

Monolithically prepared aqueous supercapacitors

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ABSTRACT

We demonstrate a novel method to manufacture non-toxic supercapacitors with aqueous electrolyte by solution processing techniques. The supercapacitors are fabricated on flexible substrates by applying ink layers on top of each other resulting to a monolithic structure. In this way the whole component including current collectors, electrodes and separator can be implemented on one substrate without the need to align and seal two separately fabricated electrodes. Biopolymer chitosan has an important role since it acts both as separator and activated carbon electrode binder. This work facilitates an easier manufacturing of thin supercapacitor structures e.g. for Internet of Things (IoT) and sensor network applications. The capacitance range of our components is 0.26–0.43 F and equivalent series resistance 12–32 Ω .

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1. Introduction

Electrochemical supercapacitors [1,2] are energy storage devices having high specific power, wide temperature range and long lifetime. An electrochemical supercapacitor has two electrodes separated by an ionically conductive electrolyte. In practical supercapacitors the electrodes are porous and filled with the electrolyte. To prevent a short-circuit between the electrodes, a porous separator is usually installed between the electrodes. The pores allow movement of ions, while the solid structure prevents a short circuit between the two electrodes. The electrodes are typically made of activated carbon (AC) powder with a binder material [3] that can be a fluorine containing polymer such as PTFE or PVDF or e.g. a biopolymer like cellulose. The alternatives for electrolytes include organic or water based solvents with dissolved ions or ionic liquids [4].

Sensor networks and Internet of Things (IoT) devices would benefit from small inexpensive energy storage components [5] that do not contain toxic materials and can thus be recycled or incinerated with normal household waste. The primary or secondary batteries currently used for these applications typically contain metals such as lithium, silver or manganese and are encapsulated inside a metal package. Battery electrodes may also be corrosive in case a leakage takes place, and some batteries contain harmful organic solvents. Using primary batteries often results to the need to replace the batteries periodically. In

applications where long lifetime is needed, the cycle life of secondary batteries may not be long enough thus making the battery change necessary. Supercapacitors, together with an energy harvesting device such as e.g. photovoltaic cell or piezoelectric generator, can solve these shortcomings since they have long lifetime and they can be made of inexpensive non-toxic raw materials using mass production methods such as printing [6–9]. If the application requires high peak power, supercapacitors can be used in parallel with a low-power energy source to meet the demands [10].

Printed energy storage devices are typically manufactured by fabricating the electrodes separately followed by an assembly step where a separator is placed between the electrodes, electrolyte is added and the package is sealed. This method is called stacked assembly [8,11]. The aim of this work is to provide a novel manufacturing process concept that makes the fabrication of supercapacitors easier by eliminating the assembling step requiring aligning and sealing of separate electrodes and separator. The result is a monolithic structure consisting of substrate, two electrodes, two current collectors and separator.

It is also possible to avoid the alignment and assembly step by using interdigitated electrodes in the substrate plane instead of arranging them vertically [12,13]. However, the interdigitated structure leads to high equivalent series resistance (ESR) due to the long current collectors. To achieve reasonably low ESR, we prefer the geometry of stacked assembly in which the electrodes are face-to-face.

The use of environmentally benign materials in energy storage devices is beneficial [14]. The materials chosen in this work are non-toxic, facilitating the use of the supercapacitors even in

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disposable applications. We present a process in which the layers of a supercapacitor are coated on top of each other using solutions as raw materials. The separator is made of chitosan solution and it is also used as binder in electrodes. Chitosan is prepared from chitin, the second most abundant natural polymer in the world. It is non-toxic, biodegradable, and biocompatible [15]. Examples of suitable applications for our supercapacitors include energy autonomous systems together with, for example, piezoelectric or RF harvester [16,17].

2. Experimental

The materials choice of the supercapacitor was largely defined by the requirement that the total system should be non-toxic, recyclable and incineratable. In addition, the need to print the parts on top of each other required compatibility of the materials with respect to adhesion and wettability. The current collectors and active material layers were made of printing inks, avoiding the use of fluorine-containing binders. The electrolyte was an aqueous, non-toxic salt solution.

PET foil (Melinex ST506 from DuPont Teijin Films, thickness 125 μm) and PET/aluminium laminate (Walki, thicknesses of the layers 50 and 9 μm , respectively) were used as substrates. In the case of PET/Al laminate, the supercapacitor structure was on the PET side and thus the aluminium layer acted only as barrier layer. The current collectors were made of Acheson PF407C graphite ink. The ink curing temperature was chosen to be 95 $^{\circ}\text{C}$. The raw materials for the electrode ink were Kuraray YP-80F activated carbon, chitosan (Sigma-Aldrich Chitosan from shrimp shells, 50494), acetic acid and deionized water (mass percentages 25.8, 1.4, 0.6 and 72.2, respectively).

The cross-section and layout of the manufactured supercapacitors are shown in Fig. 1a and b. Both the width and the length of the supercapacitor are 50 mm and the total thickness 0.5–0.8 mm. The manufacturing process of the layer-by-layer fabricated supercapacitors starts by applying the lower graphite ink to act as current collector (red in Fig. 1a, width 34 mm). On top of that activated carbon (larger black rectangle) layer (32 mm \times 10 mm) is applied. The next layer is the separator

(blue, 26 mm \times 16 mm). In one of the layer-by-layer fabricated supercapacitor types (A) we used 40 μm thick Dreamweaver Silver AR40 cellulose paper as separator to compare the properties of chitosan and paper separators. In other types (B–E) the separator materials used were chitosan (Sigma-Aldrich 50494) as such and with talc (Finntalc M15E) as filler material. On top of the separator the upper electrode (black, 24 mm \times 10 mm) and the upper current collector is applied (green, width 18 mm). When these layers are ready, the electrolyte is added. The alternatives for encapsulation (yellow) have been the same materials used as substrate or epoxy (Loctite Power Epoxy Universal) to make the supercapacitor completely solution processable. The foils used as top encapsulation were heat-sealed using Paramelt Aquaseal X2277 polyolefin dispersion.

The manufacturing process of the reference supercapacitors (F) is partly similar to the one used with layer-by-layer fabricated supercapacitors and is described in detail in the article by Keskinen et al. [8]. Two current collectors are made (graphite ink, red and green in Fig. 1b) and AC ink layers applied on them. The same Dreamweaver separator is assembled between the electrodes, the electrodes and separator are impregnated with electrolyte and the whole system is heat-sealed with Paramelt Aquaseal X2277 (gray).

There are several requirements for the separator layer. Obviously, it must be ionically conductive to facilitate the electrical operation of the supercapacitor. It also needs to guarantee the electrical insulation between the electrodes to prevent short circuits. In addition, it has to be compatible with the graphite and activated carbon inks first by adhering on them and secondly allow the application of the upper activated carbon and graphite ink layers.

A laboratory scale doctor blade coater (mtv messtechnik) was used for applying the current collector and AC inks. The AC ink was dried at room temperature resulting in films with thickness of 70–100 μm . Stencils were used to define the lateral dimensions of the current collectors, electrodes and chitosan separators. The registration accuracy in the plane of the substrate is limited in our case by the manual alignment of the stencil and is in practice of the order of 0.5 mm. The wet thickness of the current collectors

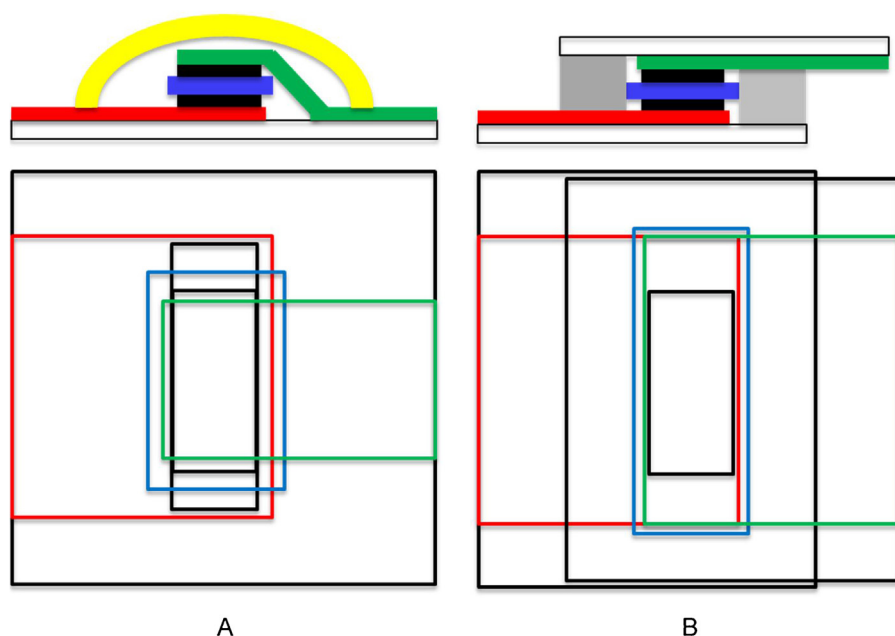


Fig. 1. Schematic cross-sections and layouts of the layer-by-layer fabricated supercapacitor (a) and the conventional supercapacitor (b) used as reference. The vertical and horizontal dimensions in the cross-section figures are not in the same scale.

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