Sustainable energy storage materials from waste hazelnut shell biomass

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Significance and Relevance

In this work, different activated carbons (ACs) were synthesized starting from hazelnut shell (HS) and employed to manufacture supercapacitor (SC) electrodes. Moreover, copper oxide post-doping was explored to further enhance the pristine ACs performances. Preliminary electrochemical tests identified two ACs (HTC-AC and PYRO-AC) and one doped-AC (CuO-HTC-AC) as the most promising ones, which were further investigated by optimizing the electrode preparation procedure. Two of the tested samples displayed a specific capacitance value of about 500 F/g, significantly outperforming commercial carbons.

Preferred and 2nd choice for the topic: 1. Sustainable and clean energy production and transport; 2. Green chemistry and biomass transformation, renewable resources conversion
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Introduction and Motivations

The urgent need to move away from fossil fuels has increased interest towards the development of alternative energy sources and storage solutions. [1] In this context, SCs are attracting much interest due to their high-power density, long life and fast charging capability. According to the charge storage mechanisms, SCs can be classified into electric double layer capacitors (EDLCs), pseudocapacitors and hybrid supercapacitors (HSCs), these latter combining both charge storage mechanisms.[1] EDLCs store energy by accumulating charges on the surface electrode, typically consisting of carbon materials, such as nanotubes, graphene and ACs. In this context, biomass-derived carbons offer a sustainable alternative for the production of EDLC electrodes. Conversely, pseudocapacitors achieve higher capacitance than EDLCs as they store energy through rapid and reversible redox reactions occurring on the electrode surface. In this case, metal oxides and conductive polymers are the most employed materials. In particular, CuO stands out for its high theoretical pseudo-capacitance, good conductivity, environmental friendliness and straightforward preparation. [2] On this basis, the combination of porous carbon materials with pseudocapacitive compounds, such as CuO, represents a promising strategy for developing new, efficient and sustainable composite electrodes for energy storage solutions. In this work, the HS waste biomass was employed as the precursor for the synthesis of three ACs and a char.[3] Moreover, the two most promising ACs were doped with CuO. The physicochemical and electrochemical properties of the synthetized HS-derived carbons were characterized to evaluate their potential for electrode fabrication in supercapacitors. This study investigates the influence of thermal treatments on the electrochemical performances of char, at the same time, proposing an eco-friendly approach for biomass repurposing with potential economic benefits within a circular economy framework.

Materials and Methods

The three ACs were obtained through chemical activation pyrolysis employing KOH as the activating agent, with the precursor/KOH weight ratio of 1/4 at 600°C per 1 h under N_2 atmosphere, according to our previously optimized procedure. [3] The first AC was directly synthesized from the raw biomass (HS-AC), the second one from the hydrochar derived from the hydrothermal carbonization (HTC) of HS (HTC-AC), performing the HTC step at 220°C for 5 hours with the biomass loading of 20 wt%. [4] The third AC sample (PYRO-AC) was obtained by a three-step procedure including 1) HTC followed by 2) pyrolysis in the absence of KOH (600°C for 1 h under N_2 atmosphere) and 3) KOH activation pyrolysis. Lastly, the char obtained after pyrolysis post-treatment of the hydrochar (HTC-PYRO) was also tested for

comparison.[3] CuO-doping of the most promising ACs was performed modifying a procedure already available in the literature,[2] by treating the selected AC with copper(II) acetate solution at pH 10, to precipitate copper(II) hydroxide. The products were recovered by centrifugation and heat-treated at 150 °C to favor the CuO deposition, yielding CuO-HTC-AC and CuO-PYRO-AC. Electrochemical measurements were carried out using two three-electrode setups. The first employed Ag/AgCl and Pt wires as reference and counter electrodes, with KNO_3 or KOH as electrolytes, and a nickel foam-based working electrode prepared by depositing a slurry of active material 80 wt%, carbon black 10 wt% and polyvinylidene fluoride 10 wt%. The second configuration employed a Swagelok cell with lithium metal as reference and counter electrode, LP30 as the electrolyte, and a Doctor Blade-prepared working electrode with a slurry containing active material 85 wt%, carbon black 10 wt%, (carboxy methylcellulose + styrene butadiene rubber at 1:2 weight ratio) 5 wt%. Cyclic voltammetry (CV) and charge/discharge tests assessed the materials' electrochemical performance.

Results and Discussion

Among the bare samples, HTC-AC and PYRO-AC exhibit pseudo-rectangular shape CV curves in both cathodic and anodic zones (Figure 1) in KNO_3, indicating good capacitive performance attributed to their superior surface properties and high specific surface area (SSA). In fact, HTC-AC and PYRO-AC showed higher SSA values (1000 m^2/g and 1421 m^2/g, respectively) than the other two tested materials ($SSA_{HS\text{-}AC}$= 815 m^2/g; $SSA_{HTC\text{-}PYRO}$= 388 m^2/g), highlighting that the pretreatment and activation of the raw biomass are necessary steps to achieve good surface properties. The corresponding CuO-doped ACs were prepared and tested. A significant improvement in the anodic region was observed for the CuO-HTC-HAC, which doubled the specific capacitance value compared to its undoped precursor due to an improved electrical conductivity and charge storage capacity. The most promising ACs (HTC-AC, CuO-HTC-AC and PYRO-AC) were further investigated to explore the electrochemical behavior of these materials and assess possible effects of the manufacturing method of the working electrode on the electrochemical performances. We focused on the cathodic region, using also the Swagelok type cell, and achieved capacitance values (HTC-AC ≅ 250 F/g, PYRO-AC ≅ 500 F/g, CuO-HTC-AC ≅ 500 F/g) much higher than those claimed for commercial carbons (100-200 F/g). [5]

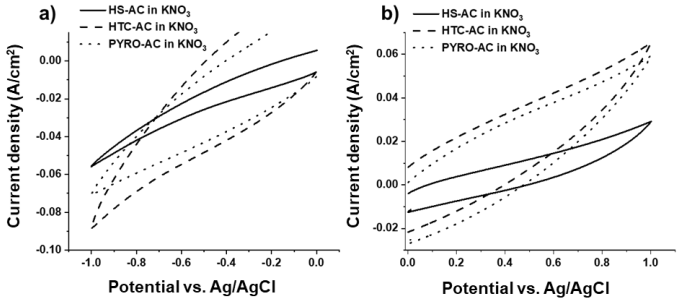

Figure 1 Cyclic voltammograms of HS-AC, HTC-AC and PYRO-AC in KNO_3 (2.5 M) in a potential window between a) -1 to 0 V (cathodic zone) and b) 0 to 1 V (anodic zone) at the scan rate of 0.1 Vs^{-1} per 1 cycle.

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