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**Report on the Doctoral Dissertation
of MSc Eng. Sylwia Ślesińska entitled "Research on the
electrode charging and carbon degradation in electrochemical
capacitors"**

This opinion is based on a letter from Prof. Ewa Kaczorek, PhD, Eng., Dean of the Faculty of Chemical Technology at Poznan University of Technology, July 1, 2025 (resolution no. RD-10/2/2024 of the Chemical Sciences Discipline Council).

Sylwia Ślesińska, MSc Eng., completed her doctoral dissertation under the supervision of Prof. Krzysztof Fic, PhD, Eng., and Jakub Menzel, PhD, Eng. The measurements presented were carried out thanks to financial support from the National Science Centre, the European Research Council and the French government's France Excellence scholarship programme.

The doctoral thesis focused on electrochemical capacitors (EC) and lithium-ion capacitors (LIC), especially studying electrode charging processes and carbon material degradation mechanisms in aqueous and non-aqueous electrolytes. This subject is crucial in the context of the energy transition and the increasing demand for reliable, safe and durable energy storage systems. EC and LIC are well known for offering very high power density and a cycle life many times longer than that of





batteries. They can also operate in a wide temperature range, despite offering lower energy density.

Therefore, improving the understanding of the processes at the electrode/electrolyte interface is fundamental for practical application, while both high efficiency and potential sources of degradation originate. To achieve this, Mrs. Slesińska employed advanced techniques and proposed new approaches. In the literature review, the PhD student examined published work on electrochemical and lithium-ion capacitors, focusing on their construction and operating principles, and the electrode materials and electrolytes used. The introduction also provides a detailed description of in situ and operando research techniques.

The justification for researching electrochemical capacitors was preceded by an analysis of the energy storage device market and its projected growth trends. A wide range of proposed research techniques has allowed find explanations for the processes taking place at the electrode/electrolyte interface in ECs and LICs with aqueous and organic electrolytes. The behaviour of activated carbon as an electrode material in various electrochemical systems was analysed in detail by Mrs Ślesińska, including an investigating the influence of factors such as surface chemistry, electrode and electrolyte composition, applied voltage and cell construction.

The doctoral dissertation submitted for review consists of 218 pages, ten figures and 1 table presented in Chapter I, and has rather classic layout. The work contains the following: Acknowledgements, abstracts in English and Polish, a list of abbreviations used in the dissertation, a list of contents, three chapters, a general conclusion, a list of scientific articles with abstracts not included in the doctoral thesis, a list of figures, scientific achievements, copyright and co-authorship statements. Both the literature and experimental chapters were





supported by detailed studies of the topic literature included in the references.

Chapter I is a literature review in which the doctoral student outlines the fundamental issues related to the subject matter of the next chapters. As mentioned, an analysis of the energy storage device market and projected growth trends was provided as an introduction. Next, energy storage devices are described, paying special attention to electrochemical and lithium-ion capacitors, their operating principles, construction, and commonly used electrode materials and electrolytes. In this chapter, Mrs Slesińska conducted a literature review of fundamental and ageing studies. A detailed description of the electrochemical techniques used in the included papers (cycling voltammetry, galvanostatic charge/discharge, current interruption, staircase potentiometric electrochemical impedance spectroscopy and step potential electrochemical spectroscopy) is presented.

The next chapters are devoted to research focused on the nature of electrochemical systems (ECs and LICs), as demonstrated by fundamental and ageing studies. The research presented in this doctoral thesis forms the basis for further work on practical technologies.

The second chapter focuses on research into the nature of electrochemical systems (ECs and LICs), as demonstrated by fundamental and ageing studies. Chapter II is based on two manuscripts: 'Operando Monitoring of Local pH Value Changes at the Carbon Electrode Surface in Neutral Sulfate-Based Aqueous Electrochemical Capacitors' and 'Fundamentals and Implications of Point of Zero Charge (PZC) Determination for Activated Carbons in Aqueous Electrolytes'. The PhD student describes charging mechanisms in electrochemical capacitors based on activated carbon and aqueous electrolytes. The first manuscript focuses on operando monitoring of pH value changes during the charging and discharging of ECs in a neutral





sulphate-based electrolyte with activated carbon electrodes. This process proved to be dynamic and strongly dependent on the applied potential, with different results observed for the two electrodes: alkalisation for the negative electrode and acidification for the other. Additionally, Mrs Ślesińska proposed GCMS (gas chromatography mass spectrometry) and EQCM (electrochemical quartz crystal microbalance) measurements to provide a more detailed explanation of the observed phenomenon of pH changes.

In the second manuscript, Mrs Ślesińska introduces the concept of the range of zero charge (RZC) instead of the point of zero charge (PZC) for porous carbon electrodes (highly microporous and micro/mesoporous) working in aqueous electrolytes. Various electrochemical techniques are used, and an improved method for determining the RZC is presented, based on step potential electrochemical spectroscopy (SPECS). The PhD student used lithium sulphate and nitrate, as well as a redox-active electrolyte with various concentrations, different cell constructions and reference electrodes, to prove that all factors are important for determining the RZC.

Chapter III focuses on measurements in organic electrolytes, which dominate commercial devices due to their wider potential windows. The PhD student conducted detailed research into both ECs (using the TEABF₄/AN electrolyte) and LICs (using LiPF₆ in carbonate solvents). The chapter consists of two manuscripts: 'Identifying the Activated Carbon Electrode Aging Pathways in Lithium-Ion Hybrid Capacitors and The Oxygen Enigma: Deciphering the Role of Carbon Surface Functionalities on Degradation at Electrified Interfaces'. In LICs, applying different voltage regimes leads to the degradation of the solid electrolyte interphase (SEI), which affects cycle life and performance. These findings were obtained through a combination of electrochemical data analysis and post-mortem surface techniques (TPD-MS, porosity





measurements, EA, XPS and Raman spectroscopy). In ECs, Mrs Ślesińska proved that the type of oxygen groups on carbon surfaces influences the degradation process more than their overall content. The influence of the electrode binder can be neglected because activated carbon cloth was used. The presence of acidic functionalities influences the formation of a protective polymer-like layer on the electrode surface, thereby improving operational lifespan. On the contrary, the elimination of carbon-oxygen functionalities promotes faster degradation. These findings highlight the need for careful control of carbon surface chemistry during electrode preparation, a process known as 'tailored functionalisation'.

The most important achievements of the dissertation submitted for review are as follows:

- The topics covered relate to processes taking place at the electrode/electrolyte interface in ECs and LICs, considering both aqueous and organic electrolytes coupled with carbon electrodes.
- Current knowledge on these processes is expanded using advanced operando and analytical techniques, and the specific causes of accelerated carbon electrode degradation are elaborated on.
- The influence of various factors (e.g. different activated carbon electrode materials, electrolyte compositions, voltage applied, surface chemistries and cell construction) on the conclusions obtained is also considered.
- The work carried out as part of Sylwia Ślesińska's MSc Eng. doctoral thesis resulted in three scientific articles being published in international journals; a fourth is under revision. The research was conducted as part of projects financed by domestic and foreign sources, as well as French Scholarship, and within an international team. The contribution of all authors is described and confirmed by





their signatures for each publication. Mrs Ślesińska is the first author on three publications.

The results obtained by Sylwia Ślesińska, MSc Eng. are presented in a coherent manner and are discussed thoroughly. This discussion is supported by figures, as well as by graphs and tables showing recorded relationships. The submitted dissertation confirms the doctoral student's theoretical knowledge and her ability to plan and conduct scientific research.

While reading the thesis, I have some general comments that do not affect my positive assessment of the dissertation. These comments could form the basis of a discussion during the public defence.

- It was proven that selected experimental conditions, especially the voltage applied, the materials used and the electrolytic solutions studied (aqueous vs. organic), influence the ageing phenomena in energy storage devices. The PhD student claims that more extensive research on this topic is required. In this case, my question relates to the statement and is connected with further measurements. Are any next steps, experiments or approaches planned?
- Improving the understanding of processes at the electrode/electrolyte interface by focusing on the effects of varied voltage and oxygen surface functionalities on ageing is fundamental to practical application. As mentioned, studies conducted at laboratory and industrial scales differ fundamentally and cannot easily be compared. However, using the international standard IEC 62391-1 as guidance for EC ageing in the doctoral work, which specifies the end of life, allows us to consider measurements that could lead to a higher TRL. In the context of producing activated carbon from biowaste for use as an electrode material, please suggest the necessary research and modifications to be carried out





to produce the final product with the best possible lifespan. Due to the scope of the doctoral thesis, analyse the research and economic aspects of both aqueous and organic electrolytes.

- There are a few editing errors in the work, mainly in Chapter I. For example, 'AN' and 'HIP' are used as abbreviations for 'acetonitrile' and 'hybrid ion capacitor', respectively. The vertical axis in Figure 1 does not include a unit description. The multiple in Equations 2 and 3 are incorrectly marked, and the descriptions of Figures 7 and 8 in the text do not match the figures provided. Additionally, the Polish and English versions of the abstract differ: the Polish version omits a short paragraph concerning the final part of the dissertation.

In summary, Sylwia Ślesieńska, MSc Eng. has achieved the following in her academic career: she is the co-author of five scientific publications in international journals with total IF=43,76. She is also the co-author of four oral presentations at national and international conferences as well as seven poster presentations at international conferences.

The doctoral dissertation submitted for evaluation by Sylwia Ślesieńska, MSc Eng., meets all the formal requirements for doctoral dissertations in accordance with: Ustawa z dnia 20 lipca 2018 r. - Prawo o szkolnictwie wyższym i nauce (tekst jednolity: Dz. U. z 2023 r. poz. 742). Therefore, I request that Sylwia Ślesieńska, MSc Eng., be admitted to the next stages of the procedure for awarding a doctoral degree in field of natural sciences in the discipline of chemical sciences.

I strongly support the distinction of the reviewed thesis, as the proposed approaches focus on electrode charging processes and the degradation mechanisms of carbon materials in both aqueous and non-aqueous electrolytes, thereby contributing to existing knowledge in this area.

