

Production of Supercapacitor Carbon Electrodes from Corn-stover via a Facile Thermal Activation

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ABSTRACT

Use of biomass is an emerging and promising alternative to produce carbon electrodes for supercapacitors. Lignin-rich unhydrolyzed solids (UHS) obtained from alkaline pretreatment and enzymatic hydrolysis of corn stover were valorized into biochar via hydrothermally liquefaction (HTL) under catalytic environment. As obtained biochar was thermally activated, pH neutralized and later converted to biocarbon using a facile one-step thermal activation process. Activation/carbonization was carried out in a tubular furnace at 850 °C (815 °C actual) for 3 hours at a heating rate of 5 °C min⁻¹ under argon flow. Electrode ink was formulated by combining 80 wt.% biocarbon, 10 wt.% high conducting carbon black (Super P), and 10 wt.% polytetrafluoroethylene (PTFE, 60 wt.% in H₂O), and a reserved amount of H₂O. Slurry was applied to Ni foam, dried, pressed, then templated and insulated with chemical resistant epoxy. Electrochemical measurements were conducted using a potentiostat, where specific capacitances determined via cyclic voltammetry (CV) and the results obtained were compared to the supercapacitors fabricated from biochar derived at non-catalytic HTL environment. The electrodes produced were well suited for use in supercapacitors.

Keywords: unhydrolyzed solids, hydrothermal liquefaction, thermal activation, supercapacitors, corn-stover

1 INTRODUCTION

Corn stover (leaves, stalks, cobs, husks and tassels) is an abundantly available biomass feedstock, typically consists of high amounts of lignin, cellulose and hemi-cellulose components, and is primarily sourced from the annual grain (corn) harvests of about 1.5 dry tons per acre.^{[1],[2]} The lignocellulosic components can be utilized for fermentation of sugars and other valuable products such as lactic acid, levulinic acid and phenols when separated from the complex cell wall of the corn stover via alkaline pretreatment and enzymatic hydrolysis processes.^{[3],[4]} The remaining solid residue which is rich in lignin can be further valorized into biochar. Among the different valorization techniques, hydrothermal liquefaction (HTL) can convert the biomass feedstock effectively compared to traditional pyrolysis and

biological techniques. However, even such technology poses several technical challenges pertaining to mixing, pressurization, transport, and pressure let down of high solid slurries which requires an optimized process intensification step to realize its full commercial potential.^{[5]-[7]}

Among the several products produced during valorization of the lignin-rich biomass feedstocks, our focus in this research work is on the hydrochar derived from the solid residue processed via HTL process under catalytic environment. From our past research, we understood that presence of Ni-based catalysts can significantly improve the quality of the biochar after HTL process, which could in turn improve the energy storage potential when converted into biocarbon.^[8] Graphitic carbons for energy storage, particularly supercapacitors can be readily generated from the solid residues of HTL. Our past investigations show that the energy storage potential of such low cost biocarbon is comparable with commercial fossil graphite.^[9] Graphitic carbon derived from biomass is an inherently benign, stable, sustainable, and economically feasible product.^[10] Due to the lignocellulosic content and the structure of these compounds themselves, they provide an excellent template for generating biocarbon, even after HTL processing. The functional group rich compounds help create porous structures post thermal carbonization.^{[11],[12]} Under thermal activation, every cleaved group creates a pore which allows for ion storage, enhancing capacitance.^[13] Given this, the material is stable and capable of cycling 10,000+ times when fabricated into a supercapacitor.

In this work, we explore the energy storage potential of the biocarbon derived from catalytic HTL of lignin-rich biomass feedstock on comparison to the biocarbon sample derived under non-catalytic HTL condition. From this preliminary study, we anticipate to get a better understanding on how the presence of catalyst can effect the electrochemical performance of the fabricated supercapacitors.

2 EXPERIMENTAL

2.1 Materials

Commercially available unhydrolyzed solids from an ammonia fiber expansion process (AFEX) for the pretreatment of corn stover were obtained from Glydia Biotech.^{[14]-[16]} Ni(NO₃)₂, as a catalytic material for HTL process was purchased from Sigma Aldrich. Acetone (analytical grade) and HCl were purchased from Fischer Scientific. Ultra high purity Argon (> 99%) for thermal activation was purchased from Airgas. Polytetrafluoroethylene (PTFE) and carbon black (Super P conductive, 99+%) were purchased from Alfa Aesar. Nickel foam cathode material was purchased from MTI corp. Henkel Loctite EA 9462 Epoxy was purchased from Ellsworth adhesives. Double distilled water was obtained from an on-demand Barnstat filtration system.

2.2 Biochar Synthesis

A slurry of commercial UHS derived from AFEX treated corn stover and DI water in biomass to solvent ratio of 1 : 10 was prepared with 5 wt.% Ni(NO₃)₂ catalyst in a 300 mL bench scale high temperature and high pressure PARR reactor and the contents in the reactor were purged with N₂ and hydrothermally liquefied (HTL) at a reaction temperature of 250°C for 1 hour.^[17] Following the reaction, the reactor contents were cooled down and the solid residue is separated from the aqueous liquid stream via vacuum filtration and later washed with several passes of acetone to remove the sticky bio-oil components from the hydro/biochar, which is later dried overnight at 65°C in conventional oven and proceeded to thermal activation in the presence of inert N₂ environment at 400°C for 2 hours. Finally, the resultant biochar is further graphitized to obtain high value biocarbon. Additional details pertaining to the HTL reactor set-up and its operation, and extraction of products are provided elsewhere.^{[18],[19]}

2.3 Biocarbon Synthesis

As-received catalytic biochar underwent a standard acid wash as reported by Shell et al. (2021).^[20] Neutralized biochar was placed in the vacuum oven at 40 °C and -10 psig overnight. About 0.33 g of biochar was placed in a ceramic boat and placed in the tube furnace. The tube furnace was set to 850 °C (815 °C actual) or 3 h with a ramp rate of 5 °C min⁻¹ under slow argon flow. Biocarbons were removed and weighed after naturally cooling. The electrochemical performance of the obtained catalytic HTL based biocarbon sample termed as H1C, is compared to the biocarbon derived from non-catalytic HTL processing as control sample, SDC5.

2.4 Electrode Fabrication

Biocarbons were first prepared into a slurry where biocarbon, carbon black (Super P), and polytetrafluoroethylene (PTFE, 60 wt.% in H₂O) were mixed into a slurry at an 8:1:1 mass ratio. The slurry was spread evenly onto reduced Ni foam electrode (1 cm x 3 cm) then dried in a vacuum over over night at 40 °C and -10 psig. Once dried, the electrodes were pressed and templated using chemical resistant epoxy. The epoxied electrodes were allowed to cure overnight. Electrode active areas were found by a ratio of geometric areas via ImageJ software. Pictures of the electrodes for active area calculations were taken prior to a post epoxying along with reference material.

2.5 Electrochemical Measurements

Electrochemical measurements were conducted in triplicate on a CH Instruments 660E potentiostat in a 3-electrode format. A working (fabricated), counter (Pt wire), and reference (sat. Ag/AgCl) were employed for the 3-electrode system. All electrochemical measurements were conducted in 2 M KOH aqueous electrolyte solution. Cyclic voltammetry (CV), galvanostatic charge-discharge (CD), and electrochemical impedance spectroscopy (EIS) were performed to give enhanced insights into electrochemical performance. Specific capacitances from CV and CD were found utilizing Equations (1) and (2).

$$C = \frac{\int_{V_1}^{V_2} I dV}{m v \Delta V} \quad (1)$$

$$C = \frac{I t}{m \Delta V} \quad (2)$$

where, V_1 and V_2 are the voltage window endpoints in V, I is the current in A, m is the active mass in g, v is the scan rate in mV s⁻¹, ΔV is $V_1 - V_2$, and t is the time to charge in s.

3 RESULTS AND DISCUSSION

Cyclic voltammetry (CV) was performed on all samples in 2 M KOH with a voltage window from -1 to 0 V vs Ag/AgCl (sat.). Cyclic voltammograms shown in Figure 1 demonstrate smooth CV curves with no reversible or irreversible reactions, indicating ideal capacitive behavior.^[21] Biocarbon H1C demonstrated the highest capacitance among all the samples as confirmed by the largest area in Figure 1. Biocarbon H1C reached a specific capacitance of 142 F g⁻¹ at 20 mV s⁻¹, while the control (SDC5) reached only 109 F g⁻¹, signifying improved ion transport within the carbonaceous framework for the catalytic material. This increase in electrochemical performance can be attributed to the Ni(NO₃)₂ utilized during the HTL synthesis of hydrochar and subsequent biochar. Ni has been cited in literature to give improved bio-oil and decreased char yields during the HTL of biomass.^[22] In turn,

this could have a positive effect on biocarbon characteristics, such as decreased O, N, and H presence, post carbonization.

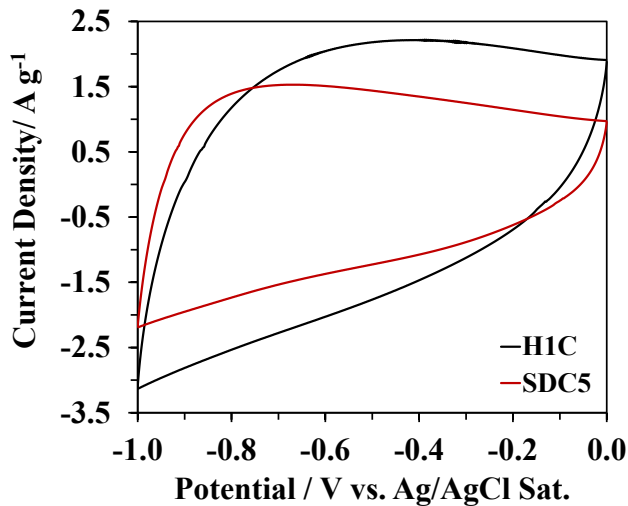


Figure 1: Cyclic voltammetry curves of prepared biocarbons at 5 mV s^{-1} .

All samples underwent galvanostatic charge-discharge (CD) to give further insights into electrochemical behavior. For supercapacitors, CD gives pseudo real world performance characteristics. Figure 2 illustrates all CD curves of H1C compared to SDC5 (control) at 0.1 and 0.05 A g^{-1} . All curves demonstrated smooth sawtooth-like curves indicating sufficient charge separation and ideal EDLC behavior.^[13] Biocarbon H1C achieved a specific capacitance of 77 F g^{-1} at 0.1 A g^{-1} . While SDC5 demonstrated a significantly longer charge and discharge time ($96 \text{ F g}^{-1}, \pm 25\%$) this is due to the decreased current density (0.05 A g^{-1}). Increasing current density causes a reduction in specific capacitance due to limited ion diffusivity, therefore it can be extrapolated that if this were increased, SDC5 biocarbon would exhibit lower capacitance.

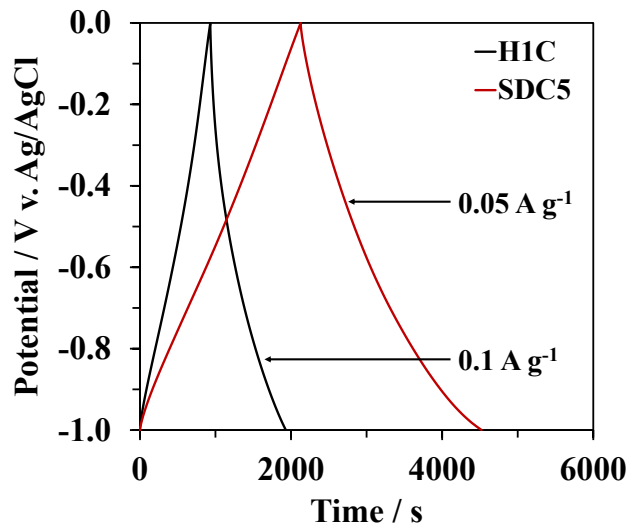


Figure 2: Charge-discharge curves for prepared biocarbons.

Further electrochemical characterizations were performed through EIS to understand internal electrode properties such as internal resistances and ion transfer characteristics. Figure 3 depicts each material's capabilities in three distinctive regions: high frequency (semi circle), medium frequency (intermediate), and at low frequency. The high frequency region denotes interfacial charge transfer resistance where a smaller region is desired.^[23] The medium, or intermediate, region signifies the ion diffusion from electrolyte to electrode surface, where a slope of 1 is desired and represents the Warburg resistance.^[24] The low frequency region corresponds to ideal capacitive behavior.^[25] An angle of 90° (slope ∞) is desired, however when comparing within a sample set, the highest slope is taken as most ideal.

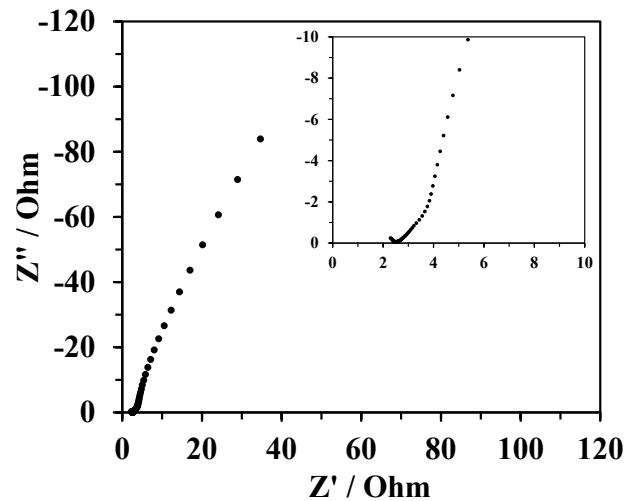


Figure 3: Electrochemical impedance spectroscopy of H1C biocarbon.

Due to the incomplete semi circle region for H1C biocarbon, only the bulk solution resistance (R_b) could be determined from the high frequency region. Biocarbon H1C achieved an R_b at 2.54Ω . In the medium frequency region H1C held a slope (S_i) of 1.72, close to the ideal slope of 1. H1C also held a slope (S_L) (2.65) in the low frequency region. Overall, catalytic HTL-derived biocarbon demonstrated enhanced electrochemical performance over the non-catalytic sample. Limitations for process scale-up exist when utilizing $\text{Ni}(\text{NO}_3)_2$ due to the high cost of $\$ 4,000 \text{ ton}^{-1}$.^[26] For this reason, it is necessary to explore alternative low-cost catalysts.

4 CONCLUSION

Corn stover derived UHS biomass underwent HTL in the presence of $\text{Ni}(\text{NO}_3)_2$ followed by low temperature annealing of biochar at 400°C for 1 h. Subsequently biochar underwent thermal activation at 850°C (815°C actual) for 3 h. The resulting biocarbon was fabricated into electrodes where electrochemical characterizations were performed. Biocarbon H1C (prepared using $\text{Ni}(\text{NO}_3)_2$ catalyst) achieved

the highest specific capacitance (142 F g⁻¹) over the control (non-catalytic HTL derived biochar SDC5), indicating the enhanced electrochemical performance of Ni-based catalysts during HTL processing.

ACKNOWLEDGEMENT

This work was financially supported by the United States Department of Energy [No. DE-EE0008252 (Pilot-Scale Biochemical and Hydrothermal Integrated Biorefinery (IBR) for Cost-Effective Production of Fuels and Value Added Products)].

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