMDs with different carbon phases is confusing. It is not so obvious to directly compare the results between NT/FeS_2 with 3DG/ReS_2 as these systems are different and may exhibit different electrochemical properties in EC (and they do).

The second article *Fast response supercapacitor based on carbon-VS_2 electrodes with a wide operating voltage range* is devoted to usage of 3DG carbon phase with other TMDs, namely VS_2, with different ratio 3DG to TMD. The aim was to investigate the effect of carbon addition on the electrochemical window stability of such electrode material. It was shown that optimized material (3DG-20 wt% VS_2) exhibited very fast electrochemical response during cycling at scan rate of 3 V/s, and was electrochemically stable up to 1.8 V. The proposed mechanism of energy storage suggested that the process is mainly controlled by surface current (pseudocapacitive) with the adsorption of lithium ions. However, according to Fig. 10c (and

S12a), the storage mechanism seems to be diffusion-controlled for low scan rates and surface-controlled for higher scan rates.

4) Did you consider to use your electrode material (3DG-20 wt% VS_2) in non-aqueous energy storage system i.e lithium-ion batteries (LIBs)?
5) If you consider to use 3DG-20 wt% VS_2 it will act as cathode or anode material?
6) Why do you think that the amount of VS_2 affects the way of lithium storage mechanism as adsorption for 3DG-20 wt% VS_2 and insertion for 3DG-50 wt% VS_2? Does VS_2 has different crystallographic structure for 3DG-20 wt% and for 3DG-50 wt% electrode material?

The third article *$Ti_3C_2T_x$ MXene as Intriguing Material for Electrochemical Capacitor* is about the synthesis and characterization of MXene as electrode material for electrochemical capacitor. This article is a continuation of a investigation of 2D material for EC. Additionally, the synthesized material exhibited the ability to adsorb and desorb proton in acidic media

7) Did consider that adsorption could occur at the surface of gold electrode?
8) Why the capacity of $Ti_3C_2T_x$ on Ti current collector was two times higher than on Au current collector?
9) Please explain the statement "*In general, it is better to avoid using Ti current collectors while evaluating the reliable performance of MXenes in acidic medium*".

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 and MXenes by addition carbon 3D or 2D phases. Mr. Masoud Foroutan Koudahi achived his goals. Moreover, he demonstrated his ability to plan and conduct experimental work, to select appropriate research techniques, to discuss the results, and to conclude. However, the title of the dissertation is slightly misleading. Under the title "Study of electrode/electrolyte interface of novel layered 2D materials" I would expect more detailed information about the phenomena occurring at the electrode/electrolyte interface. The investigation of charge storage mechanism, confirmed by the proper calculations, is shown only in Article 2.

In summary, although mentioned above comments, the doctoral dissertation submitted by Mr. Masoud Foroutan Koudahi 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. Masoud Foroutan Koudahi to the next stages of the doctoral dissertation.

Sincerely,

Andrej Nowak

Dr hab. inż. Andrzej Nowak, Profesor PG