Professor Pawel J. Kulesza,
Faculty of Chemistry, University of Warsaw
Pasteura 1, 02-093 Warsaw, Poland
Tel: (48-22) 5526344
Fax: (48-22) 5526434
E-mail: pkulesza@chem.uw.edu.pl

12th September 2021

REVIEW OF THE DOCTORAL DISSERTATION OF JUSTYNA PIWEK

The doctoral dissertation prepared by Justyna Piwek entitled „*Studies of capacitive and faradaic processes in electrochemical capacitors and in redox flow batteries*" has been performed under supervision of prof. dr hab. Elżbieta Frąckowiak as promoter (thesis advisor) and dr hab. inż. Krzysztof Fic, prof. PP as supporting promoter (subsidiary thesis advisor) at Poznan University of Technology, Faculty of Chemical Technology, Institute of Chemistry and Technical Electrochemistry.

This dissertation concentrates on important issues concerning the performance and limitations of operation of electrochemical charge storage or energy generation devices, namely, electrochemical capacitors and redox flow batteries. Special attention has been paid to studies and understanding of changes of the oxygen content with respect to the behavior of individual electrodes and such phenomena as ageing of electrochemical capacitors. Among other important issues are environmental friendliness, cost of fabrication, as well as feasibility of high output potential difference (voltage) and extension of the capacitors' lifespan. The obtained results, described and discussed in the dissertation, are certainly of importance to the development of the electrochemical energy storage and conversion devices. For example, depending on the intended technology and application, the high oxygen content may significantly reduce conductivity of the capacitor carbon electrode; on the other hand, the existence of the interfacial oxo species (on carbon electrodes) seems to affect electrochemical reactions involving vanadium species in redox flow battery. In the work, the author compares the performance of so called "aged" electrodes to the characteristics of pristine ones (before ageing). It has been clearly stated that over-oxidation of the positive electrodes results in failure of electrochemical capacitors. A unique approach utilizing molten salts have been proposed to oxidize carbon felt electrodes. Among valuable contributions is the proposal of an electrochemical protocol permitting extension of the capacitor's operation lifespan. On

fundamental grounds, the concepts of so-called “dual circuit redox flow battery” permitting hydrogen evolution upon demand and the vanadium oxygen electrochemical cell using the oxidative water splitting to generate and supply protons are of importance as well.

The doctoral dissertation of Justyna Piwek is organized in a way that it consists of five parts. The first part provides a literature review (Chapter I), in which crucial items of information concerning electrochemical capacitors and redox flow batteries 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 and electrolyte material, while emphasizing the importance of the environmental friendly water-based electrolytes and activated carbon electrodes. What is even more important, such fundamental issues as stability and lifespan of capacitors are highlighted. When it comes to the redox flow battery technology, the Author focuses on vanadium based systems. Redox flow batteries have been studied in recent years and proposed as a perspective technology for grid-scale energy storage thanks to their high power performance, flexible design and ease to scale-up. Their main advantage is that the power conversion is decoupled from energy storage, thus allowing for independent power and energy sizing. Currently, the state of the art is represented by all vanadium systems, even though they are still relatively expensive and characterized by a limited volumetric energy density. While the choice of the vanadium battery as a “model” system can be understood, it should be remembered that vanadium is a critical raw material whose origin and processing (from vanadium ores to vanadium pentoxide) have a large environmental impact. On scientific grounds, the need of carbon felt pre-treatment (oxidation) and its influence on vanadium redox processes have been correctly emphasized. Perhaps more attention should have been paid to the general electrochemical framework for understanding the vanadium redox flow battery performance, namely to self-discharge, cross-over through ion-exchange membrane, and to possible solution equilibria as well as diversity of the redox active species that can be formed. I have found the concept of “dual-circuit redox flow battery” as an additional unit in whole vanadium redox flow battery system valuable and tempting, and its extensive description justified. In Chapter II (supported with three publications, P1-P3), the author refers to the stability and failure of the carbon/carbon electrochemical capacitors operating in aqueous medium (alkali metal salt electrolytes). The systematic lifespan studies have covered different lifetime tests, effects of different potential differences applied or influence of electrolyte. To support studies of ageing, the correlation between electrochemical performance and the overall physicochemical characteristics has been addressed. It has been concluded that the oxidative degradation of the

positive electrode contributes mostly to failure of electrochemical capacitors. The origins of ageing and possible improvement actions have also addressed and discussed for different systems in Chapter II. The approaches to extend lifetime of capacitors, as well as related protocols to prolong operation of capacitors are explored in Chapter III. An interesting concept of balancing the "dual-circuit redox flow battery" through the development of the vanadium-oxygen electrochemical cell and by using the water oxidation reaction as the proton supplier is a subject of Chapter V and publication P5. The results permitting correlation between electrode conductivity, hydrophilicity and vanadium redox flow battery performance are of practical importance. In conclusion, the author matches up the performance of each electrochemical system considered with the presence of oxygen.

At the end of the doctoral dissertation, Justyna Piwek presents her scientific achievements, encloses five manuscripts (belonging to the dissertation), as well as provides statements of coauthors describing their contributions. It is noteworthy that Justyna Piwek is the first author in three publications and, judging from the statements of coauthors, she has significantly contributed to other two works. Thus, Justyna Piwek can be viewed as scientifically advanced and mature young scientist.

It should also be mentioned that research pursued toward the doctoral dissertation has been supported by *Swiss Federal Institute of Technology in Lausanne (EPFL)* - the project title „Redox flow batteries as a main player in energy storage game"; *The European Research Council* – the Starting Grant project entitled „If immortality unveil…'– development of the novel types of energy storage systems with excellent long-term performance"; and *National Science Centre*, Poland – the *Preludium* project entitled „Influence of carbon felt surface oxidation on the vanadium redox reaction mechanism in an acidic medium".

Justyna Piwek appears as coauthor of seven publications, out of which five positions constitute a basis of the doctoral dissertation. These works have been published in very good journals of international circulation (e.g., *Electrochimica Acta, Journal of Power Sources, Energy Storage Materials* or *Materials Today*). Furthermore, she holds two Polish patents and exists in two patent applications. Justyna Piwek is listed as author or coauthor of seventeen oral conference presentations (though it is not clear which she has presented herself) and seventeen poster presentations. She has completed four practical trainings, directed the Preludium (NCN) grant, and served as investigator in seven domestic or international grants. She has also acted as a member of organizing committees of three conferences. Justyna Piwek is a member of the following scientific organizations: *International Society of*

Electrochemistry and *Polish Carbon Society*. Her achievements have been recognized: she has received Poznan City Award and 3 poster prizes.

Going to the substantive evaluation of the dissertation, I would like to mention the important observations and achievements described therein. First, it has been concluded that positive electrode oxidizes over time, thus causing pore clogging and formation of the solid-state deposit on the surface. Consequently, degradation of the positive electrode in water-based electrochemical capacitors becomes the main limiting factor. Furthermore, while operation of aqueous electrochemical capacitors is feasible for only short times at larger potential differences, thousands of cycles are possible under conditions of lower potential outputs. Also transfer of active species toward the opposite electrode constitutes significantly to ageing. In this respect, the application of a proper cation exchange membrane would be helpful. Valuable observations refer also to the role of oxygen in the electrochemical charge storage devices considered in the dissertation. High oxygen content exhibits rather negative effect when it comes to the lifespan performance of electrochemical capacitors, whereas it seems to induce redox processes in vanadium redox flow battery. The author also emphasizes importance of the oxygen functional groups performing as active sites during redox reactions. Finally, the oxygen evolution reaction has been considered in "dual circuit redox flow battery" as the source of protons that are necessary for hydrogen evolution; and, consequently, the vanadium-oxygen cell has been designed as alternative to discharge the positive side of vanadium redox flow battery in "dual circuit system". The results described within the dissertation contribute to better understanding of operation and to optimization of flow batteries and electrochemical capacitors.

Upon reading the doctoral dissertation, my general impression is that the work is well-written, and the results are carefully described and interpreted. I also evaluate highly the editorial form of the dissertation. Both the results and conclusions are convincing.

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

(1) All vanadium redox flow battery operates in very strong acid medium. How problematic is the corrosion (degradation) of carbon electrode materials at more positive potentials?

(2) What is origin (chemical, kinetic etc.) of the deviation from the ideal capacitive behavior of the proposed carbons at higher charging/discharging currents?

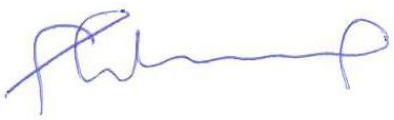
(3) The problem of cross-over and self-discharge exists in both capacitors utilizing iodine/iodide species and vanadium redox flow batteries. Fundamentally, the situations are

different. Could the recent advances in the membrane technologies be helpful in such cases?

(4) Being aware of limitations in performance of the all vanadium redox flow battery, what are the other reasonable options for this technology?

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 Justyna Piwek should be easily admitted to the public doctoral defense at Poznan University of Technology.

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



Pawel J. Kulesza