Activated Biochar: a green and low-cost electrode material for capacitor applications

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Carbon-based materials garnered significant attention in Electric Double Layer (EDL) applications (e.g., capacitors energy storage and supercapacitors) and water/wastewater purification (e.g., electrosorption and capacitive deionization), owing to their ease of processability, accessibility, and relatively low-cost. A large variety of carbonbased electrode materials have been studied such as: carbon cloth, fibers, nanotubes (CNTs), aerogels and more recently, graphene. However, many carbon electrodes employed in EDL applications showed considerable disadvantages with respect to intrinsic physico-chemical properties and/or operational conditions. Thus, a number of challenges are identified including pore mass transfer issues, significant potential drop, small capacitance, and high-cost/low-yield preparation methods [1, 2].

Our research is focused on biochar (a residual by-product of woody biomass pyrolysis with a unique carbon structure) as a low-cost and renewable precursor for electrode material preparation. The objective is to develop the biochar structure (referred to as activation) such that the activated biochar to function as a suitable electrode material for EDL application and to understand the relationship between the biochar source, activation parameters and the resulting capacitive electrode behaviour.

In the present work, we have investigated the effect of thermo-chemical activation process composed of chemical activation with 7 M KOH followed by carbonization under N_2 atmosphere at temperatures between 675 to 1000⁰C, on the activated biochar properties and electrode performance (Table 1).

Table 1. Surface area and porosity of activated biochar samples and commercial Vulcan XC-72 (for comparison)

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Sample	Surface	Mesopore	Micropore	Activation
	area	volume	volume	temperature/
	$(m^2 g^{-1})$	$(\text{cm}^3 \text{g}^{-1})$	$(cm^{3}g^{-1})$	pre-drying
			-	time
Biochar	1.66	-	-	None
Act.	990	0.59	0.31	675 ⁰ C
Biochar				72 h
1				
Act.	1294	0.09	0.62	675 ⁰ C
Biochar				12 h
2				
Act.	614	0.63	0.03	$1000^{\circ}C$
Biochar				72 h
3				
Vulcan	200	0.31	0.03	None
XC-72				

Table 1 shows that three activated biochar samples have been produced with differing porous structures and surface chemical groups (e.g., oxygencontaining groups characterized by both Elemental Analysis and FT-IR spectroscopy). Surface functional groups could be advantageous in EDL applications due to their contribution to the total capacitance of the electrodes as pseudocapacitance [1, 2]. The activated biochar samples were then mixed with different concentrations of Nafion[®] (0, 5, and 30 wt.% of Nafion[®] content) and sprayed on a flexible thin Nickel mesh (150 x 150 mesh size) acting as current collector. This electrode fabrication technique could be advantageous for the design and assembly of capacitors with various configurations, e.g., stacked or rolled screens.

The electrochemical properties of the prepared studied electrodes have been using cyclic (CV) galvanostatic voltammetry and charge/discharge experiments. The electrolyte was a mixture of 0.1 mol L⁻¹ NaCl in 0.1 mol L⁻¹ NaOH. For comparison, electrodes were also made from a commonly used carbon material in EDL application, i.e., Vulcan XC-72 carbon black. The total capacitance of each electrode was obtained from cyclic voltammograms recorded at different sweep rates (between 1 and 50 mV s⁻¹). The discharge capacitance and ohmic potential drop of each electrode was quantified using galvanostatic charge/discharge tests.

Fig. 1 shows the total capacitance as a function of Nafion content for both the activated biochar and the reference Vulcan electrode, respectively. The electrode prepared from the Act. Biochar 3 sample with 30 wt.% Nafion showed a maximum total EDL capacitance of 205 F g^{-1} , which was over an order of magnitude higher than the capacitance of the Vulcan electrode. Overall, the activated biochar samples showed promising results in both CV and charge/discharge galvanostatic experiments. Furthermore, the total capacitances of the activated biochar electrodes are competitive with much more expensive systems such as CNTs and graphene-based electrodes [4-6].

Our preliminary results suggest that activated biochars prepared with application-tailored porous structure (i.e., optimal mesoporous/microporous volume ratio) are promising, low-cost and renewable candidates for EDL-based applications including supercapacitors. Moreover, the value-added utilization of biochar would increase the overall economic outlook of woody biomass pyrolysis.



Figure 1. Total capacitances of activated biochar and Vulcan electrodes, respectively (see also Table 1).

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