



# Electrochemical behavior and stability of a commercial activated carbon in various organic electrolyte combinations containing Li-salts



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## ARTICLE INFO

### Article history:

Received 23 June 2016

Received in revised form 13 September 2016

Accepted 25 September 2016

Available online 26 September 2016

### Keywords:

Electrolyte

LiPF<sub>6</sub>+NET<sub>4</sub>BF<sub>4</sub> mixed salt

Activated Carbon

Li-ion capacitor

Ageing

## ABSTRACT

The fast development of Li-ion capacitor (LIC) technologies requires the use of low resistance and stable electrolytes. An electrolyte for a LIC not only has to provide Li for the intercalation/deintercalation of the battery-type materials, but it also needs to be compatible with the supercapacitor material. Before designing a hybrid Li-ion capacitor device containing Li-insertion and double layer-type materials, it is necessary to understand and separate the contribution of each electrode material to the resistance, capacity and stability in the chosen electrolyte. Due to the intensive research on Li-ion batteries, the interactions of Li-salt containing electrolytes combined with Li insertion materials have been extensively investigated, and a lot of literature is available on this field. In contrast, there is only little knowledge about the exclusive interaction and compatibility of Li containing electrolytes with supercapacitor-type electrode materials (in absence of battery materials). With this purpose, this paper explores the electrochemical performance of electrodes based on commercial activated carbon (AC) in various lithium salt-containing electrolytes. A standard electrolyte for Li-ion batteries (1 M LiPF<sub>6</sub> in EC:DMC, 1:1) is evaluated and compared with an electrolyte prepared with the same salt dissolved in propylene carbonate (1 M LiPF<sub>6</sub> in PC) which is a solvent typically used in commercial supercapacitors. Furthermore, two new electrolyte solutions are proposed, based on a blend of salts 0.8 M LiPF<sub>6</sub> + 0.2 M NET<sub>4</sub>BF<sub>4</sub> in EC:DMC (1:1) as well as in pure PC. The effect of the electrolyte composition is evaluated in half and full cells. Resistances, rate capabilities, the electrochemical stability window (ESW) and cycling abilities of activated carbon electrodes are compared in different electrolytes using electrochemical impedance spectroscopy (EIS), cyclic voltammetry and galvanostatic cycling techniques. Among all electrolytes, 1 M LiPF<sub>6</sub> in PC displays the best performance with the widest ESW and an excellent cycling stability, retaining 75% of its initial capacitance after 20 000 cycles. However, due to its high viscosity, PC-based electrolytes show higher resistances in comparison to EC/DMC-based electrolytes. These results are the basis for further investigation on organic Li-salt containing electrolytes for the development of hybrid supercapacitor technology in which activated carbon and Li-insertion materials are combined together.

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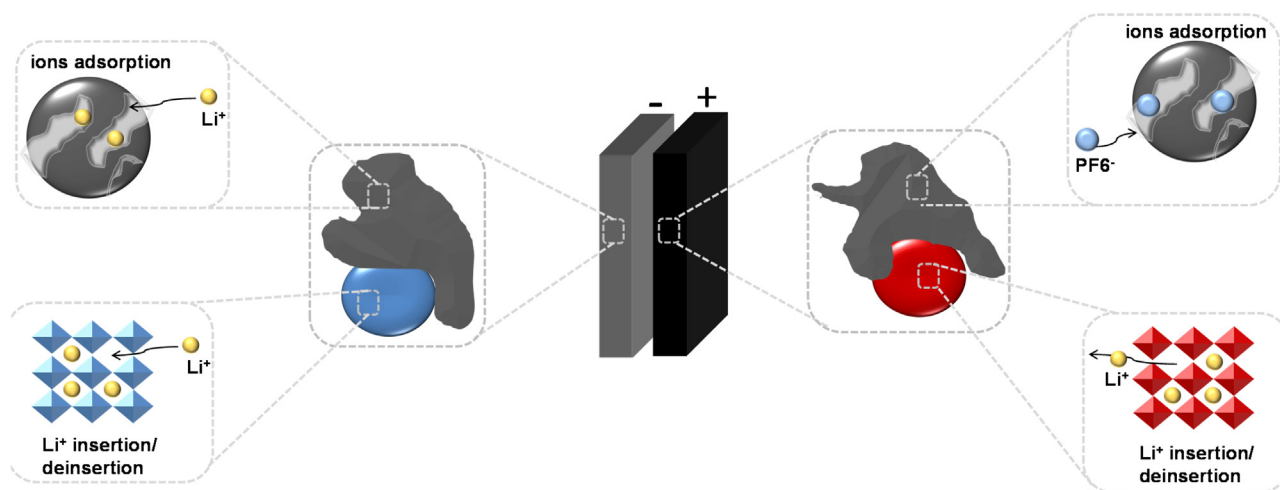
## 1. Introduction

It is currently under discussion which energy storage technology can serve as a future automotive technology where both high specific energy and power requirements can be fulfilled. Certainly, Li-ion batteries (LiBs) are one of the electrochemical energy storage systems (EESS) with the highest energy density. Even if the most recently commercialized high-power LiB systems are able to release all their energy in several minutes, they need long time to

be recharged [1,2]. On the other hand, electrochemical double layer capacitors (EDLCs) have very high power (charge/discharge in a few seconds), but they possess a low energy density [3]. The two systems can be combined in one single device employing battery and capacitor-type materials to increase the energy and power density [4–7]. As described by Cericola et al. [8], hybrid Li-ion capacitors can be divided into two main categories: the first one is the Internal Serial Hybrid (ISH) where one electrode is made with a pure capacitor and the other one with a pure Li-insertion material. The second hybridization is called Internal Parallel Hybrid (IPH) where at least one electrode consists of a bi-material electrode (capacitor and battery-type materials together in one electrode). As extreme hybridization, both electrodes are bi-material as

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**Fig. 1.** Schematic of a Li-ion capacitor based on bi-material electrodes.

depicted in Fig. 1. 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  $\text{Li}^+$  insertion-deinsertion in the lattice structure of a Li-ion material, in combination with 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 allow for ultrafast Li-insertion/de-insertion and at the same time maintain a relatively high energy density [9–12]. On the other hand, few studies have been conducted on the development of high performance electrolytes for Li-ion capacitors. The electrolyte should possess several physical-chemical properties such as high ionic conductivity (both in the electrolyte bulk and in the pores of a capacitor material) and it should display a wide electrochemical stability window [13,14]. In addition, the electrolyte must be compatible and stable with the materials contained in the electrode (e.g. high surface area activated carbon and Li-insertion materials). So far, hybrid systems have been developed using Li-salts, like  $\text{LiBF}_4$ ,  $\text{LiPF}_6$  or  $\text{LiClO}_4$  [7,15] and solvents like acetonitrile, carbonates, alkyl esters (EC, DMC, PC,  $\gamma$ -butyrolactone) and their mixtures [16,17]. However, in order to distinguish the effect of such electrolytes on the formation of the double layer, it is necessary to study the electrochemical behaviour in absence of Li-insertion materials. For this purpose, in the last few years some groups started to investigate the behaviour of battery type electrolytes on (pure) capacitor-type materials, like carbon nanofibers, carbide-derived-carbons and synthesized activated carbons [17–20]. Recently, M. Egashira et al. proposed a new interesting hybrid electrolyte based on a blend of two different salts:  $\text{LiBF}_4$  (typical Li-ion batteries salt) and  $\text{NET}_4\text{BF}_4$  (typical supercapacitor salt). This blended salt seems to have a positive effect on the capacitance of carbon nanofiber-type electrodes [21]. A similar blended salt based on  $\text{NET}_4\text{BF}_4$  and  $\text{LiPF}_6$  mixture was employed by S. Liu et al. in a full hybrid device  $\text{LiMn}_2\text{O}_4\text{-AC//Li}_4\text{Ti}_5\text{O}_{12}$  (LMO-AC//LTO) obtaining good results, especially regarding the cycling stability [22]. However, since the electrolyte has been tested in a full device containing a bi-material positive electrode (LMO-AC) and LTO as a negative electrode, its interaction with AC cannot be determined. In addition, depending on the properties of the specific carbonaceous material (surface area, porosity, functional groups, morphology etc.) the results can drastically change, if the same electrolyte is

used [23]. The Li-ion capacitor system is therefore very complex. In order to design the final device it is important to separate and analyse every possible cross-interaction of the cell components and their contribution to the stability and the electrochemical performance. Taking for example into account the three different electrode materials (LTO, LMO and AC) used to build the  $\text{LiMn}_2\text{O}_4\text{-AC//Li}_4\text{Ti}_5\text{O}_{12}\text{-AC}$  system studied by Cericola et al. [7] one has to consider the different degradation mechanisms due to the oxidation of LMO at high potentials [24], due to the gassing effect related to LTO [25] and due to the possible electrolyte decomposition on the high surface area of the activated carbon [22]. The chosen electrolyte will interact in different manner with every single material composing the electrodes. Moreover, each material/electrolyte interaction will indirectly affect the performance of the other materials in the cell [23]. A reasonable and systematic study can be performed by analysing the first material on its own (e.g. activated carbon) in various possible electrolyte combinations and then adding the next materials (for example LTO) one after another until the complete system is constructed. So far, a standard commercial activated carbon has not yet been characterized on its own in Li-salt containing electrolytes. Furthermore, no particular attention has been dedicated to the evaluation of the electrochemical stability window and to the cycling stability of the couple carbon/Li-salt containing electrolyte. This work represents the first step necessary to build a device like the one depicted in Fig. 1. The goal is to investigate the behaviour of a commercial activated carbon with various Li-salt-based electrolytes. The electrolytes of interest include a standard combination of salt/solvent normally used in Li-ion battery industry (i.e. 1 M  $\text{LiPF}_6$  in EC:DMC, 1:1) as well as a mixed salt based on  $\text{NET}_4\text{BF}_4$  and  $\text{LiPF}_6$  in two different solvent combinations: EC-DMC blend and pure PC which is a solvent used for commercial EDLCs. This study underlines the important role played by the electrolyte on the resistance response and cycling stability of the final supercapacitor.

## 2. Experimental

### 2.1. Active material

The activated carbon used in this work (HDLC-20BST-UW, coconut shell derived) was supplied by Haycarb, Sri Lanka. The declared oxygen content is  $1\% \pm 0.2\%$ . The pH value in water of the AC powder at room temperature (298.55 K) is 8.46. Physical and chemical characterization of this material is reported in the supporting information (S1–S5). The material has predominantly a

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