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Report on the doctoral thesis of Mr. MSc eng. Paweł Jeżowski

Lithium-ion capacitors based on in-situ pre-lithiation of the graphite electrode from a composite positive electrode

The work described in the thesis of Mr. MSc eng. Paweł Jeżowski is dedicated to the development of innovative lithium-ion capacitors (LICs) in which the (necessary) pre-lithiation of the negative electrode containing graphite is carried out using a sacrificial composite positive electrode. In order to realize innovative composite electrodes suitable for the goal of this work, Mr. Jeżowski utilized different types of lithium metal oxide as well as lithium salts as lithium sources for the lithiation of graphite electrodes. Le electrochemical and structural properties of these materials have been investigated in detail. Furthermore, also the influence of the composite electrodes on the electrochemical behavior of LICs has been deeply investigated.

The thesis, which is written in a clear and logic manner, contains 5 chapters, a general conclusion about the work and an annex describing the experimental techniques used in this study.

The introduction begins with a description of supercapacitors (EDLC) and lithium-ion batteries (LIB). The storage mechanisms, the materials presently used in these technologies as well as the electrochemical performance, e.g. energy, power and cycle life, are considered and compared in detail. Afterward, the concept of LIC is presented and described in many details. Particular attention is dedicated to the description of the pre-lithiation process of the graphite electrode, which is mandatory in these devices. Presently, for the preparation of commercial devices such a process is carried out using a sacrificial lithium electrode. Since the use of metallic lithium might pose safety problem, the author proposed to use a composite positive electrode as alternative source of lithium. During the charge process, this positive electrode should experience an irreversible loss of lithium, which should in turn serve as source for the lithiation of graphite. Such an approach has been already proposed in literature, but the author propose here alternative materials with respect those that have been so far investigated. The chapter supply several indications about this key aspect of LIC. However, unfortunately, many works relative to the development of advanced LIC as well as to the pre-lithiation of these devices have not been properly acknowledged.

The second chapter presents the procedure used and optimized by the author to carry out the pre-lithiation of the graphite electrode using a sacrificial positive composite electrode based on AC-$LiNiO_2$. This chapter is well written and it clearly underlines the several aspects which need to be taken into account in order to realize an effective pre-lithiation process. Particularly interesting appears the investigation about the influence of the applied C-rate on the SEI formation.

Taking into account the limitation associated to the use of the AC-$LiNiO_2$, in the third chapter Mr. Jeżowski described an investigation about the behavior of composite electrodes containing other types of lithium metal oxides, namely Li_5AlO_4, Li_6ZnO_4 and Li_8ZrO_6. All these lithium metals oxides display higher theoretical capacity compared to the $LiNiO_2$. The use of these materials in combination with carbon nanotubes (MWCNTs) is described. Although the electrodes displayed interesting behaviour, the potential at which the lithium ion extraction occurred was found not really favourable (as too high) for all of them.

The fourth chapter described the use of Li_5ReO_6 as sources of lithium in the investigated composited electrodes. The results of this investigation showed that this material represents a valid alternative for the realization of this type of electrode and that its use makes possible the realization of LIC with promising performance in term of energy, power and also a decent cycle life. Nevertheless, as Re is expensive and not largely available, the use of this lithium metal oxide appears problematic in view of the realization of commercial devices.

Considering the limitation associated to the use of Li_5ReO_6, Mr. Jeżowski proposed as alternative lithium sources for LIC the 3,4-dihydroxybenzonitrile dilithium salt (Li2DHBCN). As this lithium salt might undergo an irreversible loss of lithium (which can be obtained electrochemically), it might serve as lithium source for the graphite electrode. The results of this investigation clearly showed that this innovative material displays a good set of properties and it can be advantageously used of the realization of composite electrodes. Very interestingly, the author also realized a small LIC prototype containing the proposed lithium salt. Although not optimized, the presented system display reasonable performance in term of power and energy.

The last chapter of the thesis properly outlining the main achievement of this work as well as the main points which need to be addressed in the future.

I consider the thesis of Mr. Jeżowski a very interesting work. The thesis is well organized and the subject of this study is actual and of interest from both, the scientific and technological point of view. The materials proposed as sacrificial lithium sources for the prelithiation of graphite electrodes are interesting and their use is opening new possibilities for the development of advanced LIC. The electrochemical investigations have been carried out with care and the science appears sound through all the work.

The results presented in this work are touching several interesting and important aspects related to the development of advanced electrochemical storage devices. Some of the aspects of particular interested, which in my opinion are deserving a depth discussion and analysis, are listed below.

- Many types of hybrid, high power devices can be realized. Why LIC are considered so interesting?
- Electrolytes for EDLCs and LIBs need to fulfil different requirement. Which properties should display an electrolyte for LIC?
- The lithium insertion/extraction process in graphite is a key process for the development of LIC (and LIBs). Which factors are influencing this process?
- The formation of an effective SEI is needed for the utilization of graphite electrode (as well as of other anodes) in LIB and LIC. Which properties should display an SEI for LIC? Which is the role of the electrolyte and of the electrodes on the SEI formation? Which role might have the C-rate on the SEI formation?
- Which parameters, e.g. capacitance and/or capacity, should be considered for the optimization of the electrode balancing in LIC?
- Which structural and electrochemical properties should display a lithium metal oxide to be used as lithium sources for LIC?
- Which advantages are associated to the use of lithium salt as source of lithium in LIC? Are lithium salts always environmentally friendly?
- Is the use of positive electrode containing lithium affecting the performance, especially the cycling stability of LIC?
- Overall, the use of a positive composite electrode as source of lithium for LIC is really advantageous? This approach is technologically/economically convenient?
- Which energy and power are realistically feasible for advanced LIC?
- Which material (electrode and electrolytes) should be considered in the future for the realization of advanced LIC?

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