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 ANDRÉS CAMILO PAREJO-TOVAR

The doctoral dissertation prepared by Andrés Camilo Parejo-Tovar entitled „*Performance of symmetric and hybrid electrochemical capacitors*" has been performed under supervision of Prof. François Béguin as promoter and Dr. Eng. Paula Ratajczak as co-promoter at Poznan University of Technology, Faculty of Chemical Technology, Institute of Chemistry and Technical Electrochemistry.

This dissertation focusses on important issues concerning the performance of symmetric and hybrid electrochemical capacitors, which are crucial for advancement of the effective energy storage technologies. Special attention has been paid to studies $NaClO_4$-water eutectic electrolyte as high-conductivity water-in-salt (WIS) electrolyte for use in electrical double-layer capacitors (EDLCs) for sub-ambient temperature applications and sodium azide (NaN_3) as a sacrificial cathodic material to resolve the metal deficiency in the anodic host of sodium-ion capacitors (NICs). The Author focuses on methodology for calculating the current passing through the individual electrodes during the potentiodynamic charge/discharge of hybrid Li-ion capacitor (LIC) and explanation of the in-pore/ex-pore exchange processes in an activated carbon (AC) electrode operating within an extended potential range. The results, which has been described and discussed in the dissertation, are certainly of importance to the development of the electrochemical energy storage and conversion devices. The obtained results are also of importance from the view-point of the development of materials chemistry and engineering.

The doctoral dissertation of Andrés Camilo Parejo-Tovar is organized in a way that it consists of five chapters, which is preceded by general introduction. The first part provides a literature review (Chapter I), in which crucial items of information concerning electrical double-layer capacitors (EDLCs) and carbon-based metal-ion capacitors (MICs) have been carefully described. In the first part of Chapter The Author has described fundamental

operating principles of common electrode materials, the influence of texture and structure as well as electrolyte type on their performance. The Author concentrated on explanation of the influence of porous texture and electrochemical stability window (ESW) on EDLCs efficiency, with a focus on organic, aqueous, and water-in-salt electrolytes. The Author draws attention to study ion population dynamics within the EDLC electrodes during the charge and discharge cycles. The second part of this chapter is devoted to carbon-ion metal-ion capacitors (MICs). The Author presented fundamental operating principles and ion population changes in the positive carbon electrode of MICs. The Author discussed the effects of pairing an EDL-type positive electrode with a battery-type negative electrode and presented typical materials to use for the negative electrode in these devices. The Author described organic electrolytes used in MICs, solid-electrolyte interphase in the negative electrode of this kind of device and pre-metalation methods for the preparation of MICs. In the reviewer's opinion, the literature part of the work addresses the most important achievements in the above-mentioned fields but it does not cover pseudocapacitive systems. Perhaps this section should contain a description of preparation of materials and research methodologies.

The next chapters (II-V) refer to experimental work and results described in a form of attached four publications. All articles are preceded by short describing the most important results.

In the chapter one, Andrés Camilo Parejo-Tovar posted an article entitled "*The $NaClO_4$-water eutectic electrolyte for environmentally friendly electrical double-layer capacitors operating at low temperature*" . This publication describes electrical double-layer capacitors with activated carbon electrodes demonstrating energy storage performance at sub-ambient temperatures down to -30 °C. This devises have been developed by implementing the $NaClO_4$-water eutectic solution. Due to the properties of the eutectic solution $NaClO_4$-water, high ionic conductivity has been obtained due to the channel structures of free water molecules associated by hydrogen bonds in the entire temperature range and the liquid state of the solution has been extended at low temperature. It has also been demonstrated that, electrochemical stability window of activated carbon electrodes in high concentration $NaClO_4$ electrolyte increases potential value at -35 °C. These high values are attributed to the electrolyte's near-neutral pH and reduction of free water in the Stern layer under positive polarization.

In the article 2 (chapter III) entitled "*Ideally Realized Sodium-Ion Capacitor via Irreversible Oxidation of Sodium Azide to Pre-Metalate the Anodic Host*" special attention has been paid to use of sodium azide (NaN_3) as a sacrificial cathodic material to address metal deficiency in the anodic host, aiming to effectively prepare sodium-ion capacitors (NICs)

without producing any residual solid product. These materials have been subjected to physicochemical and electrochemical characterizations. The Author has described the preparation of electrodes consisting of NaN_3 and activated carbon (NaN_3-AC) and provided a detailed study of the effect of NaN_3 oxidation on the porous texture of the electrical double-layer positive electrode. It has also been demonstrated that, by using a mixture of hard carbons (HCM): hard carbon HC-J and hard carbon derived from glucose (HCG), compact electrodes have been obtained with optimally reduced ohmic drops. The Author has proven that sodium azide serves as an exceptionally "zero dead mass" sacrificial material with highly attractive electrochemical performance in development of sodium-ion capacitors.

The article 3 (Chapter III) entitle "*Comprehensive Potentiodynamic Analysis of Electrodes Performance in Hybrid Capacitors*", concerns the methodology for characteristics of individual electrodes in hybrid capacitors. The Author has presented methodology for calculating the current passing through the individual electrodes during the potentiodynamic charge/discharge of a hybrid Li-ion capacitor. It has been proved that, the potentiodynamic characteristics of the negative electrode obtained by applying a fixed potential scan rate, *d*, do not correctly reflect the real situation observed when a constant voltage scan rate is applied to the Li-ion capacitor, where the electrode potential sweep rate is adapted by the system. The Author has presented, that an accurate representation of the electrode CVs during real cell operation can be obtained by dynamically adjusting the potential sweep rates (calculating the electrode potential scan rate over time). This approach provides essential information on any imbalance in the contribution of the electrodes during device operation.

In the article 4 (chapter IV) entitled "*Operando tracking of ion population changes in the EDL electrode of a lithium-ion capacitor during its charge/discharge*," addresses the elucidate the in-pore/ex-pore exchange processes in an activated carbon electrode operating within an extended potential range, akin to the positive electrode of a lithium-ion capacitor during its charge/discharge. The Author has demonstrated that the molecular dynamics simulations applied to a battery-type electrolyte ($LiPF_6$ in EC: DMC), both in bulk and adsorbed within a model porous carbon, has revealed partial solvation of Li^+ cations within the pores and complete de-solvation of PF_6^- anions in both states. It has also been shown that operando, and in situ methods applied to the AC electrode, confirm the complex interplay between ionic exchange, anion adsorption/desorption, and cation trapping, which are critical for optimizing the performance and lifespan of LICs. Special attention has been paid to understanding and addressing properties of LICs related to ion desorption, the properties which could help improve the systems' performance.

At the end of the doctoral dissertation, Andrés Camilo Parejo-Tovar presents his scientific achievements, abstract and provides statements of coauthors describing their contributions. It is noteworthy, that Andrés Camilo Parejo-Tovar is the first author of four (out of five) publications and, judging from the statements of coauthors, he has significantly contributed to all works. Thus, Andrés Camilo Parejo-Tovar can be viewed as a professionally advanced and mature young scientist. It should also be mentioned that research pursued toward the doctoral dissertation has been supported by the Foundation for Polish Science under the RETURN program under the project "*New concept of a sustainable capacitor based on carbon-ion technology - CARBionCAP*". Andrés Camilo Parejo-Tovar appears as coauthor of an additional publication, which is not included to the dissertation. The above mentioned articles have been published in well-established journals of international circulation (e.g. *Electrochemistry Communication, Energy Storage Materials or Journal of Power Sources*). Andrés Camilo Parejo-Tovar is listed as author or coauthor of six oral conference presentations (four of them he presented himself) and four poster presentations. He has served as investigator in one scientific project. He received France Excellence scholarship (SSHN) on research stay, and he is a recipient of *ISEECap Poster Presentation Award* (*International Society of Electrochemistry).*

Going to the substantive evaluation of the dissertation, I would like to mention the important observations and achievements described therein. Andrés Camilo Parejo-Tovar has developed the advanced "Water-in-Salt" electrolyte for symmetric electrical double-layer capacitors which attains high voltage and stable operation, particularly in low-temperature environments, thereby enhancing energy density and extending cycle life. Among other important issues are refining the pre-metalation process in hybrid carbon-based metal-ion capacitors by employing the irreversible oxidation of a carefully selected cathodic sacrificial material, as well as enabling of the formation of solid electrolyte interphase, and the effective pre-metalation of the anodic host without forming undesired by-products. The Author also has developed an operando methodology for tracking ion population changes in the electrical double-layer positive electrode of hybrid carbon-based metal-ion capacitors during charge and discharge cycles, providing critical insights into electrode processes to optimize performance and reliability. This dissertation provides significant contributions to improving the performance of symmetric and hybrid electrochemical capacitors by addressing key challenges in energy density, cycle life, and temperature range.

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) While I find the literature review well-written, to fully describe the state-of-art of electrochemical capacitors the pseudocapacitive systems (perhaps in addition to high-power capacitive-type batteries) should also be somewhat addressed.
(2) More details would be interesting about the long-term durability of the proposed systems, not only in the context of the stability of electrolytes but carbon materials used as well.
(3) General and critical overview of the diagnostic methodology used would be helpful.

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 Andrés Camilo Parejo-Tovar should be easily admitted to the public doctoral defense at Poznan University of Technology.

Having in mind the importance of pursued research, the quality, the high scientific value and the application potential of results obtained in the area of the development of new systems for the electrochemical energy storage (presented in valuable publications onto which the dissertation is based), I would like to recommend awarding the dissertation and conferring the Ph.D. degree Andrés Camilo Parejo-Tovar with distinction (honors).

Iwona Rutkowska