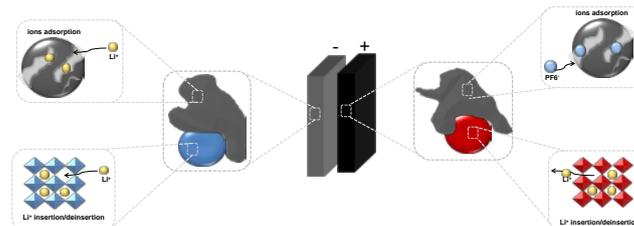


Bachelor or Master Thesis

"Role of carbonaceous materials on asymmetric-hybrid supercapacitors"

Starting date: May 2017 and later

The energy storage mechanism of Li-ion capacitors involves two simultaneous processes: the first one is based on electrostatic adsorption of ions on the surface of a carbonaceous material (e.g. high surface activated carbon, AC) forming an electrochemical double layer, while the second process involves a reversible Li^+ insertion-deinsertion in the lattice structure of a Li-ion material, attended by faradic charge transfer reactions. During the last decades the improvements of Li-ion capacitors were mainly addressed to the development of advanced electrode materials



which realize ultrafast Li-insertion/de-insertion, maintaining relatively high energy density [1,2,3,4]. On the other hand, only few studies have been conducted on the development of high performance electrolytes for Li-ion capacitors and on understanding the interactions between carbonaceous materials and Li-salt based electrolytes.

Recently, in our group we investigated the behavior of a commercial activated carbon in various Li-salt containing electrolytes [5]. This study revealed that high surface activated carbon strongly interacts with this kind of electrolytes leading to a certain capacitance fading, which has to be minimized in order to compete with the classical EDLCs. Moreover, the aging mechanism has to be further elucidated with the help of different analysis techniques (XPS, SEM, IR, Raman etc.).

It is clear that problems related to the stability of AC in Li-salt containing electrolytes have to be solved. A potential drift of activated carbon electrodes, starting from 3.05 V vs. Li^+/Li in 1M LiPF_6 in EC:DMC (1:1) to a final potential of c.a. 3.4 V vs. Li^+/Li , was observed by different research groups [6,7]. The changing of the AC potential is a clear sign of some chemical modification of the electrode surface. In order to elucidate the mechanism of degradation it is necessary to deeply investigate the phenomena which occur at the interface activated carbon/electrolyte. Modifications occur on static (without applying any polarization) and on dynamic (e.g. cycling) mode [5]. The aim of this part of the research work is to perform post-mortem analysis on electrodes treated

in different ways. Moreover, some strategies to improve the stability will be proposed, by modification of the activated carbon properties.

A second topic regards the evaluation of the same activated carbon electrodes in electrolytes containing Na- and K-salts as alternative to the previously studied Li-salts. At the state of the art there is practically any knowledge about the interactions of AC with Na-salt and K-salt organic electrolytes. This can represent a completely novel topic which can be assessed by a master student. This work will be a proof of concept for the realization of asymmetric-hybrid systems employing activated carbon and ion-insertion materials beyond the conventional Li-ion capacitor technology. The substitution of Li with the more abundant Na and K can drive the research versus novel energy storage concepts where cheaper elements can be employed as alternative to lithium [8].

Finally, the last part of the research work regards the optimization of electrodes for Na- and K-ion capacitors. The electrode processing has a crucial impact on the electrochemical performance and electrode stability. It has been recognized that Na-alginate improves the adhesive strength and reduces the resistance of activated carbon electrodes in conventional organic electrolytes (i.e. 1M NEt_4BF_4 in AN [9]). The idea of this work is to use Na-Alginate and K-Alginate-activated carbon composite electrodes in Na-ion and K-ion containing electrolytes. It is expected a positive effect played by the presence of the same ions on the electrode and in the electrolyte as already observed for hard carbon electrodes [10].

The project outlined above covers several master or bachelor theses and the work program will be finally agreed with the candidate.

Contact:

Dr. Sonia Dsoke (sonia.dsoke@kit.edu)

References

-
- [1] D. Cericola, P. Novák, A. Wokaun, R. Kötz, J. Power Sources, 2011, 196, 10305.
 - [2] K. Naoi, S. Ishimoto, Y. Isobe, S. Aoyagi (2010), J. of Power Sources, 195:6250-6254
 - [3] V. Aravindan, J. Gnanaraj, Y.-S. Lee and S. Madhavi (2014) Chem. Rev. 114:11619–11635
 - [4] N. Böckenfeld, T. Placke, M. Winter, S. Passerini, A. Balducci (2012), Electrochim. Acta, 76:130– 136
 - [5] Tong Zhang, Bettina Fuchs, Marco Secchiaroli, Margret Wohlfahrt-Mehrens and Sonia Dsoke, Electrochimica Acta 218 (2016) 163-173
 - [6] S. Dsoke, B. Fuchs, E. Gucciardi and M. Wohlfahrt-Mehrens, J. of Power Sources, 282 (2015) 385-393
 - [7] P.W. Ruch, D. Cericola, M. Hahn, R. Kötz, A. Wokaun, J. Electroanal. Chem. 636 (2009) 128-131.
 - [8] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Chem. Rev. 114 (2014) 11636-11682
 - [9] Hai Yen Tran, Margret Wohlfahrt-Mehrens, Sonia Dsoke, Journal of Power Sources, 342 (2017) 301-312
 - [10] M. Dahbi, N. Yabuuchi, K. Kubota, K. Tokiwa, S. Komaba, Phys. Chem. Chem. Phys. 16 (29) (2014) 15007-15028