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12.12.2024

Review report of the PhD thesis

„One-step assembly of metal-ion capacitors using redox-active electrolytes"
Submitted by **MSc. Adam Maćkowiak**

Electrical Double Layer Capacitors (EDLCs) are highly relevant for high-power applications and use in electric vehicles, for grid stabilization etc. However, one of the major drawbacks of EDLC is their very low energy density as compared with rechargeable batteries. One way to increase the energy density and make them more competitive in the market is to include a faradaic material and build a so-called "metal-ion capacitor", which contains one faradaic material typical for batteries and one double layer material (e.g. activated carbon). The concept of metal-ion capacitor already exists since years, but one major problem is to enable a pre-metallation step. The dissertation of Adam Maćkowiak is focusing exactly on this aspect and aims to find viable solution for an efficient and economical "one step methodology for pre-metallation. His approach is to rationally select additives to the electrolytes, which undergo an irreversible oxidation thus providing extra alkali ions (Li^+, Na^+ or K^+) to intercalate/insert either the graphite (for Li and K) or hard carbon (for Na). Moreover, this PhD thesis aimed at combining analytic methodologies for performance/side reactions evaluation with advanced electrochemical characterization (such as SPECS and GITT), thus providing a guideline for scientists and engineers in the field.

The dissertation of Adam Maćkowiak is a cumulative thesis including three published scientific articles and two manuscripts submitted to peer-reviewed scientific journals and structured into six chapters: **Chapter I** includes an introduction in the form of a literature review. This introductory background is very clear, enabling basic understanding (also for non-experts) of the topic of supercapacitors. It is very well-written and readable. It covers the motivation for the development of energy storage systems and explains in a concise and very clear/didactic manner different energy conversion and storage systems (including fuel cells, batteries, and supercapacitors). The working mechanisms of batteries and supercapacitors and the role of their key components (i.e., electrodes and electrolytes) are explained in detail. Metal-ion capacitors and the pre-metalation strategies are also reviewed. Finally, the relevant characterization techniques used in the thesis are briefly explained.
Chapter II is a very concise one. It highlights the aim and scope of the thesis, which is to optimize and facilitate the assembly of a Metal-ion capacitor. The

approach described to achieve this goal is to use redox-active molecules that can be inserted directly into the electrolyte. Here, the hypothesis (that the redox molecule can act as a charge balancer and facilitate the insertion of metal ions in the anode) is stated. This chapter concludes with an explanation of the structure of the thesis.

Chapters III, IV and V are the core of the thesis and report about the scientific findings: The journey of this PhD dissertation starts by proposing Li, Na and K thiocyanate salts as additives to the electrolyte. This is a different approach than what was proposed in the literature (i.e., the addition of a sacrificial salt to the electrode mass), and it could bring the advantage of increasing the overall energy density without adding dead mass to the positive electrode. Adam Maćkowiak proved that this type of salt is beneficial to the cells, enabling a direct in situ metallation of the negative electrode and, therefore, enhancing the overall cell's capacity and energy density. The work dives deeper into understanding the underlying mechanism by combining several techniques. A challenge encountered in the thesis is that despite the theoretical benefit of some of the possible additive candidates, they were not successful for several reasons (e.g., poor solubility in the electrolyte, clogging the pores of the activated carbon, etc.).
Salts such as Thiocyanates and Acetates are the best candidates for the one-step in-situ metallation of metal-ion capacitors. Another aspect investigated in this thesis is the possible application of "step potential electrochemical spectroscopy" (SPECS), an electrochemical technique normally used for supercapacitors to describe the storage of electric charge in systems with a battery negative electrode (i.e., graphite).
Chapter VI summarizes the whole dissertation, highlighting the main findings.

Final assessment:
Overall, the dissertation is very well-written and organized. The figures and graphics are also very well drawn, clear, and self-explaining. The candidate demonstrated excellent theoretical knowledge in the field of electrochemistry and very good planning in addressing important research questions in the short time frame of a PhD period. The thesis work and related publications are of very high scientific quality and will definitely provide important guidelines for scientists, engineers, and industries active in this field. The thesis, in fact, presented an original solution to upgrade the energy density of a metal-ion capacitor with liquid sacrificial salt additives, which can be in the future adapted to commercial devices. Moreover, Adam Maćkowiak exploited these results in 10 collaborative publications (6 of them as the first/leading author) and 7 patents (+ 3 patent applications), which is an impressive achievement for a PhD student.
In my opinion, this is an outstanding thesis work, and I recommend it with the maximum mark**.**

Best regards

Sonia Dsoke

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