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# Asymmetric and symmetric supercapacitors based on polypyrrole and activated carbon electrodes



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#### 1. Introduction

Supercapacitors [1,2] are of significant current interest since they can provide high peak power while their energy densities still are considerably higher than those of conventional capacitors. A supercapacitor consists of two electrodes separated by an electrolyte where the electrodes typically are made of activated carbon although electrodes made of electronically conductive polymers also can be employed [3–5].

Applications of supercapacitors include sensors and sensor networks [6] as well as active type RFID tags [7] which require easily scalable  $\mu$ W to mW power sources to operate under optimal conditions. In sensor applications the supercapacitors can be used to store energy and provide power peaks that primary energy sources such as photovoltaic cells or biological power sources are unable to deal with. The very good cycling stability of supercapacitors also facilitates applications involving wearable electronics and smart clothing [8] for health, well-being and sports applications. Since the supercapacitors in many of these

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#### ABSTRACT

Supercapacitors were prepared using either two polypyrrole (PPy) composite electrodes or one PPy composite and one activated carbon electrode. The PPy composite electrodes were either freestanding paper-like sheets or PPy films printed on graphite ink coated aluminium/PET laminate substrates, using *Cladophora* algae derived cellulose as the substrate or binder, respectively. The specific capacitance of the PPy electrodes was found to be about 200 Fg<sup>-1</sup> depending on the manufacturing method, yielding supercapacitors with capacitances between 0.45 and 3.8 F and energy efficiencies of over 90%. For an asymmetric device with activated carbon positive electrode and PPy negative electrode a capacitance loss of 5% was seen after 14300 cycles.

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applications are intended to be used as integrated parts of recyclable or disposable products, the supercapacitor as well as all the other components of the device should ideally be environmentally friendly and either biodegradable or combustible. For instance aqueous electrolytes are preferred to organic ones and fluorine containing electrode binders should be avoided. Furthermore, the materials and manufacturing costs should be low. As these demands generally are incompatible with the use of conventional battery or supercapacitor technology it is evident that there is a need for new supercapacitor materials and manufacturing procedures.

Recent reports of modifying the structure of polypyrrole electrodes have shown the potential of its use in supercapacitors. For instance carbonaceous coating has been reported to improve the cycle-life [9] and various graphene composites have resulted to excellent electrical properties [10,11]. As has been demonstrated recently [12], composites of cellulose and electronically conducting polymers such as polypyrrole can be used as electrode materials for supercapacitor devices. These composites can provide higher energy densities than carbon based electrode materials due to the fact that the energy storage relies mainly on redox reactions taking place throughout the volume of the conducting polymer coating rather than as a result of combined surface confined redox reactions and double layer charging effects.







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One limitation with the composite based symmetric supercapacitors described so far is that the energy density is rather low. This is a result of the fact that the cell voltage typically is limited to less than one volt and the symmetric setup which means that only half of the energy stored in the electrodes can be utilized. To be able to increase the cell voltage and the energy density it is therefore interesting to also study different asymmetric supercapacitor devices. Although asymmetric supercapacitors containing electrodes made of electronically conducting polymers have been studied frequently [3] we are not aware of any previous work with cellulose based composite electrodes.

To be able to manufacture inexpensive and environmentally friendly supercapacitor devices there is also a need for the development of new up-scalable manufacturing processes. It is therefore of significant importance to investigate the possibilities of manufacturing cellulose and conducting polymer based electrodes using approaches compatible with different printing processes. Screen printing method has been used to manufacture supercapacitors with activated carbon electrodes and aqueous [13] or ionic liquid [14] electrolytes. Xu et al. have used polyaniline/ graphene thin-film electrodes in supercapacitors made by printing [15]. Screen printing has also been used in wearable supercapacitors to produce electrodes with carbon fibre current collectors [16].

In the present work, the electrochemical performance of symmetric and asymmetric supercapacitors containing cellulose and polypyrrole composite electrodes and activated carbon are compared. The devices, which contained an aqueous electrolyte and either sheets of composite electrodes or electrode made using a printing process, are characterized employing chronopotentiometry and cyclic voltammetry.

#### 2. Experimental

#### 2.1. Electrode fabrication

#### 2.1.1. PPy Cladophora composite electrode sheets

Cellulose from the Cladophora sp. algae was extracted as described previously [17]. Pyrrole (>97%) was purchased from Sigma-Aldrich while iron (III) chloride hexahydrate (>99%) and Tween 80 were purchased from VWR international. All chemicals were used as received. To manufacture the composite, 300 mL Cladophora cellulose was first dispersed in 60 mL water by sonication during 10 min. A solution containing 1.5 mL pyrrole and one drop of Tween 80 dissolved in 50 mL of 0.5 M HClag was then added to the dispersion of the cellulose. An iron salt solution, prepared by dissolving 12.857 g FeCl<sub>3</sub> in 100 mL, 0.5 M HCl<sub>aq</sub>, was subsequently added to the cellulose-pyrrole dispersion and polymerization was allowed to continue for 30 min. The polymer composite was washed with 5L of  $0.5 \text{ M HCl}_{aq}$  and 1L of 0.1 MNaClag in a Büchner funnel. After 2 min of additional sonication, the polymer composite was dried in the funnel to form a black wet composite cake. The resulting composite material was pressed in a vise overnight and dried for at least three days at ambient conditions.

#### 2.1.2. Printed PPy electrodes

The electrodes were printed on graphite ink (Acheson PF407C) coated aluminium/PET laminate substrate made by CJI China Film. In this configuration the graphite layer protects the aluminium from corrosion caused by the electrolyte. In the manufacturing of the printed electrodes, 40 g of a 0.1 wt% *Cladophora* sp. algae cellulose (CAC) solution was first mixed with 0.6 mL pyrrole (Sigma–Aldrich 131709) under nitrogen. 40 mL of a solution containing of 0.5 M FeCl<sub>3</sub> (Merck 3943) and 0.5 M HCl<sub>aq</sub> was then added drop wise (with an addition every 10 min during 80 min) to

the solution containing pyrrole and cellulose. The polymerization reaction was subsequently allowed to proceed for three hours while stirring the solution. The resulting composite material was filtered off employing a Büchner funnel containing a nylon membrane (Merck Millipore GNWP 47 mm-d) and was then washed with 2 L of 0.5 M HCl followed by 0.4 L of 0.1 M NaCl. The composite was dried between nylon membranes until the dry matter content of ~20 wt% was reached. Printable ink was prepared by mixing CAC-PPy with chitosan (3 wt% in 1% acetic acid) and polyvinylpyrrolidone (PVP, 20 wt% in H<sub>2</sub>O) in ratio 0.54:0.32:0.14 (dry-wt%), respectively. The CAC-PPy was applied with a 20 mm × 20 mm stencil (Teonex Q51, thickness 188  $\mu$ m), and the obtained electrode was subsequently dried in a box oven at 60 °C for 2 min.

#### 2.1.3. Printed activated carbon electrodes

In the manufacturing of the activated carbon (AC) electrodes Norit DLC Super 30 activated carbon powder was used in the form of an ink. This water based ink contained activated carbon and chitosan binder in a 20:1 ratio. The activated carbon as well as the CAC-PPy sheet had geometrical areas of 15 mm × 15 mm. In the case of the printed CAC-PPy devices, the geometrical area of the AC electrodes was 20 mm × 20 mm. The activated carbon ink was dried at room temperature resulting in a thickness of about 70  $\mu$ m. A. laboratory scale bar coater (K-coater) was used for applying the activated carbon ink on the substrate.

#### 2.2. Supercapacitor assembly

#### 2.2.1. Polypyrrole sheet supercapacitors

In the similar way as with printed electrodes also with PPy sheets graphite ink coated aluminium/PET laminates were used as substrates. NKK TF40-50 cellulose paper was used as separator. The electrolyte used was 5 M NaNO<sub>3</sub> in water adjusted to pH 7 with 0.1 M phosphate.

A schematic cross-section of the supercapacitor structure is shown in Fig. 1. The dimensions of the device were about  $70 \text{ mm} \times 50 \text{ mm}$  and the total thickness varied between 0.6 and 1.5 mm depending on the thickness of the electrodes.

### 2.2.2. Printed asymmetric polypyrrole activated carbon supercapacitors

Printed electrodes were separated by Terkab Ilam 33 separator paper and moistened with a 0.67 M NaNO<sub>3</sub> gel-electrolyte. The gelelectrolyte was prepared by mixing 50 ml 0.1 M NaPBS (pH 7) with 25 mL, 2 M NaNO<sub>3</sub> solution. 55 mL of this solution was mixed with 25 g of polyethylene glycol and 20 g of PVP and mixed until a homogenous gel was achieved. Two cells containing a CAC-PPy negative electrode and an AC positive electrode and two cells with the reverse electrode set-up were characterized.



**Fig. 1.** Schematic view of the supercapacitor structure used both with sheet and printed electrodes. The horizontal and vertical dimensions are not in scale as the thickness was 0.6–1.5 mm while the length was 70 mm.

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