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Rapport on the Ph.D. thesis of Przemysław Galek (M.Sc.) entitled:

"Mathematical analysis of processes and phenomena in electrochemical energy storage and conversion systems"

The Ph.D. manuscript of M. Przemysław Galek is devoted to the understanding of the processes that occur at the carbon / electrolyte interface in the electrochemical capacitor (EC). The EC are interesting energy storage devices that are widely used in several types of applications that require high power. Along with batteries, they are crucial to accompany the transition of energy from fossil to renewable. The increase of the energy density of the EC is one of the main priorities for such devices, and this can be achieved by improving the efficiency of the electrodes and electrolytes, as well as understanding the relationship between them during the device working.

For this purpose, several key parts of the EC device (electrode, electrolyte, and system) were studied in depth by M. Galek, using both conventional and more sophisticated electrochemical techniques. For some techniques, the obtained experimental data was exploited *via* the development of novel mathematical formula and computer software. This original approach covering all parts of supercapacitors, combined with the efficient and insightful data treatment / interpretation, allows one to propose valuable directions for EC performance improvement.

The Ph.D. of M Galek was performed at Pozanan University of Technology, Faculty of Chemical Technology, under the supervision of Dr. Krzysztof Fic. The manuscript has 151 pages and is composed of a literature review part, a large experimental part that includes the main results collected in 5 articles, a description of the computer software, and a short summary. A list of abstracts corresponding to five additional articles of the author was provided, along with a description of scientific achievements. The thesis ends with an annexe illustrating the co-authorship statements for each scientific article.

After presenting the main goals of this thesis, the first part of the thesis is dedicated to the literature review. Electrochemical energy storage and conversion systems are briefly reviewed, followed by a detailed description of the electrochemical capacitors. The EC construction, working principals and performance metrics are presented, and then a focus on the state-of-the-art of carbon electrode materials and electrolyte types is provided. This section ends with a description of the main electrochemical techniques used in this work and a summary. Overall, this section is very well written and concise, providing the most important basic information and challenges of this topic. Nevertheless, for some unconventional electrochemical techniques, some illustrations could be provided to facilitate easier reading for non-specialists.

The second part of the thesis (experimental part) describes in detail the main results. The format selected for the presentation of the results is article one (double column) and each article is preceded by a short motivation and summary section. Five articles form the heart of the thesis.

Article A1 is dedicated to the fabrication of carbon electrode materials. In particular, the impact of electrode slurry components (activated carbon, binder, solvent) and preparation conditions (type of stirring) on the viscosity of the slurry is studied. Then the effect of electrode properties on electrode quality, thickness, wettability, and mechanical properties was determined. This topic is rarely investigated in the literature and highlights the original approach developed herein to better understand the factors that lead to optimal electrode materials coated on current collectors. It merits to be underlined that the state-of-the-art is very nicely presented in this article (and in the following ones) as it provides a comprehensive and synthetic overview of each investigated topic. The results obtained evidenced the viscosity threshold limits that must be respected to ensure homogeneous deposited slurry on the current collector. The viscosity parameter was found to be rather complex, as it depends strongly on the components involved, and in this direction, Galek proposed several mathematical equations that allow one to predict the viscosity and the thickness of the electrode. The importance of mixing conditions for the stability of the slurry and the dependence of the contact angle on the composition of the slurry was also underlined. An analysis of the cost of slurry fabrication is provided on the basis of the involved cost of components, their ratio in the slurry, and drying conditions. The overall results are very interesting, and the contribution of the author is significant to this topic. However, these results could be even more appreciated if PTFE binder and water solvent were used for slurry preparation, as is the case for all electrodes presented in the next articles in this thesis.

Articles A2 and A3 deal with research on different EC components, i.e. the electrolyte.
In **article A2,** concentrated aqueous electrolytes were studied in order to extend the voltage window and increase the energy density. The selected salt electrolyte was CsF, a choice motivated by its high solubility in water that allowed the study of a high concentration of up to 15.1 mol L^{-1}. The main properties of CsF electrolytes (conductivity, viscosity, and pH) were investigated and then correlated with the electrochemical performance of five activated carbons that have a distinct microporous texture.

The relationship between the electrolyte properties and the performance of selected activated carbons could not be clearly evidenced, and the improvement of the voltage window and energy was only marginal. Here, the choice of only microporous and hydrophobic carbons for this study could perhaps explain such results. The use of some carbons that have a mesopore fraction and some surface functionalities, which favor the adsorption of the electrolyte, could certainly extend the understanding of such correlations. However, some add-values of concentrated CsF, such as suppression of the leakage current and decrease in the amount of gas released during EC cycling, could be evidenced, which are important aspects for improving EC safety and cycle-life. The knowledge gained in this work was further extended in the next article.

Based on the constant that electrolytes with high viscosity and low conductivity do not necessarily penalise the performance and the literature observations highlighting that high electrolyte viscosity limits the ion mobility/performance, M Galek investigated in **article A3** the role of electrolyte viscosity on the EC performance. Aqueous electrolyte (Li_2SO_4) was used as a case study and viscosity was adjusted by using carboxymethylcellulose (CMC) and guar gum (GG). It was shown that the ion mobility is not significantly affected by the increase in electrolyte viscosity, although ion adsorption into narrow pores is affected. An original technical approach combining contact angle measurement with an electrochemical device was used, which allowed Galek to demonstrate the important role of electrolyte viscosity and surface tension, as well as polarization, on the wettability of the electrode. Finally, it was demonstrated that viscous electrolytes do not negatively affect long-term cycling, do not lead to energy decrease, but do have a positive effect on reducing electrolyte decomposition and leakage current. All of these results show the importance of electrolyte for the EC performance.

The last two articles (A4 and A5) focused on the fundamental understanding of the electrode /electrolyte interface using original electrochemical techniques, i.e., Step Potential Electrochemical Spectroscopy (SPECS) and Electrochemical Dilatometry, rarely used in the literature. It is worth highlighting that these two works are particularly complex, as they address ion sorption mechanisms in nanoporous media *via* "quasi-unexplored" techniques. The research and technical level is very high and underlines the scientific maturity of M Galek.

In **article A4**, an ionic liquid ($EMIm^+TFSI^-$) was selected as an electrolyte to avoid the contribution of the solvent to the adsorption mechanisms. Two activated carbons (micro- and micro/meso- porous) were used, and the ion sorption mechanisms depended on the type of carbon. For microporous carbon, the cations were adsorbed by ion exchange and co-adsorption mechanisms, while the anions were adsorbed by ion exchange and selective adsorption. The latter two mechanisms were found for the micro/meso- porous carbon, with no difference in behaviour for anions and cations. The adsorption mechanisms are therefore strongly dependent on the carbon porosity. This is rather intriguing considering the similar microporous character of carbons and the absence of "intrinsic" meso-porosity in the micro/meso- porous carbon. The evaluation of the morphology and chemistry of these materials would probably give some answers.

From a more general point of view, the results obtained herein illustrate that the SPECS technique combined with dilatometry offers a valuable possibility to measure ion transport mechanisms in nanoconfined spaces. These techniques were further explored in the last **article A5** to understand the effect of electrolyte pH on the ion adsorption at the electrode/electrolyte interface. The behaviour of Li_2SO_4 was found similar for pH close to neutral and different for alkaline pH, in particular at the positive electrode. Very interesting, it has been evidenced that the local pH near the polarized electrode surface might change during EC working. The lower pH ensured more stable EC operation and preserved the textural properties of carbons. The valuable and significant amount of results presented here were possible to be obtained thanks to the involvement of M Galek in the development of a specific computer software (SPECSfit) which allowed one to do the acquisition and treatment of the SPECS data in an automatic, rapid, and efficient way. This program is briefly described in the manuscript.

Overall, the presented works by Galek demonstrate very complex and interdisciplinary skills (material preparation, physicochemical and electrochemical in-depth characterisation, as well as mathematic/informatics) applied to a large pallet of systems (electrodes, electrolytes, and devices).

The manuscript ends with a brief summary of the thesis, a presentation of several abstracts corresponding to supplementary published articles, and a list of professional achievements. An important number of articles have been published (8) in journals of high quality, and some are currently being submitted. M. Galek was also involved as an author of a book chapter, co-inventor of 2 patents / 1 patent application and presented his works at many international and national conferences. All this suggests the high scientist level of M Galek.

In summary, considering the high quality of the obtained results, presented in a very clear manner in this manuscript, the complex topic at the interface of several fields, as well as the significant research contribution and the impressive scientific achievements of M. Galek, I am strongly favourable for the Ph.D. defence and for the attribution of an award.

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