Iwona A. Rutkowska, Ph.D., D.Sc., univ. professor
Faculty of Chemistry, University of Warsaw
Pasteura 1, 02-093 Warsaw, Poland
Tel: (48-22) 5526307
Fax: (48-22) 5526434
E-mail: ilinek@chem.uw.edu.pl

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REVIEW OF THE DOCTORAL DISSERTATION OF MASOUD FOROUTAN KOUDAHI

The doctoral dissertation prepared by Masoud Foroutan Koudahi entitled „*Study of electrode/electrolyte interface of novel layered 2D materials*" has been performed under supervision of prof. dr hab. Elżbieta Frąckowiak as promoter (thesis advisor) at Poznan University of Technology, Faculty of Chemical Technology, Institute of Chemistry and Technical Electrochemistry.

This dissertation is devoted to the study of design and performance during electrochemical charging of electrochemical capacitors. Special attention has been paid to preparation and characterization of novel materials including three-dimensional graphene with metal disulfide (iron and vanadium), and transition metal carbides (MXenes) as electrodes in electrochemical capacitors operating in aqueous media and ionic liquids. In the dissertation, the Author shows electrochemical performance of electrode materials based on transition metal dichalcogenides (TMDs) and carbons fabricated using hydrothermal reactors. In the case of study of transition metal carbides (MXenes), the Author addresses the fundamental aspects of charge storage in aqueous media to explain of the effectiveness of charging/discharging mechanism at the electrode/electrolyte interface. In order to comment on the volumetric expansion of different MXenes in ionic liquids, an advanced operando technique, such as electrochemical dilatometry, has been applied. The results, which has been described and discussed in the dissertation, are certainly consistent with the present trends in materials chemistry and technical electrochemistry, in particular, with the recent developments in the area of electrochemical capacitors. The obtained results are also of importance from the view-point of the development of materials science.

The doctoral dissertation of Masoud Foroutan Koudahi is organized in a way that it consists of three parts. The first part provides a literature review (Chapter I), in which crucial items of information concerning electrochemical capacitors have been carefully described. In addition to general characteristics, the Author concentrates on the critical overview and addresses the operation principles, choices of the electrode material and electrolyte for electrochemical capacitors. In the reviewer's opinion, the literature part of the work addresses the most important achievements in the above-mentioned fields. At the end of Chapter I, the Author describes electrochemical cells and electrochemical techniques, such as cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge-discharge approach. This section could have been more thoroughly and precisely prepared.

Chapter II refers to experimental work and results described in a form of attached publications, out of which three articles have already been accepted and one manuscript has been submitted and is still under consideration. All articles are preceded by short summaries addressing motivation and describing the most important results. In the article 1 entitled "*Electrochemical Capacitor Performance of Nanotextured Carbon/Transition Metal Dichalcogenides Composites*", a novel material based on the 3D-graphene-network-like structure to serve as a matrix for iron sulfide has been described and compared to multi-walled carbon nanotubes acting as a support for ReS_2. Transition metal dichalcogenides are promising systems for potential applications for electrochemical capacitors due to their layered structure, a feasibility of large variety of metal-dichalcogenide combinations, and existence of the exposed active sites. But the systems exhibit moderate conductivity and stability; the latter feature limits their long-term operation in charge storage devices. The materials have been subjected to physicochemical and electrochemical characterizations. Such parameters of electrochemical capacitors as capacitance values, charge/discharge efficiency, capacitance retention, charge propagation, cyclabilty, and potential-output limits with carbon/sulfide composites in aqueous neutral solutions (Na_2SO_4) have been addressed. Special attention has been paid to energetic efficiency of capacitive charge/discharge processes. It has also been demonstrated that, in aqueous medium, the extension of potential output is affected by structure of materials, and importance of the type of metal, as well as the existence of high roughness and defect-rich surfaces or edge sites with respect to the potential operational window has been emphasized. In the article 2 entitled "*Fast response supercapacitor based on carbon-VS_2 electrodes with a wide operating voltage range*" the Author has proposed composite electrodes based on three-dimensional graphene-like and transition metal-dichalcogenide (TMD), namely, VS_2, as hybrid electrodes. Such electrodes differing in sulfide contents (from 20% to 50% of VS_2) have been prepared using a one-step hydrothermal treatment. The ultimate goal of this research has been to expand the working potential output of the TMD-based electrochemical capacitor in an aqueous medium (1 mol dm^{-3} $LiNO_3$). The expansion of the working potential difference has been achieved via designing a highly porous structure based on free-edge graphene capable of inhibiting the aqueous medium decomposition, as well as through designing the hybrid electrochemical capacitors by integrating VS_2 with an optimum amount of graphene, and by choosing a proper electrolyte, including an anion with a chaotropic nature, decreases the degree of H-bonding between the water molecules, and therefore, increases the stability of the aqueous medium at high potentials. The article 3 entitled "*$Ti_3C_2T_x$ MXene as Intriguing Material for Electrochemical Capacitor*" concerns the mechanism behind the hydrogen storage of titanium carbides. The Author has addressed the performance of titanium carbide, as an important example of the MXene family, and the valuation has been based on full cells operating in different aqueous media and at distinct pH values. The Author has postulated that hydrogen adsorbs at the surface of MXene layers with different bonding strength. Because the actual bonding is dependent on pH, a choice of electrolyte and potentials applied, differentiation between contributions originating from the weak and strong interactions within the total hydrogen storage of MXenes has become feasible. Based on the obtained information, the Author has addressed the problem of the narrow potential difference of symmetric $Ti_3C_2T_x$-based electrochemical capacitors, as well as pointed out a lack of the stability of the positive electrode. It has been postulated that a combination of capacitive and faradaic currents is responsible for the energy storage within the titanium carbide during the negative polarization. On the other hand, a high disproportion with the negligible capacitive charge has been observed in the positive potential range. These factors are the two main reasons behind the narrow working potential output of MXene-based electrochemical capacitors. The article 4 entitled "*Charge storage and operando electrochemical dilatometry of MXene electrodes in ionic liquids*", which has been submitted for publication, addresses the electrochemical performance of two key members of the MXene family, titanium carbide and molybdenum titanium carbide, in three ionic liquids characterized by different ionic sizes. The Author has monitored energy storage performance of all MXene samples in a broad potential range under negative and positive polarization. He has used operando electrochemical dilatometry studies to comment on the effect of ionic diffusion on the structural properties of samples. The Author has postulated that different MXenes show diverse structural and electrochemical behaviors. The high accessible surface and quantity of functional groups in titanium carbides improve their charge propagation dynamics and facilitate the redox responses. On the other hand, the compact structure of molybdenum-based samples imposes a restriction on the rate of insertion/deinsertion of ions and, therefore, what leads to lower capacitance values.

At the end of the doctoral dissertation, Masoud Foroutan Koudahi presents his scientific achievements, and provides statements of coauthors describing their contributions.

It is noteworthy, that Masoud Foroutan Koudahi is the first author of three (out of four) publications and, judging from the statements of coauthors, he has significantly contributed to all works. Thus, Masoud Foroutan Koudahi can be viewed as a scientifically advanced and mature young scientist. It should also be mentioned that research pursued toward the doctoral dissertation has been supported by National Science Centre, Poland – the OPUS project entitled "Study of electrode/electrolyte interface of high stability and quick charge response" and the PRELUDIUM project "Preparation and characterization of novel 2D MXenes material". Masoud Foroutan Koudahi appears as coauthor of an additional publication, which is not included to the dissertation. The above mentioned articles have been published in well-recognized journals of international circulation (e.g., *Small, Energy and Enviromental Science or Energy Storage Materials*). Masoud Foroutan Koudahi is listed as author or coauthor of five oral conference presentations (two of them he presented himself) and four poster presentations. He has directed the Preludium (NCN) grant, and has served as investigator in one domestic grant.

Going to the substantive evaluation of the dissertation, I would like to mention the important observations and achievements described therein. Among the important observations is that integrating of carbon substrates with redox-active materials, such as FeS_2 and VS_2, constitutes a valuable approach leading to the enhancement of both energy and power density of electrochemical capacitors in aqueous media. A carbon constituent affects the electrochemical response of the active material, and it can function as either the substrate or the conductive additive. In the case of highly conductive transition metal dichalcogenides characterized by the box-like cyclic voltammetric profiles, it has been possible to increase the loading of redox-active materials and employ carbons only as the conductive agent. Consequently, safe potential limits with no electrolyte decomposition have been determined for both electrodes of electrochemical capacitors. The Author also emphasizes the need for fundamental understandings of the charge storage within transition metal carbides (MXenes) in aqueous media. Furthermore, titanium carbide MXenes have only been found to be active at negative potentials, i.e., under conditions where a combination of capacitive and faradaic currents (electrochemical sorption of hydrogen) contribute to the energy storage. Different mechanism has been proposed to explain the nature of interactions involved in the hydrogen storage of MXenes. The cell potential output has significantly been improved by applying asymmetric electrochemical capacitors based on MXenes as negative and positive electrodes together with activated carbons. Finally, for the first time, the charge/discharge phenomena of Mo/Ti carbides have been studied in ionic liquids using operando electrochemical dilatometry. The dilatometry studies have provided important information permitting to correlate the growing capacitive response of negatively polarized titanium carbides with their volumetric expansion. The Mo/Ti carbides have exhibited a significant strain increase in a case of the positive electrode what has correlated with high capacitance values. The results described within the dissertation contribute to better understanding of operation and to optimization of electrochemical capacitors.

I believe that the work has been prepared correctly, and I no doubt that the measurements have been carried out carefully, as well as the results obtained are convincing. A similar statement applies to conclusions.

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

(1) What is the overall stability and the resistance of the proposed hybrid materials against corrosion at positive potentials?

(2) For the systems studied in article 1, what is origin (chemical, kinetic etc.) of the deviation from the ideal capacitive behavior of the proposed materials at higher charging/discharging currents?

(3) I would like the Author to discuss how capacitive currents can be distinguished from Faradaic (surface and bulk) responses under voltammetric conditions.

(4) In article 1, two novel materials, namely the 3D-graphene-network-like structure (as a matrix for iron sulfide) and multiwalled carbon nanotubes (as a support for ReS_2), are described. The Author addresses only one (FeS_2) in Ph.D. thesis. Comparison to the performance of ReS_2 would also be informative.

In conclusion, I would like to express my 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 Masoud Foroutan Koudahi should be easily admitted to the public doctoral defense at Poznan University of Technology.

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