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# Coniferous pine biomass: A novel insight into sustainable carbon materials for supercapacitors electrode

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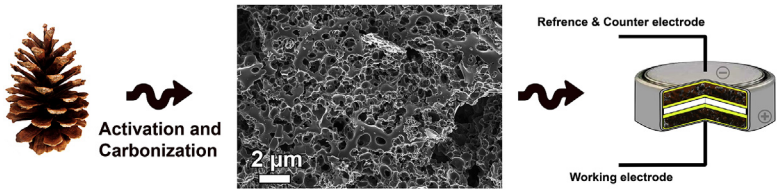
## HIGHLIGHTS

- Sustainable carbon materials from pine cone biomass.
- Hydrothermal treatment of the pine cone to produce hydrochar.
- KOH activation and carbonization of the hydrochar to produce porous carbons.
- Symmetric supercapacitor based on the porous carbon exhibit good electrochemical performance.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Low-cost biomass-derived activated porous carbon from natural pine cones is synthesized using hydrothermal approach followed by KOH activation and carbonization. The produced carbon materials have a high surface area of 1515 $m^2\ g^{-1}$ with a well-developed meso/micropores structure which is advantageous and favorable for mass transfer and ion accommodation for fast rate performance by providing pathways for electrolyte permeation and contact probability. Symmetric device fabricated using the obtained carbon material as electrode, exhibited good electrochemical performance with no degradation of capacitance after voltage holding at 1 V for about 60 h demonstrating good rate capability of the fabricated device. The results demonstrate the exciting potential of the pine cone derived carbons as a promising candidate for high-performance electrode materials for supercapacitors if fully explored.


## 1. Introduction

Considering the increasing demand for energy and the rapid depletion of fossil fuels, the development of green and sustainable eco-friendly energy-storage systems that are highly efficient is imperative to meet the increasing energy demand for the socio-economic development of our society [1,2]. Electrochemical capacitors (ECs) also known as supercapacitors, ultracapacitors are a new class of electrochemical energy storage system which store energy by charge accumulation, and are excellent power devices that suffer from low energy density when compared with their battery counterparts which store energy using a faradaic reaction and providing high energy with moderate power [3,4]. They hold a considerable promise for a wide range of applications, including portable electronics, uninterruptable power sources, braking systems and hybrid electric vehicles [5,6]. Several research activities are focused on improving the energy density of ECs by developing novel nanostructured electrode materials because the electrochemical performance of the electrode is highly dependent on the properties of the produce materials and electrolyte. Thus the design and optimization of nanostructured active electrode materials for the optimum balance between energy and power properties is an

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on-going process. To improve and achieve high energy storage capacity and high power density in ECs, carbonaceous nanomaterials such activated carbons (AC) are used to fabricate electrodes, this is because they possess nanoporous structure with high specific surface area (SSA), suitable pore size distribution, good conductivities and have high chemical stability [7,8]. Recently it has been shown that advanced form of carbon such a carbon nanotubes (CNT) [9], onion-like carbons (OLC) [10], carbide derived carbons (CDC) [6,11] and graphene [12] exhibit high capacitance, high energy and power densities as electrodes in ECs and hybrid ECs systems operating in various aqueous, organic and ionic electrolytes [6,13]. Unfortunately, the production of these advanced forms of carbon materials is significantly limited by the high cost, which is greater than the production of porous carbon derived from pyrolysis/hydrothermal treatment of biomass or bio-waste [14,15]. Hence, the need for a paradigm shift from the production of porous carbons for ECs electrodes from the conventional technique to a relatively low-cost and green carbonization approach, to meet the demand for growing global energy and sustainable development, and further to reduce the depletion of the fossil fuel raw materials [16].

Different methods like hydrothermal [17], direct pyrolysis [18], chemical vapor deposition (CVD) [19], gas-solid displacement reactions [20], and wet chemistry techniques, such as sol–gel processes [21], have been employed to produce diverse porous carbons from biomass or waste materials such as egg shell [22], seaweeds [18], dead leaves [8], hemp basts [15], wood sawdust [17], pistachio nutshells [23], cigarette filter [24], sunflower seed shell [25], cypress [26] and rice husk [27]. Aside the low cost and sustainability benefits of these carbon-based nanomaterials they also possess high specific surface area, optimal pore size distributions, suitable average pore sizes and pathways for easy accessibility of electrolytes and rapid transportation of ions during electrochemical measurements.

In this work we have pioneered the production of porous of carbon materials from pine cone biomass as electrode for electrochemical energy storage. Pines are coniferous trees in the genus Pinus family of the Pinaceae which materialize in a wide range of environmental conditions. It sprouts up to 50 m in height with dark green needles and 5–10 cm length cones with rounded scales. Large amount of cones are produced yearly throughout the world, especially in pine plantations grown for the pulp and paper industry. They are mainly composed of cellulose, lignin and resins that contain a variety of organic compounds [28,29]. Although in the course of the literature review porous carbon from pine biomass have been studied extensively as biosorbent for metal, dye waste waters, nitrate uptake and removal of lead (II) ions from aqueous solutions by adsorption [30–32], they have never been studied as electrode for electrochemical energy storage to the best of our knowledge. Here, we report a two-step integration of hydrothermal and activation processes that uses coniferous Pines as the starting precursor for the production of porous carbons. The as-prepared products are used as the electrode materials for supercapacitors; they exhibit excellent performance with high specific capacitance of 90 F $g^{-1}$ at the current density of 0.1 A $g^{-1}$, and good stability even after voltage holding for about ~3 days.

## 2. Experimental section

### 2.1. Materials synthesis

The porous activated carbon powder was derived by hydrothermal process from the ground pine cones (PC) materials by a slight modification of the procedure in Ref. [33]. Scheme 1 shows the transformation of PC into porous carbons. PC was collected from the University of Pretoria campus Hatfield, South Africa. The cones were washed repeatedly with acetone and distilled water to remove adhering dirt and soluble impurities and dried at 60 °C. After drying, the cleaned PC was crushed and eight grams was dispersed in 80 ml of distilled water containing 0.5 ml of sulphuric acid. The dispersion was transferred into a stainless steel autoclave and was heated up to 160 °C for 12 h and then allowed to cool to room temperature. The resulting solid black product was filtered and washed with distilled water and dried overnight at 80 °C. The dried solid black product was activated using KOH with a mass ratio of 1:1. The mixture was then placed in a horizontal tube furnace ramped from room temperature to 800 °C at 10 °C/minute under argon flow and annealed for 1 h for the carbonization process. A series of temperatures (600, 700, and 900 °C) were examined to investigate the effect of temperature on the structural evolution of the produced carbon materials. The materials were denoted as activated pine cones (APC), and APC-600, APC-700, APC-800 and APC-900 with the number denoting the carbonization temperatures.

### 2.2. Characterization

The samples were characterized using powder X-ray diffraction (XRD). An XPERT-PRO diffractometer (PANalytical BV, Netherlands) with theta/theta geometry, operating a cobalt tube at 35 kV and 50 mA, was used. The XRD patterns of all specimens were recorded in the 10.0°–80.0° 2θ range with a counting time of 5.240 s per step. Fourier-Transform Infrared (FTIR) spectra were recorded on a Vertex 70v (Bruker) spectrometer in the 4000-600 $cm^{-1}$ range with 4 $cm^{-1}$ resolution and analyzed with the Opus software. Raman spectra of samples were recorded using a WiTec-alpha 300R+ confocal Raman spectrometer (WiTec GmbH) with the laser power of 1.5 mW in order to minimize heating effects. The excitation source was a 532-nm laser through a numerical aperture of 0.9 and 20× magnification. The morphologies of the activated porous carbons were observed by Zeiss Ultra Plus 55 field emission scanning electron microscope (FE-SEM) operated at an accelerating voltage of 2.0 kV. The surface area measurements of the produced samples were performed by liquid Nitrogen adsorption–desorption isotherms at −196 °C using a Micromeritics TriStar II 3020. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method.

### 2.3. Electrochemical performance measurement

The electrochemical experiments were carried out using a two-electrode cell with a 1 M $Na_2SO_4$ aqueous electrolyte. The electrodes were prepared by mixing 80 wt% sample, 10 wt% carbon black and 10 wt% Polyvinylidene fluoride (PVDF) binder in *N*-methylpyrrolidone (NMP) solution and pasted onto the Ni-foam current collector, which was dried at 80 °C overnight in an electric oven to ensure complete evaporation of the NMP. Each electrode has a mass loading of about 4 mg per electrode. The symmetric devices were assembled such that two electrodes were separated by a glass microfiber filter paper in CR2025-type coin cells. The cyclic voltammetry (CV), galvanostatic charge-discharge (CD), and electrochemical impedance spectroscopy (EIS) measurements were performed on a Bio-logic VMP-300 potentiostat. CV tests were conducted between 0 and 1 V at different scan rates of 10–200 mV $s^{-1}$. The EIS plots were obtained in the frequency range from 100 kHz to 0.01 Hz at open circuit potential. The specific capacitance was calculated from the galvanostatic charge-discharge tests based on a two-electrode cell, the gravimetric specific capacitance ($C_{sp}$: F $g^{-1}$), the maximum energy density ($E_{max}$: Wh $kg^{-1}$), and the power density ($P_{max}$: kW $kg^{-1}$) of the cell