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**REFREE REPORT**

of the thesis

**DESIGN OF HIGH VOLTAGE AC/AC ELECTROCHEMICAL CAPACITORS IN AQUEOUS ELECTROLYTE**

by **mgr Paula Ratajczak**

The thesis was prepared in the Institute of Chemistry and Technical Electrochemistry of the Faculty of Chemical Technology of Poznan University of Technology with Professor François Béguin as the Supervisor.

The significant novelty of the thesis is the development of the concept of the voltage range increasing of the working current and the reduction of the material costs of the electrochemical capacitors (ECs) working in water electrolytes by using porous carbon materials as electrodes. Applying environmentally friendly electrolytes, current collectors of common metals and exploiting asymmetrical configurations of carbon electrodes the author suggested the design of the electrochemical capacitors working in a wide range of operating voltage with a satisfying cycle life. In the research the author took into consideration the usability of structurally diverse carbon materials and the factors responsible for the corrosion of metallic current collectors and water electrolyte decomposition during a long-term work of the capacitor under high voltage operation. In spite of numerous research works these problems are still an object of interest of many scientific research centers.

The author assumed to achieve the main purpose of the research consisting in developing cheap and environmental friendly electrochemical capacitors by using commercially available carbon active materials as electrode materials. In

investigations the author applied the typical experimental techniques: cyclic voltammetry, galvanostatic loading/unloading of electrodes (chronopotentiometry) and the impedance spectroscopy. Accelerated ageing tests were applied for the evaluation of the proposed capacitors (the usefulness of their work time).

The reviewed thesis has been written in the traditional system covering more than 170 pages and consists mainly of 140 pages of the thesis text followed by the experimental appendix (6 pages), 14 pages of the bibliographical list (216 references) and the scientific achievement statement of the author. The text of the trial is divided into five chapters preceded by the introduction in which the purpose of the dissertation is formulated (upper paragraph). The first chapter (35 pages) is devoted to the references review closely connected with the subject of the thesis and consists of the contents concerning the classifying of electrochemical capacitors and the role of active carbon materials as of high capacity electric double layer electrodes. The vast majority of quotations (216) refer to the works published after the year 2000, which emphasizes the topicality of the research subject and an excellent knowledge gained by the author of the world scientific literature concerning the research subject. A reliable literature study enabled the author to formulate more precisely the aim of her research actions and the presentation of the manners of their execution (last paragraph of chapter I)

***It is to be regretted that the aims of the work are not distinguished in the text as a separate chapter.***

Chapter II is devoted to the electrochemical research techniques applied to the reviewed work. The adopting of the techniques used for testing commercial super capacitors allowing to indicate their functional parameters deserves emphasis. Reliability and lifetime are two major factors deciding about the usability of the electrical storage system.

***It is to be said that the dissertation lacks an attachment containing the list of acronyms, abbreviations and symbols used in the work. It might have facilitated the reading, the comprehension and the evaluation of the thesis and this way the mistakes caused by marking the same material with different symbols might have been avoided.***

The three chapters (III-VI) presenting the results of the examinations and their analysis are the most extensive. Each of them ends with a brief summary. All these chapters present the experimental outputs in the form of 55 figures (mostly multipart type and of collective nature) and 5 tables.

Chapter III contains the results of the behavior of carbon electrochemical capacitors (ECs) with steel current collectors in neutral water electrolyte. Application of the test of accelerated ageing of ECs by floating revealed a fall in the electric capacity and an increase in the electrical resistance of electrode materials and also an increase in work time of the system at voltage higher than 1,5 V. Such a limit of the anode potential is lower than in the case of using gold collectors but it is significantly higher than for ECs with acidic or alkaline electrolytes. The major achievements of this part of the thesis are the examination results of the gases evolved during the galvanostatic cyclisation and ageing method by floating indicating the electrolyte decomposition and the fact of the parameter changes characterizing the porous structure and the surface chemism of the electrode carbon materials. Carbon electrode material oxidiation leads to reduction of its specific surface and modifies the selective adsorption of the ions. The electrolyte decomposition results in ionic starvation. Both these processes cause a capacity decrease and an increase of electrical resistance. Reliability decreases and effective work time of the examined capacitors shortens.

The following chapter is devoted to strategy development of the elimination or reduction of negative effects appearing during the capacitor work. The author took two factors into consideration: corrosivity of the metal current collector and the potential range of the device action. The ECs lifetime was extended by useing: a non corroding nickel collector, covering the steel collector by nickel – plated foil, adding an inhibitor to the electrolyte solution. Of great importance was the ascertainment that covering the metal collector with a conducting layer of a carbon ink prevents the accumulation of corrosion products at the limiting layer between the metal and carbon substrate. Another important result was achieved during the electrochemical examination of the electrochemical behavior of the asymmetric electrode system. Coupling two selected carbons as cathode and anode electrode

materials shifts the operation potential of the system towards the lower values. An equally important result of the research is the proof of the possibility of preventing the carbon electrodes from oxidation even during work at high voltage by using neutral aqueous electrolytes and molybdate inhibitor.

***My remark on this part of the thesis is the question concerning the data in Table 5 containing some copied data from Table A2. A question to the author arises: what was the way of reckoning the percentage oxygen content (wt%) in the examined carbon materials basing on the TPD method. My concern applies mostly to the TPD results for B800 carbon obtained from the thermal process to 800 C degrees while examining it by TPD method until 950 C degrees.***

In the last experimental part the author basing on the gained experience about the factors which influence the behavior of the construction materials and the achieved current ranges presents a new concept of the asymmetrical carbon capacitor cell design. The increase of the operating potential range was achieved by applying a neutral electrolyte in the anodic part and base in the cathodic part of the capacitor separated by a cation exchange membrane as separator. The results obtained allow it to be supposed that the concept may indicate the direction of further search for cheap super capacitors working in a long cycle life with high power density – that is of devices (products) with potential functional advantages.

***I must remark that there is the mistake in the numbering of the subsections (repeated in the table of contents)***

An analysis of the reviewed dissertation clearly indicates the high quality of the achieved experimental results and the way of their evaluation. The assessed trial constitutes a fully substantiated and original solution to an important scientific problem and contributes crucial elements of novelty to world science in its research subject both on its cognitive level and its practical applications alike. The contents introduced in the succesive chapters prove a wide general knowledge of chemistry particularly in the field of active carbon material technology of assumed properties which are most suitable for charge collecting processes and construction of electrochemical capacitors (“super capacitors”). Clear design, precise description of the conducted experiments performed with the application of modern research

methods but most of all, convincing evaluation of the results of the succesive work stages indicate fully formed personality of the researcher, her analytical ability and skills to combine the basic research results with its applied character. The author fulfilled the assumed research aims, which was stated in the final conclusions at the end of the experimental part of the work.

**Summary**

I certify that the author is to be regarded as a fully grown scientific personality, well prepared for independent research work, being able to set research objectives and find adequate tools and methods of their implementation as well as evaluate the achieved results. The above mentioned editorial shortcomings and minor editorial mistakes in the text do not diminish the value of the thesis.

I can state in fully confidence that the customary and legal requirements (Bill of 14 March 2003 on university degree titles and university academic titles and titles in the field of art – Act No. 65 Item. 595, as amended) applicable to doctoral candidates are fully met. The reviewed thesis constitutes an indisputable reason for applying for a university title of the Doctor in the field of technical science, chemical technology. Therefore, I am addressing the Council of the Faculty of Chemical Technology of Poznan University of Technology to table a motion to accept the thesis and to allow Paula Ratajczak, M. Eng. to follow the further stages of the doctoral degree procedure.

Prof. dr hab. Stanisław Biniak