



## Original Research Paper

## High-capacitance KOH-activated nitrogen-containing porous carbon material from waste coffee grounds in supercapacitor



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## ABSTRACT

Waste coffee grounds were activated by KOH at various pyrolysis temperatures, changing the ratio of the area of the mesoporous structure to that of the microporous structure, the surface area, the amount of oxygen and nitrogen functional groups in the grounds, and their chemical structure. At a pyrolysis temperature of 700 °C, the KOH-activated waste coffee grounds had a specific capacitance of 175 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and 475 F g<sup>-1</sup> at 0.1 A g<sup>-1</sup> from the discharge profiles. Assembling the KOH-activated waste coffee grounds in a coin cell yielded an energy density and power density of 11 W h kg<sup>-1</sup> and 7500 W kg<sup>-1</sup>, respectively, with an operating potential of 1.5 V, making waste coffee grounds a viable feedstock for manufacturing energy materials.

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## 1. Introduction

Electrochemical capacitors and supercapacitors are well-known energy storage devices, which have high power density, high stability, and a long cycling lifetime. Electrochemical capacitors can be separated into two types by their electrochemical mechanism – electrochemical double-layer capacitors (EDLC) and pseudocapacitors. The former are non-Faradaic, and their active ions are ad-/desorbed on/from the electrode surface. Ideally, the EDLC exhibits no electron transfer across the electrode surface and the energy storage is electrostatic. The latter are Faradaic, and their energy is stored during the redox reaction of electroactive species that are related to the electrode potential. Thus, pseudocapacitors exhibit electron transfer across the electrode surface and the energy density depends on the oxidation state of electroactive species. Accordingly, electrochemical capacitors have high power density but low energy density, and so are favorable for use in electric vehicles, integrated with batteries or fuel cells of high energy density.

Porous materials, e.g. porous carbon materials and porous silica materials, have been used for electrochemical capacitors [1–3]. Carbon-based materials are the most popular electrodes owing to their high electrical conductivity, relatively low price, stable performance, and good polarization [4–6]. Therefore, a wide range of carbon-based materials have been studied for use as electrodes

for electrochemical capacitors, including activated carbons [7–9], carbon aerogels [10–12], single-walled carbon nanotube [13], multi-walled carbon nanotube [14–17], carbon nanofibers [17–21], carbide-derived carbons [22–24], mesoporous carbons [25–27], graphene [28–30], graphene oxides [31] and others. The specific capacitance of carbon-based materials is believed to be a function of both porosity and surface area [32,33]. Rufford et al. evaluated the specific capacitances of activated carbons in terms of contributions by micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm) [34]. They found that the contribution of micropores to specific capacitance was rapidly decreased by fast charging and discharging, and the specific capacitance depended on the number of mesopores that were present during that process, owing to the ion transport through the pore network. Moreover, some investigations have investigated nitrogen-, oxygen- and phosphorous-enriched carbon materials for use in electrochemical capacitors, in which the nitrogen-, oxygen- and phosphorous groups undergo stable and reversible pseudocapacitive reactions, which enhance the overall capacitance [20,35–38].

Activated carbons or carbon blacks are frequently manufactured by the channel process, the oil furnace process, or the thermal process, of which oil and natural gas are the carbon precursors [39]. Waste biomass contains more carbon, oxygen and nitrogen than oil or natural gas, and so can be used as a low-cost carbon precursor to reduce the environmental impact of the process. Yu and his colleagues used some biomass-derived materials, e.g. seaweed and hair, which were pyrolyzed at high temperature to form the heteroatom-doped highly porous carbon as the metal-free catalyst

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for the oxygen reduction reaction [40,41]. They also used cow dung derived activated carbon as the electrode material for EDLC [42]. Balathanigaimani et al. utilized corn-based activated carbons, whose specific capacitance was  $257 \text{ F g}^{-1}$  at  $1 \text{ mA cm}^{-2}$  in  $6 \text{ M KOH}$  [43]. Liu et al. used crab shells as templates of carbon precursor: they grew mesoporous carbon nanofibers in the pores of the shells, producing capacitive behavior in organic solution [44]. Hong et al. demonstrated the formation of nitrogen-doped porous carbon by endothelium corneumgigeriaegalli, with a large surface area of  $2149.9 \text{ m}^2 \text{ g}^{-1}$  and a specific capacitance of  $198.0 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  in  $6 \text{ M KOH}$  [45]. In some studies, fish scales [46], coffee endocarps [47], chicken eggshells [48], animal bones [49], egg whites [50], and human hair [51,52] have all been used as carbon precursors in the fabrication of biomass-derived electrochemical capacitors. However, in most studies in this field, animal proteins and foodstuffs have been used as a carbon precursor: these are not widely available and some spoil easily in air. Biomass-derived electrochemical capacitors should preferably be developed from widely available materials that can be easily collected and stored over the long term.

Coffee is a well-known beverage. Roasted coffee comprises carbohydrates (38–42% dry basis), melanoidins (23%), lipids (11–17%), protein (10%), minerals (4.5–4.7%), chlorogenic acid (2.7–3.1%), aliphatic acids (2.4–2.5%), caffeine (1.3–2.4%), and other components [53]. After coffee seeds are ground and brewed to create a beverage, the waste coffee grounds are typically discarded, although a few are reused in agriculture, construction, biofuel, and sorption [54–59]. Waste coffee grounds clearly contain high volumes of organic carbon and caffeine. In 2008, Hulicova-Jurcakova and his colleagues have begun research into the treatment of waste coffee grounds for use in electrochemical capacitors [34,60–63]. They typically mixed  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ , or  $\text{MgCl}_2$  with waste coffee grounds, and carbonized the mixture in an atmosphere of nitrogen at  $900 \text{ }^\circ\text{C}$  for several hours. These treated waste coffee grounds exhibited a specific capacitance of  $368 \text{ F g}^{-1}$  at  $0.05 \text{ A g}^{-1}$  and of  $320 \text{ F g}^{-1}$  at  $1.0 \text{ A g}^{-1}$  in  $1 \text{ M H}_2\text{SO}_4$ . The authors concluded that the capacitance arose primarily from the mesopores in the treated waste coffee grounds. Jisha et al. similarly treated coffee shells for use in electrochemical capacitors, obtaining a specific capacitance of  $150 \text{ F g}^{-1}$  at  $1 \text{ mV s}^{-1}$  in  $6 \text{ M KOH}$  [64].

This work extends the work of Hulicova-Jurcakova et al., by treating and activating waste coffee grounds using KOH without the addition of any metal salt as an activation agent, to form KOH-CG with a large BET surface area of  $1622 \text{ m}^2 \text{ g}^{-1}$ . The specific capacitances of KOH-CG are  $475.0 \text{ F g}^{-1}$  at  $0.1 \text{ A g}^{-1}$ ,  $175.7 \text{ F g}^{-1}$  at  $1.0 \text{ A g}^{-1}$ , and  $148.6 \text{ F g}^{-1}$  at a very high current density of  $10 \text{ A g}^{-1}$ , exhibiting almost no decay over 10,000 cycles.

## 2. Experimental

Waste coffee grounds were collected from compost that contained exclusively coffee beans (Kirkland Signature Rwandan and dark roast bought from Costco) that had been ground and used to brew coffee in an automatic coffee machine (ENA Micro 9, JURA Inc.). The collected waste coffee grounds were dried at  $40 \text{ }^\circ\text{C}$  for 48 h and then immersed in  $1 \text{ M KOH}$  solution with stirring for six hours to remove contamination and oil. Then, the grounds were washed in deionized water and dried at  $50 \text{ }^\circ\text{C}$  for 24 h. They were then mixed with an equal weight of KOH, and the mixture was then introduced to a furnace for pyrolyzation at particular temperature in an atmosphere of nitrogen for two hours. The pyrolysis temperatures were set to 600, 700, and  $800 \text{ }^\circ\text{C}$ , and the corresponding samples were denoted as KOH-CG-600, KOH-CG-700, and KOH-CG-800, respectively. The KOH-activated waste coffee grounds were washed using large amount of  $1 \text{ M H}_2\text{SO}_4$  solution to remove residual KOH and then rinsed in de-ionized water. They were then filtered and dried for the use.

Brumauer–Emmett–Teller (BET) measurements were made using a Tristar 3000 to estimate the specific surface area ( $S_{\text{BET}}$ ) of the grounds. The distribution of mesopore volumes ( $V_{\text{pore}}$ ) was estimated using the Barrett–Joyner–Halanda model. The Raman spectrum was recorded using a Jobin-Yvon LabRAM HR800-Confocal micro-Raman spectroscope with a 633 nm He–Ne laser as the excitation source. High-resolution scanning electron microscopy (HRSEM, JEOL-6700F) was used to elucidate the morphology of the samples. Thermal gravimetric analysis (TGA) of the samples was conducted in an atmosphere of  $\text{N}_2$  with a flow rate of  $20 \text{ mL min}^{-1}$  at a heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$ . X-ray photoelectron spectroscopy (XPS, VG ESCA Scientific Theta Probe using  $1486.6 \text{ eV Al K}\alpha$  source) was used to study the surface chemistry of the sample.

An electrode was prepared by mixing KOH-activated waste coffee grounds and polyvinylidene chloride in a 9:1 ratio in N-methyl-2-pyrrolidone to form an ink (sediment content:  $0.01 \text{ g mL}^{-1}$ ), which was hand-painted onto carbon paper (NOS1005 CeTech Co., Ltd.), such that typically  $2 \text{ mg cm}^{-2}$  of the active materials was applied to the electrode. Thereafter, the electrode was heated to  $120 \text{ }^\circ\text{C}$  for 12 h to eliminate the solvent.

To make measurements of the capacitance in three-electrode cell, the electrode was placed in a holder as a working electrode, which was connected to an electrochemical instrument (Solartron 1280C) via a gold wire in  $6 \text{ M KOH}$ . The reference electrode was an Hg/HgO electrode ( $0.098 \text{ V vs. SHE}$ , 20% KOH) and the counter electrode was a piece of platinum foil. To make measurements of the capacitance in two-electrode cell, a sandwich-type cell (CR2032 size) was assembled from two electrodes, which were separated by a separator. A  $6 \text{ M KOH}$  solution was added as an electrolyte to the cell. Each sample was weighed before the electrochemical measurements were made and the cell was constructed, and each electrode was found to weigh  $1.80 \text{ mg cm}^{-2}$ .

## 3. Results and discussion

Fig. 1 plots the TGA curve of the KOH-activated waste coffee grounds in an atmosphere of nitrogen. The curve indicates that approximately 50% of their weight was lost at  $250\text{--}350 \text{ }^\circ\text{C}$ , indicating that KOH strongly activates waste coffee grounds in this range of temperatures. When the temperature exceeded  $600 \text{ }^\circ\text{C}$ , the percentage residual weight was an almost constant 22%. Fig. 2a presents HRSEM images of the original waste coffee grounds. Owing to their poor electrical conductivity, charging caused the image to be of poor quality. Fig. 2b–d shows HRSEM images of KOH-activated waste coffee grounds that were heated at 600, 700, and  $800 \text{ }^\circ\text{C}$ , respectively. The original waste coffee grounds

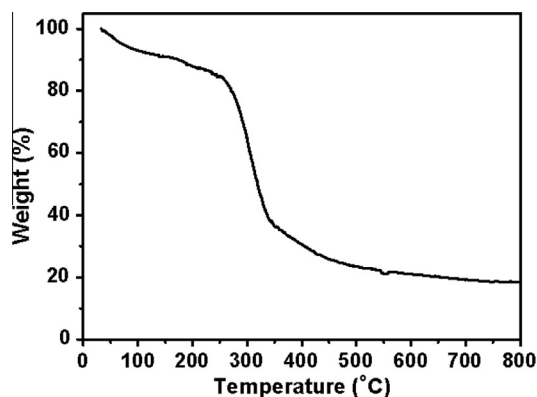


Fig. 1. The TGA curve for treating KOH-activated waste coffee grounds in nitrogen atmosphere.

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