

Bio-Based Materials for Supercapacitor

M. Cadek¹, O. Oettinger¹, M. Wachtler¹, E. Raymundo-Piñero², F. Béguin²

¹SGL Group – The Carbon Company, Meitingen, Germany

*²Centre de Recherche sur la Matière Divisée, CNRS-University, 1B rue de la Férellerie, 45071
Orléans Cedex 02, France*

Email: martin.cadek@sglcarbon.de

Introduction

Due to a strong growth of the energy storage market in applications such as portable electronics and hybrid electric/electric vehicles (HEV/EV), an increasing demand for light-weight and compact electric power sources is developing. Electrochemical double layer capacitors (EDLC) are excellent candidates for applications demanding high charging rates and cycleability, above 1 million cycles, while storing a moderate amount of energy at high power densities. The energy storage mechanism in this case is mainly based on an accumulation of charges in the electrical double layer formed at the electrode/electrode interface. In general, the specific capacitance of EDLC is approximately $10 \mu\text{F}/\text{cm}^2$ ^[1]. Classical materials used in EDLC are activated carbons based on coke, char or pitch, with high specific surface area but relatively low volumetric capacitance. Production and purification of these materials are time consuming, expensive and have a large environmental impact.

Materials presenting pseudo-faradic properties are promising candidates to replace the above mentioned activated carbons. Here, specific capacitance values of $100\text{-}400 \mu\text{F}/\text{cm}^2$ were observed^[2-3], which is related to the charge/mass transfer between the electrode and the electrolyte. Since the surface functionality is involved in pseudo-faradic reactions, a high pore volume is therefore not necessary, and consequently the materials conductivity is not too much reduced.

In this work, experimental values of gravimetric capacitance will be shown up to $250 \text{ F}/\text{g}$ ($>200 \text{ F}/\text{cm}^3$) at energy densities above $20 \text{ Wh}/\text{kg}$ ($>10 \text{ Wh}/\text{L}$) while using an aqueous electrolyte at a potential window up to 1.4 V .

Keywords: Carbonisation, Porous carbon, Electrochemical properties

Experimental

The raw material used in this work is an oxygen rich regenerative bio-based seaweed material^[3], which is available at low cost and industrial scale. Carbonaceous materials were produced under controlled inert atmosphere at 600°C .

The porous texture was investigated by using N_2 adsorption at 77K and CO_2 adsorption at 273K (Autosorb-6 and Autosorb-1MP, Quantachrome). Imaging of the materials was performed using a transmission electron microscope (Phillips CM20). Analysis of surface functionalities was done by X-ray photo electron spectroscopy (XPS) with a VG ESCALAB 250 spectrometer (Al $K\alpha$ monochromatic source). The electrochemical characteristics were determined in $1 \text{ mol}/\text{L} \text{ H}_2\text{SO}_4$ electrolytic medium, in two- or three-electrode cells, using the galvanostatic, voltammetric and impedance spectroscopy techniques (VMP multi channel potentiostat-galvanostat, Biologic, France)

Results and Discussion

As shown in figure 1, the carbons from seaweeds exhibit some tubular morphology. Here, it is expected that the tubular shape will lead to an improved electrical conductivity of the electrode material.

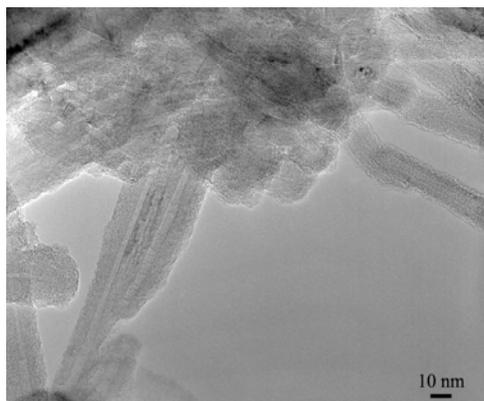


Figure 1. Transmission electron microscopy micrograph of carbonized seaweed at 600°C in inert atmosphere.

Furthermore, as shown in figure 2a, we compared the capacitance performance of both lab-scale and pilot scale produced materials. It can be observed that the voltammetry curves are overlapping almost exactly. The achieved capacitance values for the lab-scale sample was determined to be 255 F/g and for the pilot scale sample 252 F/g. The voltage windows for the plotted measurements were found to be 1.2V, resulting in energy densities of 14.7 Wh/kg for the lab-scale carbonized seaweed sample and 13.5 Wh/kg for the pilot-scale carbonized seaweed sample. Figure 1a shows that both materials exhibit much higher capacitances and voltage windows than a commercial available activated carbon for supercapacitors. The commercial material (based on KOH activated petrol pitch) was achieving only a capacitance of 203 F/g at voltage window of 0.7 V resulting in an energy density of only 4.1Wh/kg.

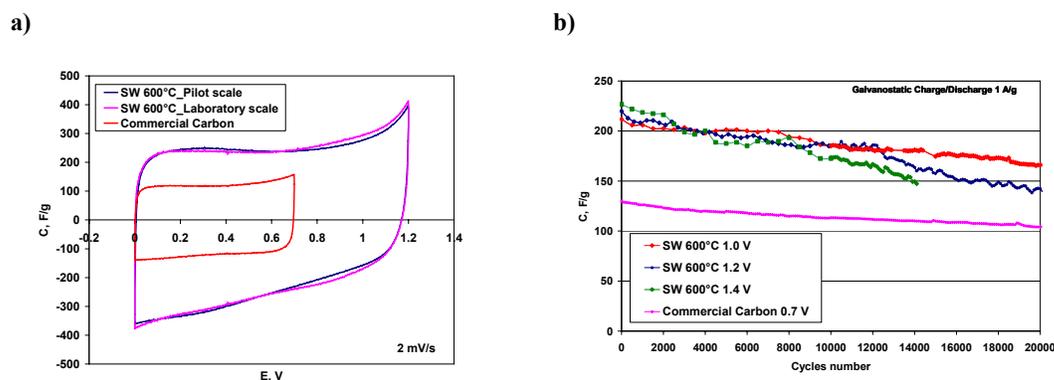


Figure 2. a) Voltammetry curves of lab-scale and pilot-scale carbonized seaweeds. Measurements were performed at 2 mV/s; **b)** Galvanostatic cycling performed at a regime of 1 A/g with different voltage windows: 1.0 V, 1.2 V and 1.4 V. The results were compared to a commercial carbon, based on KOH activated petrol pitch, at a voltage window of 0.7 V.

Figure 2b shows the galvanostatic cycling at a relative high regime of 1A/g for a pilot-scale produced sample of carbonized seaweeds at several voltage windows: 1.0 V, 1.2 V and 1.4 V. It can be observed that the capacitance losses are 15% and 20% at 20.000 cycles for the 1.0 V and 1.2 V windows, respectively, and 20% for the 1.4 V

window at 15.000 cycles. By comparison, for the commercial sample, the capacitance loss reached 10% after 20.000 cycles at 1 A/g, but with a voltage window of only 0.7 V.

Shown in figure 3 are Ragone plots for the pilot-scale seaweed sample carbonized at 600°C and a commercially available activated carbon sample. The values shown in this graph were re-calculated into volumetric energy and volumetric power densities, using densities values of 0.79 g/cm³ for the carbonized seaweeds and 0.47 g/cm³ for the commercially available activated carbon sample. It can be clearly observed that the carbonized seaweed samples are showing a much higher energy density and power stability compared to the activated commercial sample. At the 10 second diagonal, it was found that the energy values were 6.0 Wh/L for measurements at 1.4V, 5.4 Wh/L for measured values at 1.2 V and only 0.9 Wh/L for the commercial activated carbon at 0.7 V.

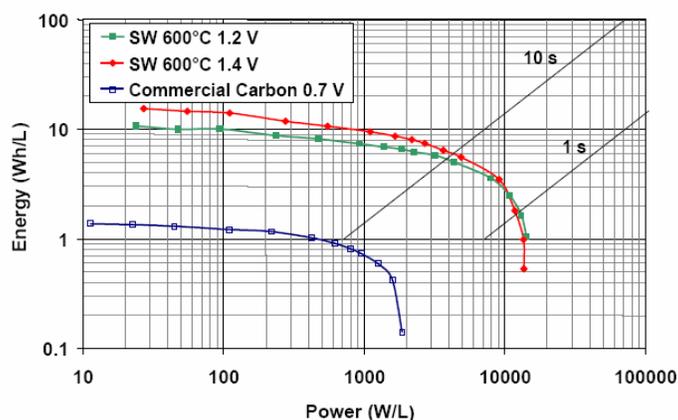


Figure 3. Ragone plot of pilot-scale carbonized seaweeds at 1.2 V and 1.4 V compared to a commercial activated carbon at 0.7 V.

Conclusions

The production method for these novel supercapacitor electrode materials does not involve any environmental unfriendly ingredient. In addition, an aqueous electrolyte, environmental friendly electrolyte, was used for getting the above mentioned results, up to a voltage stability window of 1.4 V. Compared to commercially available activated carbons, this material shows a much better performance combined with high cycleability.

Further work is in progress at present to additionally allow organic media, such as acetonitrile, to be applied as electrolyte.

References

- [1] Conway, B. E. 1999. Electrochemical capacitors, Kluwer Academic, Plenum Publishers, New York.
- [2] Frackowiak, E. and Béguin, F. 2001. Carbon materials for the electrochemical storage of energy in capacitors, *Carbon*, 39: 937-950.
- [3] Raymundo-Piñero E., Laroux, F., and Béguin F. 2006. A High-Performance Carbon for Supercapacitors Obtained by Carbonization of a Seaweed Biopolymer, *Advanced Materials*, 18: 1877 – 1882.