Energy Storage

KEYWORDS: Energy Storage / Supercapacitors/ Biomass-derived carbon electrodes / Flexible supercapacitors

Biomass-derived carbons were prepared and modified by introducing heteroatoms (O, P) and/or incorporating carbon nanotubes (CNTs) during the synthesis/activation procedure. The use of CNT materials as electrodes in flexible energy storage devices was investigated. Cork-based electrodes are under investigation for the development of new eco-conscious supercapacitors to enable the energetic transition.

Introduction

Supercapacitors are energy storage devices capable of supplying high power density, that is, fast energy delivery. The capacitance of a supercapacitor is directly related to the properties of the electrode material; further breakthroughs in the development of advanced materials are required to increase the amount of stored energy without compromising the power density. Nanostructured porous carbons can play a decisive role in the development of efficient and cost-effective electrochemical devices for energy conversion and storage. The various methods that have been reported for the synthesis of nanostructured carbons were reviewed [1].

Current Development

Glucose-derived carbons The valorization of biomass (glucose) as a source of electrode carbon materials through hydrothermal processes was investigated [2]. Two strategies have been addressed during the synthesis of the glucose-derived carbons: the incorporation of carbon nanotubes (CNTs) into the initial precursor solution [2] and the incorporation of phosphorus functionalities [3].

Glucose-derived carbon/carbon nanotube (CNT) hybrid materials were prepared by hydrothermal carbonization of glucose in the presence of CNTs and subsequent carbonization, physical activation, or chemical activation [2]. The proportion of CNTs added during the hydrothermal polymerization of glucose was varied to ascertain the optimum dose to maximize the performance of the carbon hybrids in supercapacitor applications. Both the thermal treatment applied and the addition of CNTs lead to changes in the textural and chemical properties of the activated carbons. It was observed that samples bearing CNTs exhibit a higher number of nucleation centers for glucose oligomers to polymerize, and consequently, the behavior of the hydrothermal carbon toward activation differs according to the activating agent employed. Moreover, the initial chemical speciation dominated by acidic groups shifts to more basic functionalities (quinones and carbonyl groups) with the addition of CNTs. The effect of the different physicochemical properties of the prepared carbons on their electrochemical behavior was evaluated. The addition of 2 wt % of CNTs and subsequent chemical activation leads to electrode materials yielding 206 F g^{-1} and 78% of capacitance retention up to 0.8 V and 20 A g^{-1} and high rate cyclability (97% after 5000 cycles) (Fig.1). The outstanding performance is ascribed to the high surface area, narrow mesopores, and phenol/carbonyl surface functionalities, which enhance molecular diffusion, the amount of stored energy, and electronic transportation, respectively.

P-doped carbon hybrids were prepared by hydrothermal carbonization of glucose in the presence of CNT, followed by chemical activation with phosphoric acid. The role played by phosphoric acid on the final textural and chemical properties of the samples was thoroughly investigated by varying the activation temperature. Temperatures above 700 °C were needed to chemically activate the samples, while 800 °C is the optimum temperature to generate the largest amount of micropores. In addition to oxygen functional groups such as carboxylic acids, anhydrides, lactones, phenols and carbonyl quinones, several phosphorus functional groups are also detected. At 700 °C, only C–O–P–O_3 and C–P–O_3 groups are observed; meanwhile, C_3–P=O and C_3–P groups appear at 800 °C and 900 °C, respectively. The oxygen moieties bonded to carbon and the phosphates (C–O–P–O_3) contribute significantly to the pseudocapacitance; the oxygen groups linked to phosphorus (C–P–O_3 and C_3–P=O) enhance the electrostatic charge and the non-oxygen functional group (C_3–P) increases the capacitance retention. The P-doped hybrid treated at 800 °C resulted in a porous carbon material with 806 m^2 g^{-1} active surface area and high phosphorus content (6.6%) that increases the total capacitance from 26 (non-doped hybrid treated at 700 °C) to 133 F g^{-1} at 1 A g^{-1} (Table 1).

Table 1. Specific capacitance determined from the cyclic voltammograms using the glucose-derived carbons in a two-electrodes cell.

Samples	Specific Capacitance, C_s/ F g^{-1}
CG-CNT	26±3
CG-CNT-P700	82±3
CG-CNT-P800	116±6
CG-CNT-P900	101±6
CG-CNT-P_{op}700	8±2

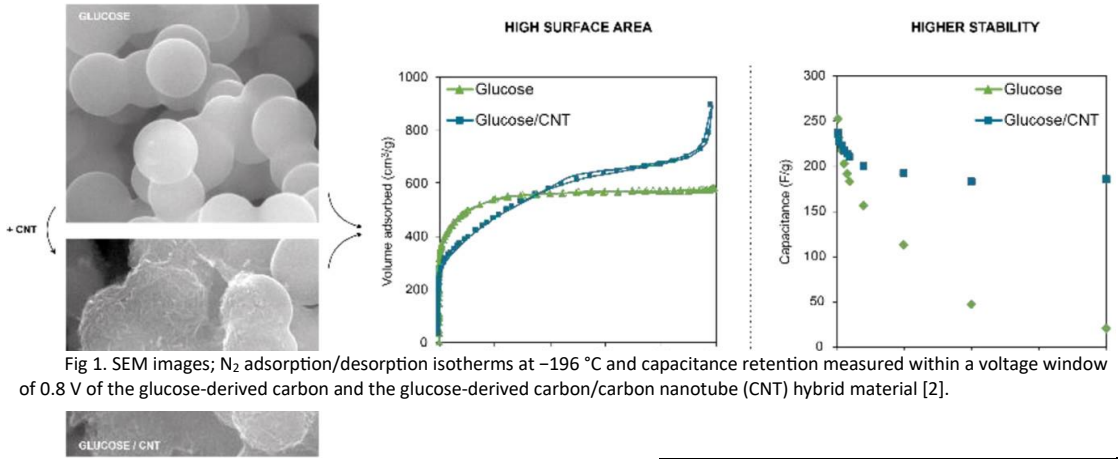

Fig 1. SEM images; N_2 adsorption/desorption isotherms at −196 °C and capacitance retention measured within a voltage window of 0.8 V of the glucose-derived carbon and the glucose-derived carbon/carbon nanotube (CNT) hybrid material [2].

CG-CNT-P_{op}800	61±7
CG-CNT-P_{op}900	42±3
AG-CNT	89±9
AG-CNT-P800	133±2

Carbon-based materials for flexible supercapacitors Wearable electronic gadgets have appeared as an interesting application and carbon nanomaterials are the most proficient and most studied electrode materials in flexible supercapacitors. CNTs have been extensively studied owing to their excellent mechanical and electrical properties. A short review focused on the progress in the use of CNT materials as electrodes in flexible energy storage devices was published [4]. Under the project SmarText4Estore, in collaboration with the Associated Laboratory for Green Chemistry (LAQV) of the Network of Chemistry and Technology (REQUIMTE) and the Institute of Physics for Advanced Materials, Nanotechnology and Photonics (IFIMUP) Research Unit of the University of Porto, the performance of carbon nanotube-based cotton textile supercapacitors (TSCs) was investigated [5]. The CNTs were oxidized using three agents, HNO_3, H_2SO_4 and HNO_3/H_2SO_4, to unveil their role in the performance and energy storage mechanism of the resulting TSCs. The TSCs based on the oxidized MWCNTs exhibited up to 106% enhanced energy density than the device based on pristine MWCNTs (up to 3.48 W h kg^{-1} vs. 1.69 W h kg^{-1}) and up to 98% capacitance retention over 5000 cycles. A balance between the extent of oxidation of the MWCNTs, their specific surface area, and electrical conductivity was required to boost the performance. The MWCNT oxidation with HNO_3 promoted the highest increase of the specific surface area, the creation of redox-active surface oxygen-based groups, and optimum surface oxygen loading (4.0%). The synergy between these features endowed a pseudocapacitive contribution to the energy storage mechanism, leading to the TSC with the best performance.

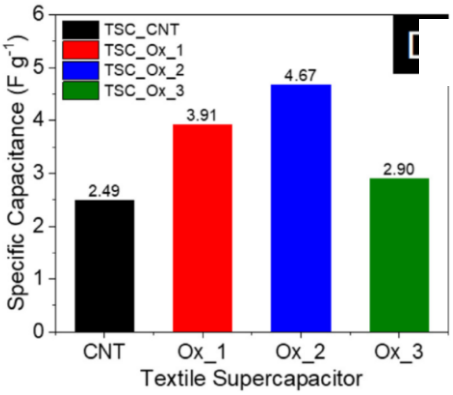

Fig 2. Specific capacitance of all textile supercapacitors at 1 mVs^{-1} [5].

Cork-based electrodes A novel generation of cork-derived carbon and its hybrids with MnOx are being investigated to create electrodes for asymmetric supercapacitors (ASCs) under the aim of the CORKCap project in collaboration with the Association of Instituto Superior Técnico for R&D (IST-ID) and the Instituto Superior de Engenharia de Lisboa (ISEL). The overarching vision is to deliver an eco-conscious ASC based on cork. Different methodologies to activate cork are under investigation, combining eco-friendly routes such as chemical K_2CO_3 activation and physical (CO_2) activation.

Future Work

Low-cost biomass-based materials synthesis (such as cork-based activated carbons) will be investigated. We will be focused on designing and optimizing the physical/chemical activation route to develop extended and tailored porosity and to increase the specific surface of the carbon material. The introduction of different functionalities and heteroatoms to modify the surface's chemical nature, control its electronic properties, and further increase the affinity with the MnO_x for asymmetric supercapacitors.

Related Sustainable Development Goals

Outputs

Master Dissertation

Miguel Â.C. Granja, Functionalized phosphorous carbon materials derived from biomass for supercapacitor application, MIEQ, FEUP, 2018.

Selected Publications

[1] J.L. Figueiredo, Surface & Coatings Technology 350, 307 (2018).
[2] N. Rey-Raap et al., ACS Appl. Mater. Interfaces 11, 6066 (2019).
[3] N. Rey-Raap et al., Electrochimica Acta 354, 136713 (2020).
[4] G. Queiróz et al., U.Porto Journal of Engineering 7, 151 (2021).
[5] R.S. Costa et al., Carbon Trends 5, 100137 (2021).

Team

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