HTL Derived Biochar for Supercapacitor Electrodes

K. Huynh, B.K. Maddipudi, V.S. Amar, J. D. Houck, and R.V. Shende*

Department of Chemical and Biological Engineering,
South Dakota School of Mines & Technology
Rapid City, SD 57701 USA, *Rajesh.Shende@sdsmt.edu

ABSTRACT

In this study, biochar samples were prepared by conversion of biomass feedstock (corn stover) via catalytic hydrothermal liquefaction (HTL) and later used as electrode material in conjunction with sol-gel derived perovskite based mixed (Mn,Ti)-oxides (Mn:Ti precursors 65:35 wt%) for asymmetric supercapacitors. The HTL reaction was performed with 5wt%. $Ca(NO_3)_2$ at 250ºC for 1 hour. The biochar obtained after the HTL reaction was activated with KOH and further thermally treated at 400ºC for 1 hour. The activated porous biochar samples were analyzed by BET surface area analyzer. In asymmetric supercapacitors (ASC) configuration, the energy storage potential was studied using cyclic voltammetry.

Keywords: Porous carbon, supercapacitor, cyclic voltammetry

1. INTRODUCTION

With increase in the world population, the demand for energy is steadily rising. Primarily, this energy demand is currently being fulfilled by the use of fossil fuels such as coal, oil and gas, which is contributing to the greenhouse gas (CO_2) emission. According to the International Energy Agency, 33.4 gigatons of CO_2 has been released to the environment in 2019. This prompts researchers to find alternative and novel methods of energy generation and storage that are friendlier to the environment [1].

Various carbon-based materials such as porous carbon, activated carbon, carbon nanotubes, and graphene have been investigated for energy storage due to their high surface area and good conductivity [2-5]. The global market for carbon was $1.67 billion in 2020 and it is projected to be $14.66 billion by 2024 [6]. Carbon or porous carbon is used as an electrode material in supercapacitor or electrochemical capacitor, which finds application in electric vehicles (EV), portable devices, and others. Moreover, supercapacitors also possess some advantage over conventional batteries such as fast charging/discharging cycles and long cycle life. [4,7]. Asymmetric supercapacitor (different electrode materials as anode and cathode) is observed to perform better than traditional symmetrical supercapacitor due to an additional charge transfer within a region of applied potential. As per the Ragone plot [8], asymmetric supercapacitors (ASCs) possess higher power density as compared to batteries, fuel cells, and symmetric supercapacitor. ASCs also possess a better energy density as compared to conventional capacitor. The performance of ASC depends upon the carbon materials such as graphene, carbon nanotubes, and activated carbon used as one of the electrode materials [9-13]. Among the carbon materials, graphene has emerged as the desired material [14]; however, it is expensive. Biochar derived from biomass can be cost effective, which is currently being investigated for supercapacitor application [15].

In this study, porous carbon derived from corn stover was used as anode in ASC whereas sol-gel derived (Mn, Ti)-mixed oxide was used as the cathode. BET analysis was performed on the anode material, and the fabricated ASCs were characterized using cyclic voltammetry to determine their specific capacitance.

2. EXPERIMENTAL

2.1 Materials

All reagents were analytical grade and used as received. Ti-isopropoxide (98%, Acros Organics), Mn-nitrate tetrahydrate (98%, Alfa Aesar) and Pluronic 123 (MW-5800, BASF) were used for the sol-gel synthesis. Ethanol (200% proof) was obtained from AAPER and concentrated HCl (35.5%) was purchased from Fisher-Scientific. Corn stover (avg. particle size 1.12 mm) was supplied by Idaho National Laboratory (INL), Idaho.

2.2 Preparation of Electrode Material

A slurry of corn stover (10 wt%) in de-ionized water with 5 wt% $Ca(NO_3)_2$ catalyst was loaded in the PARR high-temperature high-pressure (HTHP) reactor (300 ml capacity). It was heated to 250°C to perform HTL reaction, which was carried out for 1 hour. Following the HTL reaction, the processed slurry was filtered, and the solid residue was recovered. Next, the residue was washed with acetone to separate bio-oil and the resultant solids were dried in the conventional oven at 80°C. Hydrochar obtained was then chemically activated with KOH in presence of CTAB, cetyltrimethylammonium bromide surfactant. Later, the solids were recovered and thermally activated in a Carbolite horizontal tubular furnace at 400°C for 1 hour in presence of ultrahigh purity N_2. Following the thermal activation, the mixture was acid washed with 0.1 M HCl to remove the impurities. Finally, the activated hydrochar was washed to pH neutral with DI water and dried. A schematic of this process is presented in Figure 1 below. Additional details of this process can be found elsewhere [16].

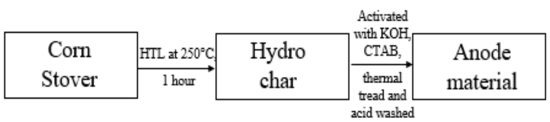

Figure 1: Schematic of the process used to obtain porous carbon as anode for ASCs.

As for the cathode side, (Mn, Ti)-oxide electrode material was synthesized using sol-gel approach. Sol-A was prepared by sonicating Ti-isopropoxide precursor in ethanol containing Pluronic 123 (5 wt.%), which was acidified with HCl. Sol-B was prepared by dispersing Mn-nitrate tetrahydrate in ethanol. The two solutions were mixed for 10 minutes. To the mixed solution, de-ionized water was added to achieve the gelation. The gel was aged, dried, and calcined at 500° and 1000°C. Additional details can be found elsewhere [17-19].

2.3 Fabrication of the asymmetric supercapacitors (ASC)

Two identical copper plates (0.5 inch x 0.5 inch) were sanded on one side to achieve better adhesion of electrode material. Sol-gel derived (Mn, Ti)-oxide and porous carbon materials were applied on the sanded side of the copper plate using fast drying polyurethane. The system was then sealed tightly with vacuum sealer roll and duct tape to avoid dust contamination. Then, it was charged using a DC power supply at 5 volts and 0.03 amps for 10 minutes. After fully charged, the asymmetric supercapacitors were analyzed by cyclic voltammetry using a G-300 potentiostat/ galvanostat/ZRA from Gamry. Detailed fabrication of ASCs can be found elsewhere [20].

3. RESULTS AND DISCUSSION

Activated porous carbon material derived from corn stover was analyzed by BET specific surface area analyzer to investigate the nitrogen adsorption-desorption isotherms, which is shown in Figure 2 below. It can be observed that the isotherm is type-IV isotherm with a hysteresis loop at a relatively high P/Po range. This signifies a capillary condensation in the mesoporous. The average pore diameter and BET SSA was ~3 nm and 102 m^2/g, respectively.

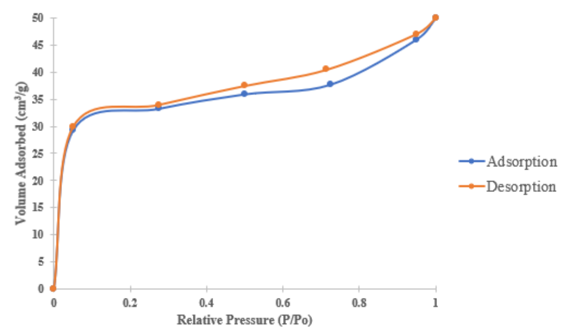

Figure 2: Nitrogen adsorption and desorption isotherm for the KOH activated and thermally treated porous carbon derived from HTL of corn stover.

Cyclic voltammetry (CV) was performed on the ASCs fabricated with (Mn,Ti)-oxide and porous carbon electrodes. CV measurements were repeated multiple times. Figure 3 shows 4 CV cycles for the ASC. Multiple oxidation and reduction peaks can be observed, which can be explained as the oxidation of Mn^{+2} to Mn^{+6}. The following equation was used to determine the specific capacitance $C_{ASC} = \frac{I.t}{m.\Delta V}$, in which I is the current in amps, t is the discharge time in sec, m is the mass of the working electrode in grams and ΔV is the voltage, in volts [21].

Specific capacitance of 92.3 F/g was observed for the ASC fabricated with (Mn, Ti)-oxide electrode consists of TiO_2-Rutile (R) phase (47.3 wt%) and $TiMnO_3$-Perovskite (P) phase (52.7 wt%) revealed via X-ray diffraction (XRD) analysis, which was synthesized via 2-step calcination (step-1: heated to 500°C, followed by cooling to 50ºC and in step-2, calcined to 1000ºC followed by cooling to room temperature). Further details on the phase formation w.r.t. calcination conditions can be found elsewhere [20]. The specific capacitance was found to decrease with increase in number of charge-discharge cycles (Figure 4).

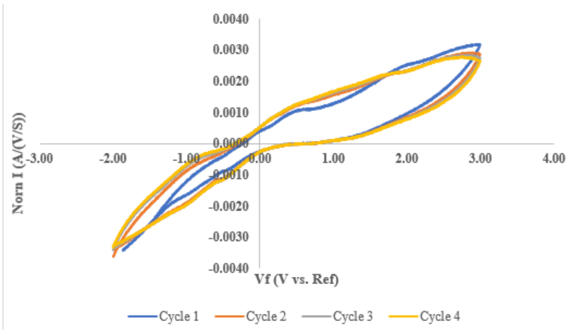

Figure 3: Cyclic voltammetry plots of the ASCs.

For the ASCs prepared with (Mn,Ti)-oxide calcined at 500 ºC, the specific capacitance was found to be lower as compared with the (Mn,Ti)-oxide calcined with 2-step method. Regardless of the calcination tempeture, the specific capacitance was found to decrease with increase in charging-discharging cycles.

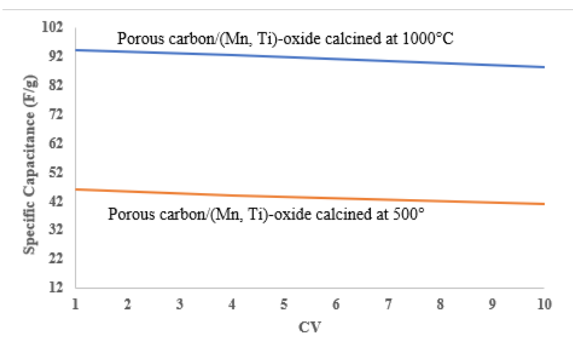

Figure 4: Specific capacitance as a function of CV cycles.

Currently, we are investigating the effect of surfactant on porous carbon characteristics and electrochemical charge storage.

4. CONCLUSION

Pulverized corn stover was treated with HTL and the hydrochar derived was successfully activated by KOH and thermally treated at 400ºC. The BET specific surface area analysis of the derived porous carbon showed SSA of 102 m^2/g and average pore diameter of ~3 nm. When used as anode for asymmetric supercapacitor (ASC) with (Mn, Ti)-oxide (calcinated at 500°C), the specific capacitance of 43 F/g was observed in first CV cycle. For the ASCs prepared with porous carbon/(Mn,Ti)-oxide (step 1- calcined at 500ºC followed by cooling to 50ºC; step-2, calcined at 1000ºC and cooled down to room temperature), average specific capacitance of 92.3 F/g was observed. The specific capacitance was found to decrease with increase in charging-discharging cycles.

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