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A 4 Farad high energy electrochemical double layer capacitor prototype operating at 3.2 V (IES prototype)

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HIGHLIGHTS

- An innovative high energy EDLC prototype is reported as result of the IES project.
- The prototype has nominal capacitance of 4 F and operative voltage of 3.2 V.
- Maximum specific energy and power of 37 Wh kg^{-1} and 65 kW kg^{-1} are achieved.
- Promising electrochemical stability is observed upon cycling and floating tests.
- The IES components are suitable alternative to the state-of-the-art materials.

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ABSTRACT

In this manuscript we report about the realization and testing of a high-voltage electrochemical double layer capacitor (EDLC) prototype (IES prototype), which has been assembled using innovative electrode and electrolyte components. The IES prototype displays a nominal capacitance of 4 F, a maximum voltage of 3.2 V and its maximal energy and power are in the order of 37 Wh kg^{-1} and 65 kW kg^{-1}, respectively. Furthermore, it also displays good cycling stability, high capacitance retention after 80 h float test and acceptable self-discharge. Taking into account substantial improvements of the cell design and assembly procedure, the performance of the IES prototype indicates that the components utilized in this device might be suitable alternatives to the state-of-the-art materials used in high energy EDLCs.

1. Introduction

Electrochemical double layer capacitors (EDLCs) are nowadays considered among the most important electrochemical energy storage devices [1–6]. Commercially available EDLCs can be charged-discharged in seconds (or less), display high power (5–10 kW kg^{-1}) and extraordinary cycle life (up to 1 million of cycles) [1–6]. These features make EDLCs suitable for a large number of applications, including uninterruptible power supply (UPS) systems, power tools and start-and-stop systems [1]. Presently, the market of EDLCs has been evaluated in the order of more than 500 M USD [1–7]. Although smaller than that of lithium-ion batteries (LIBs), the EDLC's market represents an important reality within the global energy storage market, experiencing a constant growth in the last decade [7]. As a matter of fact, EDLCs have been indicated as interesting devices for several applications in the transportation as well as in the stationary sector [1–7]. It has been forecast that the introduction of EDLCs in these new applications would lead to a dramatic increase of their market. Nevertheless, it has been also shown that, in order to be effectively introduced in these latter applications, the energy of these devices

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should be at least 10 Wh kg^{-1} [1–7]. This value of energy, although significantly lower than that delivered by high power LIBs, is almost the double of the one delivered by state-of-the-art EDLCs, which is about 5 Wh kg^{-1}. For this reason, the development of high energy EDLCs is nowadays considered of crucial importance for the future of this technology. A proof of this is the recent commercial release of a 3 V and 3000 F cell from the worldwide leading company “Maxwell Technology” [8].

In EDLCs the charge is physically stored at the interface between the electrodes and the electrolyte, through the formation of an electrochemical double layer [1–3]. This physical storage is responsible for the high power and long cycle life but, also, for the (limited) energy previously mentioned. State-of-the-art EDLCs are based on composite electrodes containing activated carbons (AC) as active materials, carbon blacks as conductive agents and, in most of the cases, polytetrafluoroethylene (PTFE) or polyvinylidene difluoride (PVdF) as binder. The electrolyte is generally based on a solution of tetraethylammonium tetrafluroroborate (Et_4NBF_4) in acetonitrile (ACN) or propylene carbonate (PC). Using these conventional electrode-electrolyte combinations, the maximum operative voltage achievable ranges between 2.7 and 2.8 V [1–3].

In the attempt to improve the energy of EDLCs, several innovative electrode and electrolyte materials have been proposed in the past years [2,3]. Carbon nanotubes, carbide derived carbons (CDC) and, more recently, graphene, have been widely investigated as alternative to activated carbons and/or conducting agents [2–4]. Also, sodium-carboxymethyl cellulose (CMC), natural cellulose (NC) and other natural polymers have been proposed as alternative binders [2,3,7]. Regarding the electrolytes, many studies have been dedicated to ionic liquids (ILs), but also alternative solvents and salts have been recently proposed [2,3,7,9,10].

It has been shown that the use of the abovementioned alternative components might lead to the realization of devices with improved performance with respect to the state-of-the-art [1–3]. However, it is important to remark that the vast majority of the works dedicated to these new components have been carried out using small lab-cells (with a typical area of ca. 1 cm^2). The realization of such small devices represents a mandatory intermediate step towards the realization of new EDLCs (and any other electrochemical devices), but we should be aware that the performance of small systems cannot be transposed “one-to-one” to real devices. As a matter of fact, the performance of small devices is typically much higher than those of real systems (at least of a factor of 4) [11]. Taking this point into account, it is evident that the realization of prototypes of larger dimension than classical lab cells represents a very important and necessary step to understand the real impact of new materials on the performance of EDLCs.

In this manuscript we report about the realization and testing of a high voltage EDLC prototype (IES prototype) realized using innovative electrode and electrolyte components. Initially, the selection of the used materials is explained and motivated. Afterwards, the realization of the IES prototype is described in detail. Finally, the electrochemical performance of the investigated prototype is reported and critically analyzed. The work here described has been carried out within the frame of the project “Innovative Elektrochemische Superkondensatoren” (IES), which has been funded by the German federal Ministry of Education and Research (BMBF).

2. Experimental

The selected materials, namely activated carbon “P4” (provided by SGL carbon GmbH, Germany), *N*-butyl-*N*-methylpyrrolidinium tetrafluroborate ($Pyr_{14}BF_4$, provided by IoLiTec, Germany) and propylene carbonate (PC, BASF, Germany), were used as received for the preparation of the electrodes and the electrolyte, respectively.

Double-side and single-side coated electrodes were prepared following a recipe similar to that indicated in Ref. [12]. Double side coating was performed by casting the active layer on one side of the Al foil and, after drying at room temperature for two hours, applying the second coating on the opposite surface of the Al foil. After another drying step at room temperature for 24 h, the coated Al-foils were calendered. Electrodes were stamped out of with a coated area of 40 × 40 mm and dried in vacuum at 180 °C for 24 h. The composition of the final electrodes was 90 wt% active material (activated carbon “P4”), 5 wt% conductive additive (carbon black, SuperC65, Imerys Graphite & Carbon) and 5 wt% binder (sodium carboxymethyl cellulose, CMC, Walocell CRT 2000, Dow Wolff Cellulosics).

The electrolyte (1.5 M $Pyr_{14}BF_4$ in PC) was prepared in the dry room (dew point < -70 °C, i.e. R.H. <2 ppm). After dissolving the conductive salt, the electrolyte was filtered and repeatedly dried over molecular sieves (3 Å) until its water content was below 20 ppm, as measured by Karl-Fischer technique.

Electrochemical tests were performed using the VMP multichannel potentiostatic-galvanostatic system equipped with a 10 A current booster (Biologic Science Instruments, France). The cells were kept at 20 °C inside climatic chambers (KBF 115, Binder). In order to evaluate the performance of the prototype, electrochemical impedance spectroscopy (EIS), galvanostatic charge-discharge cycling, float tests as well as self-discharge investigations were carried out. Notice that all prototypes were made without reference electrode (two-electrode configuration) Impedance spectra were recorded with 5 mV AC perturbation in the frequency region from 500 kHz to 10 mHz. Galvanostatic charge-discharge cycling was performed using different current densities ranging from 0.1 A g^{-1} to 20 A g^{-1} (considering the activated carbon mass of both electrodes). The values of capacitance (C), equivalent series resistance (ESR) and coulombic efficiency (η), have been calculated as indicated in Ref. [12]. Specific energy (E) and power (P) values, based on the total activated carbon content of the prototype (i.e. m_{AC}), have been calculated according to the following equations:

$$E\left(Wh\ kg^{-1}\right) = \frac{1}{2}C\frac{V^2}{m_{AC}\cdot 3600}$$

$$P\left(W\ kg^{-1}\right) = \frac{V^2}{4ESR\cdot m_{AC}}$$

It is worth noticing that, in order to provide numbers of practical interest, both energy and power have been estimated considering the maximum usable voltage ($V = V_{max} - iR$ drop), rather than the upper cell cut-off voltage (V_{max}). Float tests were carried out with the aim of assessing the stability of the prototype. For this purpose, the prototype was charged to its maximum voltage and kept there for 180 h. Every 20 h, EIS measurements followed by short charge-discharge steps were performed to determine changes in specific capacitance and ESR. Similarly, during the self-discharge tests, charge-discharge steps were alternated to open circuit voltage (OCV) periods (each lasting 1 week) while the voltage monitored over time.

3. Results and discussion

3.1. Materials selection

The aim of the IES project was the realization of innovative EDLCs displaying higher energy and improved safety with respect