DIPARTIMENTO DI CHIMICA "GIACOMO CIAMICIAN"

Bologna 16/12/2022

OBJECT: Evaluation of PhD Thesis "Mathematical analysis of processes and phenomena in electrochemical energy storage and conversion systems" by Przemysław Galek, Institute of Chemistry and Technical Electrochemistry at Poznan University of Technology.

This is an excellent work that addresses very challenging fundamental and applied studies on supercapacitors.

The experimental results are original and of high significance and might pave the way towards the design of novel electrode and electrolyte components of electrical double layer capacitors. Specifically, this work sheds light on the interplay among electrode architecture, electrode manufacturing, and electrolyte formulation.

The candidate demonstrates a deep knowledge about the processes that drive supercapacitor operation, on the key components of the supercapacitor cells, such as high surface area carbons and electrolytes, on the advanced analytical techniques and on the theoretical approaches adopted to get insight into the chemical-physical properties of these devices.

The work is excellently described and the dissertation very well organized. The document is of high standard with respect to technical detail and the language is appropriate. The introduction chapters are exhaustive and review the recent research works on the Thesis topics, which clearly proves high familiarity of the candidate with the field of research in question. Furthermore, the candidate has adequately mentioned and interpreted the relevant literature on his dissertation topic.

Research approaches and results are original and innovative and rely on different activities, even supported by modeling. They span from the study of the optimization of the electrode manufacturing by ink casting, to the analysis of the carbon/electrolyte interfaces with different high surface area carbons and aqueous, water-in-salt and ionic liquid

ALMA MATER STUDIORUM • UNIVERSITÀ DI BOLOGNA
VIA SELMI, 2 - 40126 BOLOGNA - ITALIA - TEL. 0512099797 - FAX 0512099365 francesca.soavi@unibo.it

electrolytes. The systems are deeply studied by combining chemical physical and morphological analyses and electrochemical investigations. The methods include advanced techniques like N2 sorption at 77K, Raman, along with cyclic voltammetry, gavalnostatic and cycling tests, and electrochemical impedance spectroscopy. Innovative is the proposed technique that combines Step Potential Electrochemical Spectroscopy and Electrochemical Dilatometry and the 'SPECSfit' software developed to reduce data elaboration time.

The scientific rigor with which these studies are reported and commented demonstrate the high skills acquired by the PhD student in the different techniques of characterization of supercapacitor materials and cells. The Experimental part is organized referring to papers published and/or in preparation, and the main findings are briefly summarized in the conclusive part of the dissertation. A deeper and critical conclusive section would have further demonstrated the candidate ability to critically examine and compare his work with literature, and to delineate and suggest directions for future work in this topic.

The research work has been carried out under a Researcher in European Research Council (ERC) project and published in high impact-factor, peer reviewed Journals, presented at several international conferences, and the candidate was recipient of scientific awards, therefore supporting the interest of the international scientific community to this work. The candidate is even co-author of 2 patent applications. It would be interesting to know which is the topic of these patents. In addition, I suggest to clearly mention eventual collaborations with groups from different Universities and periods spent abroad.

In addition, I would suggest the following minor revisions:

- Pages 42 and 66: the candidate reports that in water-in-salt electrolytes capacitance is improved. However, this is not a general behavior and I suggest removing the related sentences. Indeed, the work reported in article A2 does not clearly support this

statement.

- -Page 45. It is reported that "it is not recommended to use noble metal foil or other unstable materials in an aqueous solution because they are sensitive to corrosion". This is not totally correct. Nobel metals are expected to be more stable than others. However, I agree that noble metals are not usable in aqueous electrolyte. But one of the main reasons is also that they often promote the electrochemical decomposition of the electrolyte solutions (like water electrolysis).

- -Page 47. The comments about voltammetric peak shift are not fully correct. The statement "The peak shift can be caused when the redox processes at this electrode site are limited by mass transport" is wrong. Indeed, during a cyclic voltammetry, peaks are observed because the current is limited by mass transport (diffusion). Electrochemical processes that are not limited by diffusion do not give rise to voltammetric peaks. In addition, the sentence "Another possibility is electrode/electrolyte instability (decomposition particularly at the extreme potentials) or the resistivity of processes" is ambiguous. The main reasons for peak shift are: i) electrochemical irreversibility of the process (Not-Nernstian processes), ii) adsorption of products or reagents, iii) increase of the electrode or electrolyte resistance. Please revise this part.

- Pages 61-62. It seems that some text has been missed. Comments to Figure 4 are not completed (what happens above 0.3 Pa s?) and the introductory part to the following section (cost analysis) is missing. Indeed Figure 5 is not commented and after Figure 5 the paragraph starts with "In conclusion,…". Please check.

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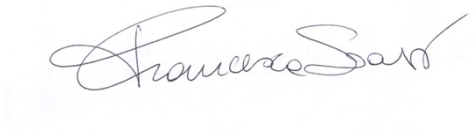
In conclusion, overall, the candidate presents the theoretical knowledge and the skills required to conduct scientific activity on his Thesis topic, and proposes original solutions of the scientific and applied problems required for a doctoral degree in a chemical sciences discipline. Hence, I positively evaluate this dissertation.

Sincerely,



Francesca Soavi

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