

## ACTIVATED CARBON FIBERS DERIVED FROM SEA BALLS FOR THE USE AS SUPERCAPACITOR ELECTRODES

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### Abstract

Sea balls (*pillae marinae*) were impregnated with diammonium hydrogen phosphate (DAHP), carbonized, and activated using carbon dioxide or steam. Thus, activated carbon fibers (ACFs) with unique morphology and specific surfaces of 243 m<sup>2</sup> g<sup>-1</sup> were produced. These ACFs were studied as electrode materials for supercapacitors that achieved specific capacities of 38 F g<sup>-1</sup> in an organic electrolyte, resulting in specific energy for the supercapacitor of 9.7 W h kg<sup>-1</sup>.

**Keywords:** Activated carbon, electrode materials, supercapacitor, energy storage, sea balls, *pillae marinae*

### 1. INTRODUCTION

Energy storage is a key technology in the ongoing efforts to combat climate change. Supercapacitors are highly regarded energy storage devices due to their ability to absorb and release large amounts of energy very quickly. They are also characterized by their long service life of over 1 million charging cycles and low maintenance costs [1-3]. In this type of energy storage, the mostly carbon-based electrode materials are of central interest.

A promising material for supercapacitor electrodes is activated carbon fibers (ACFs). These ACFs have a high specific surface area, a well-suited pore structure, and possess excellent conductivity in the electrode due to their fiber shape, as we were able to find out in previous work [4-6]. When ACFs are used in electrode materials, high-purity substances such as viscose fibers, pitch fibers, or polyacrylonitrile fibers are usually used. These precursors have to be synthesized in advance in a complex process.

In this study, sea balls will be used as a starting material for the production of ACFs. In contrast to other starting materials for ACFs, no complex manufacturing process is required here; the sea balls are a naturally occurring, biological raw material. They are produced by the wave action in the sea by tearing out and felting dead parts of the seagrass (often neptune grass). When they are washed up on beaches they are removed by heavy machinery. Apart from its use as an insulating material, there are no known industrial applications for this raw material.

### 2. MATERIALS AND METHODS

The sea balls were collected on the beach of Talamone, Italy. They were washed in distilled water in a drum hoop mixer for 1 h and dried at 80 °C in a drying oven. Depending on the sample, treatment with a 10 wt.% DAHP solution was performed (see **Table 1**). For this purpose, the samples were soaked in the 10 wt.% DAHP solution for 15 min and then dried at 80 °C overnight. Carbonization was carried out in a chamber furnace (HTK8, Gero, Germany) with a heating rate of 10 °C min<sup>-1</sup> to 850 °C under nitrogen atmosphere. Before cooling, the samples were held isothermally at the target temperature for 30 min. Activation was carried out in a rotary

kiln (RSR-B 120/500/11, Nabertherm GmbH, Germany). Prior to use, N<sub>2</sub> was used to purge the apparatus at a flow rate of 100 l h<sup>-1</sup>. Samples were then heated from room temperature to the desired activation temperature T under an N<sub>2</sub> flow rate of 50 l h<sup>-1</sup>. To ensure that the temperature was uniform throughout the reaction chamber, the sample was kept isothermal under the nitrogen flow for 30 min. Then, the N<sub>2</sub> flow was terminated and replaced by CO<sub>2</sub> at the desired flow rate Q (80 l h<sup>-1</sup>). The completion of the activation process was marked by stopping the CO<sub>2</sub> flow and restarting the N<sub>2</sub> flow until the oven cooled down to room temperature.

**Table 1** Overview of the prepared samples

Sample	Sample treatment	Activation conditions
SB_165	Washing, drying; carbonization	T = 870 °C; Q = 80 l h <sup>-1</sup> ; t = 165 min
SB_DAHP_165	Washing, drying; impregnation with a 10 wt.% DAHP solution; drying; carbonization	T = 870 °C; Q = 80 l h <sup>-1</sup> ; t = 165 min
SB_DAHP_285	Washing, drying; impregnation with a 10 wt.% DAHP solution; drying; carbonization	T = 870 °C; Q = 80 l h <sup>-1</sup> ; t = 285 min

The morphology of the samples was investigated using Scanning Electron Microscopy (SEM) with Phenom ProX (Thermo Fisher Scientific, USA). The chemical composition was determined by using energy dispersive X-ray spectroscopy (EDX) by using the same instrument. The acceleration voltage was 15kV and a backscattered electron detector (BSD) was used.

The specific surface area of the activated sea balls was determined using physical adsorption of nitrogen at -196 °C on an automatic volumetric sorption analyzer AutosorbIQ MP-XR (Quantachrome Instruments, USA) using the Brunauer-Emmet-Teller (BET) method. The adsorbed gas volume was measured at a relative pressure range of 0.1 - 0.3 using 40 – 50 mg of sample. Prior to the measurements, the samples were outgassed at 300 °C for 4 h under vacuum.

The electrode production can be found elsewhere [6,7]. The cells were assembled using a Swagelok®-type 2-electrode test cell with two symmetrical ACF electrodes as a counter and working electrode soaked with a 1 M triethylmethylammonium tetrafluoroborate (TEMA BF<sub>4</sub>, >98.0%, TCI Deutschland GmbH, Germany) solution in propylene carbonate (PC, 99.5%, Acros Organics N.V., Belgium) as an electrolyte with a separator (Celgard® 3401, Celgard, USA) between them. A C-coated aluminum foil (z-flo 2651, Coveris Management GmbH, Austria) was used as a current collector. All cells were assembled under nitrogen atmosphere avoiding moisture and oxygen. Cyclic voltammetry (CV) and galvanostatic discharge curve (GDC) measurements were performed using a potentiostat (Vertex.One, Ivium Technologies BV, The Netherlands). The gravimetric capacitance C<sub>S</sub> was determined by CV and GDC using the following equations (1) and (2):

$$C_S = \frac{\int_{V_1}^{V_2} i dV}{2 m_E v} \quad (1)$$

$$C_S = \frac{2 I t}{m_E \Delta V} \quad (2)$$

The specific capacitance C<sub>S</sub> of one electrode is determined by the integral  $\int_{V_1}^{V_2} i dV$  of the positive part of the 5<sup>th</sup> CV curve, limited by the V<sub>2</sub> and V<sub>1</sub> of the cell voltage ΔV, scan rate v and the mass of the active material m<sub>E</sub> of one electrode. For the GDC measurements, C<sub>S</sub> is calculated using the current I, the discharge time t, m<sub>E</sub> and ΔV. Energy density E<sub>S</sub> and power density P<sub>S</sub> for the device were calculated using equations (3) and (4):

$$E_S = \frac{1}{8} C_{S,GDC} (\Delta V)^2 \quad (3)$$

$$P_S = \frac{E_S}{t} \quad (4)$$

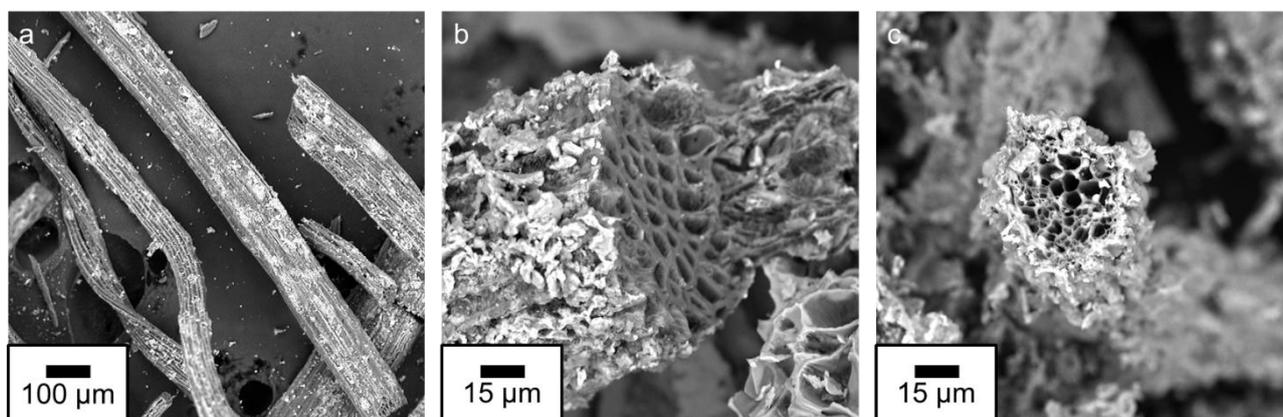
### 3. RESULTS AND DISCUSSION

The sea balls are 3 - 7 cm in diameter before carbonization and consist of a dense mesh of fibers (**Figure 1**). This structure is retained even after carbonization.



**Figure 1** Impregnated sea ball before and after carbonization

The morphology of the sea balls after carbonization and after activation (SB\_DAHP\_165) was studied by SEM (**Figure 2**). In the case of the impregnated samples, the fiber structure is preserved both after carbonization and after activation by carbon dioxide. Without the DAHP treatment, the sea ball disintegrates during activation, leaving only ash and no carbon structure. The fibers differ strongly in thickness and length (see **Figure 2a**). At the fracture points of the fibers, it can be seen that the fibers possess a unique honeycomb-like structure.



**Figure 2** SEM micrograph of the carbonized (a and b) and the activated sea ball (b)

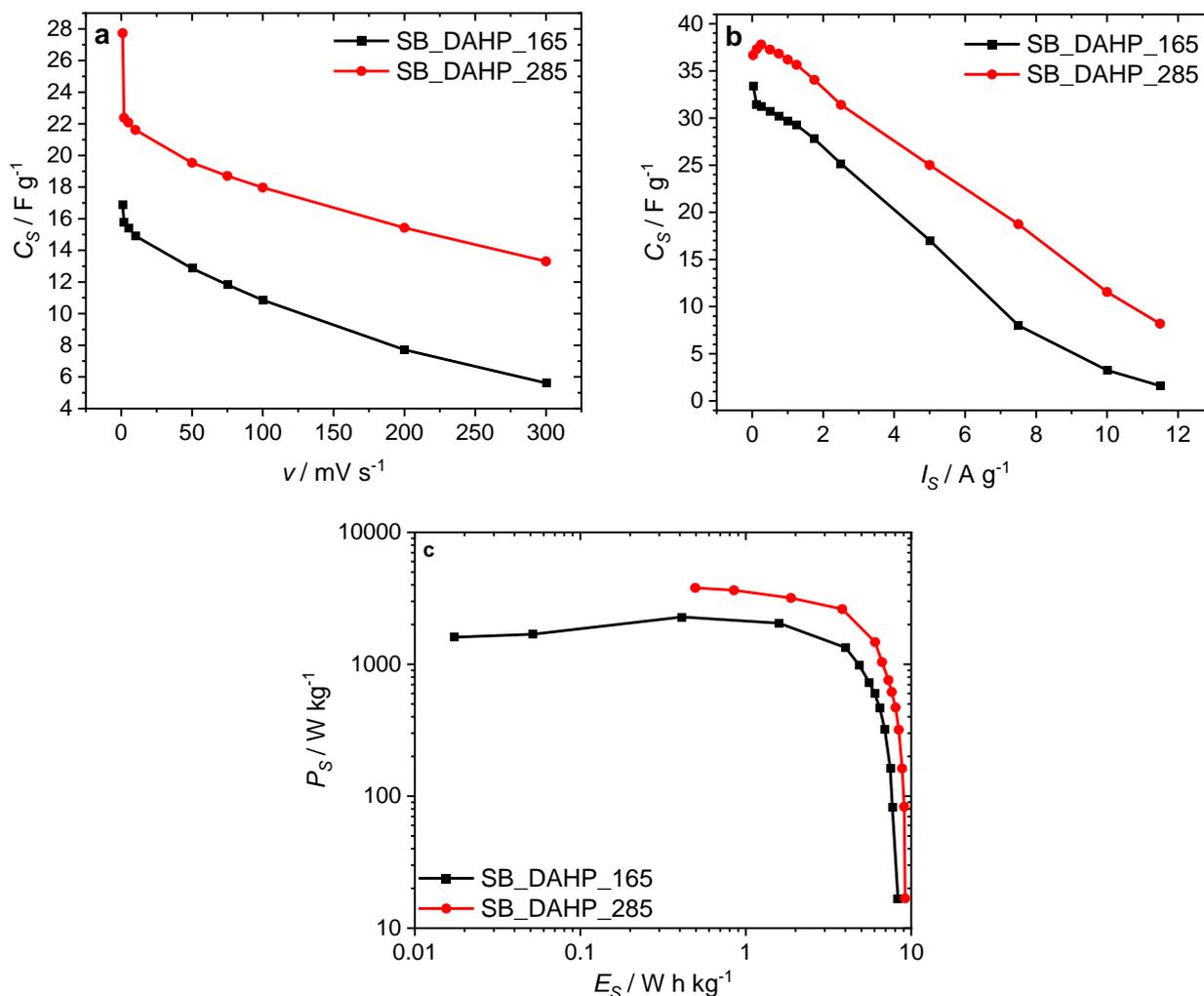
After activation, only the samples treated with DAHP form a carbon structure. The yield after 165 min activation time is 68.4 %, the specific surface area of the sample is 200 m<sup>2</sup> g<sup>-1</sup>. With the longer activation time, the activation yield decreases to 33.9 %, but the specific surface area increases to 243 m<sup>2</sup> g<sup>-1</sup>.

**Table 2** Yield of the activation step, specific surface areas, and total pore volumes of the activated samples.

Sample	Yield of the activation / %	Specific surface area / m <sup>2</sup> g <sup>-1</sup>	Total pore volume / cm <sup>3</sup> g <sup>-1</sup>
SB_165	-	-	-
SB_DAHP_165	68.4	200	0.13
SB_DAHP_285	33.9	243	0.15

For further characterization, test cells were prepared from the ACFs and examined by CV and GDC. The sample activated for 165 min reached a maximum specific capacitance of 17 F g<sup>-1</sup> at CV at the lowest scan rate of 2 mV s<sup>-1</sup>. The sample activated for 285 min showed a maximum specific capacitance of 28 F g<sup>-1</sup>. With

increasing scan rate the specific capacitance decreased to  $13 \text{ F g}^{-1}$  at  $300 \text{ mV s}^{-1}$ . For the specific capacitances calculated from the galvanostatic measurements (**Figure 3b**), the sample SB\_DAHP\_165 reaches a maximum value of  $33 \text{ F g}^{-1}$ , while the sample reaches a value of  $38 \text{ F g}^{-1}$ . The longer activated DAHP-impregnated sea ball also reaches the highest specific energies, calculated per test cell, of  $9.7 \text{ W h kg}^{-1}$  and the highest specific power of  $3800 \text{ W kg}^{-1}$  (**Figure 3c**).



**Figure 3** Specific capacitance per electrode  $C_s$  derived from CV (a) and from GDC (b) as well as specific power  $P_s$  and specific energy  $E_s$  derived by GDC (c)

#### 4. CONCLUSION

Sea balls could be successfully used to produce ACFs that can be used as electrode material for supercapacitors. It was shown that the use of an impregnate is essential, otherwise no ACFs could be obtained. In the prepared ACFs, the unique honeycomb-like porous macroporous structure from the precursor remains intact. Overall, it can be easily seen that the higher specific surface area achieved by the longer activation results in higher specific capacities, powers, and energies. The achieved capacities per electrode of  $38 \text{ F g}^{-1}$  are relatively low compared to other precursors, but the achieved specific energy density of  $17 \text{ W h kg}^{-1}$  per test cell is promising.

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