Microwave-Assisted Hydrothermal Preparation of Corn Straw Hydrochar as Supercapacitor Electrode Materials

Dongdong Liu, Yiting Wang, Boyin Jia, Jintao Wei, Junhao Zhu, Shanshan Tang, Zhihai Wu,* and Guang Chen*

ABSTRACT: In this work, we propose the microwave-assisted hydrothermal activation method to synthesize supercapacitor electrode materials from corn straw under a small amount of the potassium catalyst (30 wt %), which can meet the environmental protection and low-cost requirement. With the extension of radiation time from 40 to 100 min, the pore structure of hydrochar expands from the micropore to hierarchical pore, and the microstructure evolves from an amorphous structure to graphene-like sheets. Microwave-assisted hydrothermal activation can control the synergistic development of hierarchical pore and graphene-like sheets of hydrochar under the condition of using a lesser amount of the catalyst. The as-obtained HTC-40/70/100 shows an excellent graphitization degree and the developed hierarchical pores. By comparing the electrochemical performance of the symmetrical capacitor devices composed of corn straw hydrochar and pyrochar in organic electrolytes, we have found that the hydrochar is suitable for organic system symmetric capacitance, and the pore structure and graphitization degree are closely related to the transmission of ions and electrons in the electrolyte. Therefore, HTC-100 with a high specific surface area (1781 m²/g) and highly ordered microstructure has the best electrochemical performance.

1. INTRODUCTION

A supercapacitor is an electrochemical capacitor with high energy density, which has the characteristics of quick charge and discharge of a capacitor and energy storage characteristics of a battery.1 Electrode materials are the critical components of energy storage devices, and the pore structure and conductivity are the crucial factors to determine its electrochemical performance. More concretely, the pore structure provides diffusion channel, adsorption, and a storage place for electrolyte ions. The ordered graphitic crystallite structure can help the electron transport, showing excellent electronic conductivity.2 Therefore, the preparation of ideal electrode materials (including the developed pore structure and ordered graphitic crystallite) has become the focus of research. Porous carbon has become a promising electrode material for supercapacitors because of its high specific capacitance, long cycle life, and abundant resources.4 Usually, the production of porous carbon is based on the biomass/coal and chemical activation method. Zhang et al.5 and Xia et al.6 prepared three-dimensional porous carbon nanosheets with a few layer graphite structure by KOH and K2CO3 activation using a banana peel as a carbon source. Muramatsu et al.7 prepared nanosheets with a graphene domain structure by KOH activation of corn husk ash. Chen et al.8 found that the rapid increase of the specific surface area (S_BET) and ordering degree of the as-obtained sample mainly depended on the addition of excess chemicals (about 4–5 times of the raw material). Many scholars had explored the reason about the excessive addition of chemical reagents. Olsson et al.9 found that the alkali metals (such as Na and K) began to release at 180 °C, and when the temperature was higher than 500 °C, the release rate increased significantly. Kowalski et al.10 found 53–76% alkali metals and 27–40% alkaline earth metals released with the increase of heat treatment temperature to 800 °C, which was mainly due to the substitution reaction between a lot of free radicals and carbon radicals. Li et al.11 found that there were two temperature peaks (300–400 °C and above 600 °C) during the release of alkali metals, the former was the decomposition of organic salts and the latter was the evaporation of inorganic salts. From the above analysis, large amounts of alkali metals in the samples were released in the gaseous form under an open...
pyrolysis environment. Therefore, the addition of excessive chemical agents is to supplement the release of the catalyst during the traditional activation process. Generally, the addition of excessive activation agents can improve the physicochemical properties of porous carbon as electrode materials, but it also inevitably leads to high cost and environmental pollution. Only a closed environment can effectively prevent the release of alkali metals to play its catalytic role, which realizes the preparation of ideal electrode materials using a small number of chemical agents.

Hydrothermal carbonization (hereafter as HTC) can convert biomass into functional carbon materials and liquid fuels using the sub/supercritical water in a closed environment. HTC has the advantages of mild reaction conditions, low energy consumption, a wide range of raw materials, and environmental friendliness. Microwave irradiation can accelerate hydrolysis and different types of polymerization. Besides, microwave irradiation also promotes the movement of alkali metals between graphite sheets because of the excellent microwave absorption effect of alkali metals. Therefore, microwave-assisted hydrothermal treatment is an excellent method to hinder the release of alkali metals from samples and can give full strength to its catalytic role. It is significant to study the effect of microwave-assisted hydrothermal activation on the physicochemical structure of hydrochar and its electrochemical properties.

In this work, the feasibility of preparing ideal electrode materials from biomass using microwave-assisted hydrothermal activation and a small number of chemical reagents was studied. The changes of the physical–chemical structure of hydrochar prepared by microwave-assisted hydrothermal activation and pyrochar prepared by traditional chemical activation were discussed and analyzed in detail. The electrochemical properties of the obtained hydrochar and pyrochar were tested using an organic electrolyte system.

2. RESULTS AND DISCUSSION

2.1. Surface Morphology Analysis of Corn Straw Hydrochar and Pyrochar. Figure 1 shows the scanning electron microscopy (SEM) images of corn straw hydrochar and pyrochar. The surface of HTC-40(K) presents some pores with different shapes, and its surface is loose and rough. The surface of HTC-70(K) and HTC-100(K) has a lot of pores with different sizes and shapes, and their surface becomes rougher. From further observation, the pore edge of HTC-100(K) is concave inward to expose more internal structure, and the phenomenon of multilayered pores with “holes in the hole” can be found in Figure 1c. The analysis shows that a lot of cellulose and soluble sugars in corn straw are dissolved and separated from the fiber skeleton in a hydrothermal environment, which makes the loose skeleton structure open and exposed. Then, a lot of volatile components (such as CO, CO2, C2H4, etc.) become more comfortable to escape from this free framework structure, resulting in the formation of pores of different sizes and shapes. Also, the hydrothermal reaction is enhanced gradually by the extension of microwave radiation time from 40 to 100 min. In this process, high-temperature and pressure water can also remove the impurities in the original pores of straw hydrochar to open some of the blocked pores.

AC-500(K) presents a regular and compact surface morphology, which is related to the softening of straw during dehydration and degassing. With the increase of heat treatment temperature from room temperature to 500 °C, the macromolecular structure of straw begins to depolymerize and produce a lot of tar components. Some of them are released in the form of gas, and the other part reaggregates, precipitates, and continuously diffuses on the particle surface to form the metaplast, resulting in the plugging of pores and a smooth surface morphology. Then, AC-800(K) presents a slightly rough surface, and there are some pores on its particle surface. The production of many pores is related to the rapid release of a lot of volatile compounds formed by the continuous depolymerization of the molecular structure. The surface of AC-1000(K) presents the silver-grey metallic lustre and a small number of pores and cracks. The shrinkage of straw pyrochar promotes the collapse of some pores and the formation of cracks, resulting in the more compact surface morphology.

2.2. Microstructure Analysis of Corn Straw Hydrochar and Pyrochar. Figure 2 shows the transmission electron microscopy (TEM) images of corn straw hydrochar and pyrochar. There are some parallel microcrystalline layers with well the perfection and stacking degree. Besides, there are the potassium-based compound nanoparticles with a similar circular or elliptical shape in HTC-40(K), HTC-70(K), HTC-100(K), AC-500(K), AC-800(K), and AC-1000(K).
gradually increases, indicating that microwave-assisted hydrothermal activation can retain more catalysts in straw hydrochar. The analysis shows that the potassium-based compounds with good permeability can intercalate into the carbon structure to form potassium carbon complexes. These complexes can be further decomposed into potassium and graphite carbon under certain conditions. In this process, an amorphous carbon structure can transform into microcrystalline layers. Microwave irradiation can accelerate the movement of the potassium-based compounds between the carbon layers, which is beneficial to the uniform distribution of the catalyst on the surface of the particles and inside the particles. In this process, the contact between the catalyst and the carbon layers becomes closer and closer, which further promotes the formation of ordered graphitic crystallite. The HTC can hinder the rapid volatilization of a potassium-based catalyst to play its role in catalytic graphitization.

AC-500(K) is mainly composed of amorphous carbon, as shown in Figure 2d. Our previous studies found that the potassium-based compounds played their role in catalytic cracking instead of graphitization at low temperatures. With the increase of heat treatment temperature from 500 to 1000 °C, the condensation, aromatization, and dehydrogenation of hydrogenated aromatics of straw pyrochar can lead to the formation of more microcrystalline layers. However, AC-500/800/1000(K) contains only a small area and few layers of microcrystalline layers, which is related to the release of more potassium-based compounds in an open environment.

2.3. Crystal Structure Analysis of Corn Straw Hydrochar and Pyrochar. Figure 3 shows the X-ray diffraction (XRD) profiles of corn straw hydrochar and pyrochar. There are two diffuse diffraction peaks in the XRD patterns of all samples, namely, 002 peak (2θ = 20−30°) and 100 peak (2θ = 35−55°). The 002 peak and 100 peak reflect the stacking thickness and the condensation degree of the aromatic layers. Further observation, AC-500/800/1000 shows two broad peaks at 24 and 43°, respectively, indicating the small size and low degree orientation of straw pyrochar. The 002 and 100 peaks of HTC-40/70/100 are high and narrow, indicating the large size and good degree orientation of straw hydrochar. To further study the crystal structure changes of straw hydrochar and pyrochar, the 002 and 100 peaks of all samples are treated by fitting method, and the specific parameters [such as layer distance (d002), stacking height (Lc), width (La), and layer number (N = Lc/d002)] are calculated by the Bragg law and Scherrer formula, as shown in Table 1.

According to the data in Table 1, the Lc, La, d002, and N of straw hydrochar increase significantly. A large number of side chains, functional groups, and other unstable components in corn straw dissolve out in the hydrothermal environment.
which makes the carbon skeleton more easily disintegrate into many "small microcrystalline units". With the extension of irradiation time from 40 to 100 min, the strong hydrolysis reaction and the catalysis of the potassium-based compounds can further induce the rapid polymerization or cross-linking reaction between these "small microcrystalline units", resulting in the significant changes on the structural morphology of straw hydrochar. In addition, many scholars found that the optimization of the stacking morphology and the expansion of the interlayer spacing were conducive to the adsorption and embedding of electrolyte ions. Alternatively, the $I_D/I_G$ and $I_{2D}/I_G$ values of all samples are shown in Table 2.

The Raman spectrum of straw hydrochar presents high and narrow peaks of D band, 2D band, and G band. According to the data in Table 2, a decreasing $I_D/I_G$ value from 0.41 to 0.11 and an increased $I_{2D}/I_G$ value from 0.48 to 0.91 for HTC-40/70/100 imply an increasing graphitization degree. Sevilla and Fuertes found that biomass was first hydrolyzed to a large number of acids, aldehydes, and phenols by hydrogen hydrate. The polymerization or polycrystallization reactions were further induced by intermolecular dehydration or aldehyde alcohol condensation, thus forming the graphite structures. Besides, our previous study found that the free movement of potassium-based compounds between layers could promote the growth and condensation of microcrystals. Based on the characteristics, the aliphatic/aromatic structure of HTC-40/70/100 is rapidly transformed into graphene-like flakes with the extension of microwave radiation time from 40 to 100 min. Therefore, microwave-assisted hydrothermal activation is favorable to the rapid formation of the majority of graphene-like sheets under a small amount of potassium-based catalysts.

For straw pyrochar, the widening D and G bands and the increase of the ratio of the I_D/I_G value indicates that the disordered degree of the microstructure of carbon materials is stronger. In addition, AC-1000 and HTC-40/70/100 all have the 2D band at 2692 cm⁻¹, which is more sensitive to the rapid increase of graphene layers. The increase of the $I_{2D}/I_G$ value indicates the highly ordered degree of carbon materials. The $I_D/I_G$ and $I_{2D}/I_G$ values of all samples are shown in Table 2.

### Table 2. Relative Intensity Ratio ($I_D/I_G$) and ($I_{2D}/I_G$) of Corn Straw Hydrochar and Pyrochar

|         | HTC-40 | HTC-70 | HTC-100 | AC-500 | AC-800 | AC-1000 |
|---------|--------|--------|---------|--------|--------|---------|
| $I_D/I_G$ | 0.41   | 0.25   | 0.11    | 1.16   | 1.25   | 0.87    |
| $I_{2D}/I_G$ | 0.48   | 0.77   | 0.91    | 0.33   |        |         |

**Figure 4.** Raman spectrum of corn straw hydrochar and pyrochar (a) HTC-40, (b) HTC-70, (c) HTC-100, (d) AC-500, (e) AC-800, and (f) AC-1000.

2.4. Hybrid Carbon Structure Analysis of Corn Straw Hydrochar and Pyrochar. Figure 4 shows the Raman spectrum of corn straw hydrochar and pyrochar. All samples have the D band (1350 cm⁻¹) and G band (1590 cm⁻¹). The D band represents the defect structure with more than six large aromatic rings connected by C−C, which is related to the in-plane vibration of the edge carbon atom, heteroatom, and sp² carbon atom with structural defects. The G band represents the stretching vibration of the lamellar carbon atoms in the ideal graphite crystal, which is related to all paired sp² carbon atoms in the aromatic ring structure. The increase of the $I_D/I_G$ value indicates that the disordered degree of the microstructure of carbon materials is stronger. In addition, AC-1000 and HTC-40/70/100 all have the 2D band at 2692 cm⁻¹, which is more sensitive to the rapid increase of graphene layers. The increase of the $I_{2D}/I_G$ value indicates the highly ordered degree of carbon materials. The $I_D/I_G$ and $I_{2D}/I_G$ values of all samples are shown in Table 2.

The Raman spectrum of straw hydrochar presents high and narrow peaks of D band, 2D band, and G band. According to the data in Table 2, a decreasing $I_D/I_G$ value from 0.41 to 0.11 and an increased $I_{2D}/I_G$ value from 0.48 to 0.91 for HTC-40/70/100 imply an increasing graphitization degree. Sevilla and Fuertes found that biomass was first hydrolyzed to a large number of acids, aldehydes, and phenols by hydrogen hydrate. The polymerization or polycrystallization reactions were further induced by intermolecular dehydration or aldehyde alcohol condensation, thus forming the graphite structures. Besides, our previous study found that the free movement of potassium-based compounds between layers could promote the growth and condensation of microcrystals. Based on the characteristics, the aliphatic/aromatic structure of HTC-40/70/100 is rapidly transformed into graphene-like flakes with the extension of microwave radiation time from 40 to 100 min. Therefore, microwave-assisted hydrothermal activation is favorable to the rapid formation of the majority of graphene-like sheets under a small amount of potassium-based catalysts.
The rapid transformation of isolated sp² carbon atoms (the silicon-based compounds at higher temperatures can promote microstructure. The strong catalytic graphitization of potassium-based compounds at higher temperatures can promote the rapid transformation of isolated sp² carbon atoms (the large aromatic ring system and disordered sp² carbon atoms (small aromatic ring system) into crystal sp² carbon atoms, and Pyrochar.

Figure 5. N₂ adsorption isotherms of corn straw (a) hydrochar and (b) pyrochar.

Table 3. Pore Structure Parameters of Corn Straw Hydrochar and Pyrochar

|                | HTC-40 | HTC-70 | HTC-100 | AC-500 | AC-800 | AC-1000 |
|----------------|--------|--------|---------|--------|--------|---------|
| S_BET (m²/g)   | 1065   | 1534   | 1781    | 135    | 312    | 224     |
| V_t (m³/g)     | 0.58   | 0.94   | 1.21    | 0.10   | 0.21   | 0.15     |
| V_mic (m³/g)   | 0.44   | 0.51   | 0.60    | 0.07   | 0.16   | 0.12     |
| D_ap (nm)      | 2.61   | 3.18   | 3.86    | 2.51   | 2.92   | 2.70     |

**Note:** S_BET: specific surface area; V_t: total pore volume; V_mic: micropore volume; and D_ap: average pore diameters.

further produce pyrolysis gas and tar. Still, the combination of small free radicals and large free radicals or between large free radicals could form various aromatic structures. AC-1000 contains the narrowing D and G bands and a sudden presence of the 2D band. The I_D/I_G and I_{2D}/I_G values of AC-1000 are 0.87 and 0.33, implying its order development of the 2D band. The strong catalytic graphitization of potassium-based compounds at higher temperatures can promote the rapid transformation of isolated sp² carbon atoms (the large aromatic ring system and disordered sp² carbon atoms (small aromatic ring system) into crystal sp² carbon atoms, which leads to the increasing graphitization degree of AC-1000. Still, a small number of the catalyst cannot effectively play its role in catalytic graphitization during traditional chemical activation.

### 2.5. Pore Structure Analysis of Corn Straw Hydrochar and Pyrochar

Figure 5 shows the N₂ adsorption isotherms of corn straw hydrochar and pyrochar. Table 3 gives the corresponding pore structure parameters. First, the adsorption isotherms of HTC-40/70/100 all exhibit type I and IV. The high adsorption capacities of hydrochar at low pressure (P/P₀ < 0.2) indicate the existence of a large number of micropores. The adsorption and desorption curves begin to diverge and present a crescent-shaped hysteresis loop with the increase of relative pressure from 0.4 to 1.0. This is related to the capillary condensation caused by rich mesopores in the sample. These changes mean that there are both mesopores and micropores (namely the hierarchical pores) in straw hydrochar. From further observation, the adsorption capacities of HTC-70/100 at low pressure increase evidently, and their isotherms and hysteresis loops become steeper and larger with the increase of relative pressure. According to the data in Table 3, there is a significant increase in all pore structure parameters with the extension of radiation time. The analysis shows that hydrolysis makes cellulose and hemicellulose in straw decompose gradually, leading to the weakening of van der Waals forces between layers. When the pressure generated by the rapid movement of potassium under the longer radiation time exceeds the van der Waals force, the layers are peeled off to form different pores (including the micropores and mesopores). In addition, the yield of gaseous products increases in the hydrothermal process, and the jet pressure caused by these gaseous products can open some blind or closed holes. Under the shorter microwave irradiation, the strong hydrolysis also makes the micropores expand obviously into mesopores. Therefore, microwave-assisted hydrothermal activation is favorable to the development of hierarchical pores under a small amount of potassium-based catalysts.

Then, the N₂ adsorption isotherm of AC-500 is type I, and its adsorption capacity at low pressures and the corresponding pore parameters are low, showing the underdeveloped pore structure. The analysis shows that a lot of tar substances aggregate on the surface of the particles and cover the pores, leading to the rapid reduction of porosity. Compared with AC-500, the N₂ adsorption isotherm of AC-800 evolves from type I to type I/IV. The adsorption capacity of AC-800 increases at low pressure, and its curvature of the inflection point becomes larger. These changes indicate the formation of hierarchical pores and rapid increase of micropores. Besides, the pore structure parameters of AC-800 are the highest in all straw pyrochar, as shown in Table 3. With the increase of heat treatment temperature from 500 to 800 °C, more volatiles (including tar components and other small molecules) are released from the interior of the particles to produce a large number of pores. However, the adsorption capacity of AC-1000 decreases at low pressure, and its adsorption and desorption curves coincide and become stable. The V_t, V_mic, and S_BET values of AC-1000 also decrease significantly. When the heat treatment temperature continues to rise to 1000 °C, the yield of the volatile matter reduces greatly. Meanwhile, the strong thermal condensation behavior can cause the collapse of the pore structure at higher temperatures. Therefore, the ideal porous material (such as HTC-1000), with a high S_BET of 1781 m²/g, V_t of 1.21 m³/g and V_mic of 0.60 m³/g, can be prepared...
2.6. Evolution of the Potassium-Based Catalyst during Different Activation Methods. The weight loss behavior of corn straw hydrochar and pyrochar without acid treatment [HTC-40/70/100(K) and AC-500/800/1000(K)] during the temperature-programmed process is shown in Figure 6. AC-500/800/1000(K) all show a sustained and slow weightlessness during the temperature-programmed process, and the weight loss ratio from large to small is as follows: AC-500(K), AC-800(K), and AC-1000(K). The analysis shows that the weight loss of straw pyrochar is mainly related to the generation and release of a certain amount of the volatile matter because of the repeated depolymerization of the molecular structure during the temperature-programmed process. Remarkably, the cross-linking and polycondensation reactions at the higher preparation temperatures are conducive to the formation of the high-stability macromolecular structure, resulting in a small change in weight loss for AC-800(K) and AC-1000(K) during the temperature-programmed process. The weight loss curves of HTC-40/70/100(K) show no obvious change from room temperature to 700 °C and a sudden decrease from 600 to 1000 °C. According to the literature, the decomposition temperature of potassium and its compounds was more than 600 °C. Therefore, the significant weight loss of HTC-40/70/100(K) is related to the decomposition of potassium and its compounds. In this process, a series of redox reactions can occur between the potassium-based catalyst and the coal matrix, resulting in the release of a large number of volatile components. Remarkably, the weight loss curves of HTC-40/70/100(K) are similar from 600 to 1000 °C, indicating that the potassium-based catalysts can be retained in straw hydrochar by microwave-assisted hydrothermal activation. However, there is a slight decrease in the weight loss of AC-500/800/1000(K) from 600 to 1000 °C, indicating the release of many catalysts during the traditional activation stage.

Figure 7 shows the phase analysis of HTC-40/70/100(K) and AC-500/800/1000(K). Figure 7a−c shows that the potassium-based compounds form the main characteristic peak of HTC-40/70/100(K), indicating the presence of many catalysts during the microwave-assisted hydrothermal activation stage. From further observation, the peak height of K, K₃C₂, KC₈, and K₄C₆O in HTC-40/70/100(K) increases, but the peak height of K₂CO₃, KHCOS, and KO₂ reduces gradually. First, a series of redox reactions occur between the potassium-based catalyst and biomass matrix, resulting in the formation of K₂CO₃, KHCOS, and KO₂. The potassium-based catalyst can provide a relatively homogeneous thermal environment in the process of continuous “impregnation” into the molecular structure of the biomass, which accelerates the structural depolymerization and the release of the volatile matter to form the developed pores. Then, with the extension of microwave radiation time from 40 to 100 min, potassium-based oxides melt and react with the carbon structure to form a large amount of potassium (such as K₂CO₃ + C → K + CO). Because of its good permeability, potassium can intercalate into the carbon structure to form potassium carbon complexes.
(K₂C₂, K₃C₈, and K₄C₆₀). These complexes can further decompose into potassium and graphene sheets under certain conditions. Therefore, the peak intensities of K, K₂C₂, K₃C₈, and K₄C₆₀ are also positively proportional to the graphitization degree. However, AC-500/800/1000(K) show the relatively obvious characteristic peak of the carbon-based component ([002 peak and 100 peak) and a small number of potassium compounds, as shown in Figure 7d–f. These changes are related to the release of the potassium-based catalysts during the traditional activation stage. Further investigation reveals that AC-800(K) and AC-1000(K) mainly contain a small amount of K, K₂C₂, K₃C₈, and K₄C₆₀, indicating their improvement of graphitization degree.

2.7. Electrochemical Measurements. According to the results and analysis from Sections 2.1 to 2.6, HTC-40/70/100 are more suitable as the electrode material owing to the developed pores and highly ordered microstructure. To determine the electrochemical advantages of straw hydrochar and pyrochar, we construct a 1 M TEA BF₄-PC organic electrolyte system symmetrical supercapacitor device and test the corresponding electrochemical performance.

Figure 8 shows the electrochemical performance analysis of a symmetrical capacitor composed of HTC-40/70/100 and AC-500/800/1000 electrodes in a 1 M TEA BF₄-PC organic electrolyte system. Figure 8a shows the cyclic voltammetry (CV) curve of HTC-40/70/100 and AC-500/800/1000 at a charge–discharge current density of 1 A/g; (c) CV curves at various scan rates of HTC-100-based capacitor; (d) GC curves of HTC-100-based capacitor at various charge–discharge current densities; (e) Nyquist plot of HTC-40/70/100; and (f) Ragone plots of HTC-70- and HTC-100-based capacitors.
densities. At a current density of 0.5 A/g, the power density of the symmetrical capacitor composed of HTC-40 and HTC-100 at different current densities. At a current density of 0.5 A/g, the power density and energy density of the organic symmetric capacitor device with HTC-70 are 120 W/kg and 10.3 W h/kg, respectively. Still at 20 A/g current density, the organic symmetric capacitor device can only provide 3600 W/kg and 4.37 W h/kg, indicating that energy density attenuation of HTC-70 is severe under high current density. Remarkably, the power density and energy density of HTC-100 are 340 W/kg and 96 W h/kg at a current density of 0.5 A/g. HTC-100 still provides 9500 W/kg and 77 W h/kg at 20 A/g current density. These changes indicate that the attenuation of HTC-100 is not obvious even at high current density. The above results indicate that the organic series capacitor devices of samples with developed hierarchical pores and high graphitization characteristics have higher specific capacitance and rate performance.

3. CONCLUSIONS

This paper has demonstrated a novel microwave-assisted hydrothermal activation method using a small amount of the potassium-based catalyst (30 wt %) to obtain a series of corn straw hydrochar as electrode materials. In the preparation stage, we compare the difference of the physical–chemical properties of hydrochar (HTC-40/70/100) and pyrochar (AC-500/800/1000). A large amount of the catalyst is retained within the carbon material under a hydrothermal environment. Still the traditional activation method accelerates the release of the catalyst from pyrochar. Also, microwave irradiation not only can accelerate the hydrolysis, which is conducive to the strong depolymerization and reorganization of the carbon framework, but also can promote the movement of the potassium-based catalyst between the carbon layers to give a graphitization effect. Therefore, the different pores and the ordered microcrystalline layer can be formed by the depolymerization and rearrangement of the molecular structure of corn straw during microwave-assisted hydrothermal activation. A series of hydrochar with a highly ordered microstructure and developed hierarchical pores can be obtained by extending the microwave radiation time and using a small amount of potassium-based catalysts. By comparing the electrochemical performance of hydrochar and pyrochar in organic electrolytes, the matching relationship between the pore size and electrolyte ion size determines the specific capacitance of organic symmetric capacitor devices. The graphitization degree of the samples has an important impact on the transmission of ions and electrons in the electrolyte. Therefore, HTC-100 with a large number of developed hierarchical pores and high graphitization degree show the highest specific capacitance and the best rate performance of the symmetrical capacitor devices constructed.

4. EXPERIMENTAL SECTION

4.1. Sample Pretreatment. Corn straw from the Jilin province in China was crushed and sieved to 60–80 mesh, the results of the proximate and ultimate analysis are given in Table 4. In order to remove the inorganic impurities in corn straw, 6 mol·L⁻¹ HCl (200 mL) was mixed with 15 g of the sample and magnetically stirred at room temperature for 12 h.
The mixture was filtered and washed with deionized water until no chloride ion was detected. Then, HCl-treated samples were mixed with 40 wt % HF (120 mL) and magnetically stirred at room temperature for 12 h. The acid-treated samples were repeatedly washed with deionized water until the solution was neutral. Finally, the demineralized samples dried in a 105 °C blast drying oven for 12 h, and then denoted CS.

4.2. Experimental Arrangement. For the preparation of corn straw hydrochar, 6 g of CS and 3 g of KOH powder weighed in a hydrothermal tank, and 50 mL of deionized water was mixed. The reaction tank was then closed tightly, put into the microwave reactor, heated at 1000 W and 2450 MHz, and held for a specific time (40, 70, and 100 min, respectively). After this process, the reactor cooled down to 60 °C. The solid phase of the mixture was collected by filtration, then washed with 30 mL of ethanol one time, 30 mL of deionized water three times, and dried at 100 °C for 8 h. The as-obtained hydrochar was marked as HTC-diifferent time (K). After the potassium-based compounds in samples were removed by using 0.2 mol·L⁻¹ HCl, the as-obtained hydrochar was marked as HTC-diifferent temperature (K). For the preparation of corn straw pyrochar, the mixture (including 6 g of CS and 3 g of KOH powder) was raised to the setting temperature (500, 800, and 1000 °C, respectively) at 5 °C/min under a N₂ atmosphere of 400 mL/min in a horizontal tube reactor, and held for 2 h. After naturally cooled it to room temperature, the as-obtained pyrochar was marked as AC-diifferent temperature (K). The potassium-based compounds in samples were removed by 0.2 mol·L⁻¹ HCl and deionized water, then a series of reference pyrochar was obtained after drying and marked as AC-diifferent temperature. 

4.3. Measurement Analysis. SEM (Hitachi, Regulus 8200, 200 kV) and TEM (Hitachi, H-9500, 300 kV) used to obtain the surface morphology and microstructure of the samples. The pore structure of the samples was characterized by a nitrogen adsorption analyzer (Micromeritics instrument, ASAP2020) at −196 °C in liquid nitrogen. The adsorption/desorption isotherms, pore size distribution curves, and specific pore parameters (including specific surface area, total/micropore/medium and large pore volume, average pore size, etc.) were obtained. The microcrystalline structure and phase composition of the sample were characterized by Raman spectroscopy (Renishaw inVia, 532 nm wavelength) and XRD (Shimadzu, 6100). A thermogravimetric analyzer (Beijing Hengjiu, HCT-4) was used to monitor the weight loss of the samples from room temperature to 1000 °C at 5 °C/min under a N₂ atmosphere of 400 mL/min. The conversion and normalized reaction rates of samples were calculated by $X_t = W_t/W_0$ and $K_t = (dX/dt)/(1 - X)$ to evaluate the reactivity of different samples. Where, $X_t$ was the carbon conversion rate, $W_0$ was the initial mass of the sample, $W_t$ was the sample mass at time $t$, $K_t$ was the normalized reaction rate (min⁻¹), $dX/dt$ was the reaction rate, and $X_t$ was the carbon conversion rate of the sample measured at time $t$.

4.4. Electrochemical Measurements. The preparation of electrode materials follows the steps: in anhydrous ethanol, porous carbon samples, conductive carbon black (Super P), and 60 wt % polytetrafluoroethylene were ground evenly into the film according to a mass ratio of 8:1:1, and then dried in a vacuum drying oven (the drying temperature was 120 °C and the drying time was 12 h). Each time, 2 mg of the film used to prepare the single electrode, with an area of about 1 cm². The assembly process of the symmetrical supercapacitor was as follows: two mass plates of the same quality were selected and pressed on a foam nickel collector with a diameter of 1.2 cm and dried in a vacuum drying oven (120 h at 120 °C) for positive and negative electrodes. In the process of assembling organic capacitors, 1 M TEA BF₄-PC was selected as electrolytes, and the glass fiber membrane (Whatman) with a diameter of 1.6 cm was cut as the diaphragm. The button cell was assembled in the vacuum. The electrochemical performance test process of the capacitor device was as follows: electrochemical workstation (Biologic-VMP3) used to test the electrochemical performance, including CV curve at different scanning rates (10–200 MV/s), charge discharge curve, and AC impedance curve (frequency: 10²–10⁶ Hz) at different current densities (0.5–20 A/g). The specific electric capacity, energy density, and power density of the single electrode are calculated by $C = 2\Delta T/(m \Delta V)$, $e = C V^2/8$ and $P = E/\Delta T$, respectively. Where $\Delta V$ is the voltage range after the voltage drop is removed.

# AUTHOR INFORMATION

**Corresponding Authors**

Zhihai Wu — Faculty of Agronomy, Jilin Agricultural University, Changchun 130118, China; Email: wuzhihai1116@163.com

Guang Chen — Key Laboratory of Straw Biology and Utilization, The Ministry of Education, Jilin Agricultural University, Changchun 130118, China; orcid.org/0000-0003-4413-2358, Email: jlauchenguang@163.com

**Authors**

Dongdong Liu — Key Laboratory of Straw Biology and Utilization, The Ministry of Education and College of Engineering and Technology, Jilin Agricultural University, Changchun 130118, China

Yiting Wang — College of Engineering and Technology, Jilin Agricultural University, Changchun 130118, China

Boyun Jia — College of Animal Science and Technology, Jilin Agricultural University, Changchun 130118, China; orcid.org/0000-0002-7901-6675

Jintao Wei — College of Engineering and Technology, Jilin Agricultural University, Changchun 130118, China

Chang Liu — College of Engineering and Technology, Jilin Agricultural University, Changchun 130118, China

Junhao Zhu — College of Engineering and Technology, Jilin Agricultural University, Changchun 130118, China

Shanshan Tang — Key Laboratory of Straw Biology and Utilization, The Ministry of Education, Jilin Agricultural University, Changchun 130118, China; orcid.org/0000-0002-2944-0873

**Complete contact information is available at:**

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**Notes**

The authors declare no competing financial interest.

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REFERENCES

(1) Lo, A.-Y.; Chang, C.-C.; Lai, Y.-W.; Chen, P.-R.; Xu, B.-C. Improving the supercapacitor performance by dispersing SiO2 Microspheres in electrodes. ACS Omega 2020, 5, 11522–11528.

(2) Peng, X.; Peng, L.; Wu, C.; Xie, Y. Two dimensional nanomaterials for flexible supercapacitors. Chem. Soc. Rev. 2014, 43, 3303–3323.

(3) Wang, D.-W.; Li, F.; Liu, M.; Lu, G. Q.; Cheng, H.-M. 3D aperiodic hierarchical porous graphitic carbon material for high-rate electrochemical capacitive energy storage. Angew. Chem., Int. Ed. 2008, 47, 373–376.

(4) Ma, F.; Ma, D.; Wu, G.; Geng, W.; Shao, J.; Song, S.; Wan, J.; Qiu, J. Construction of 3D nano-structure hierarchical porous graphitic carbons by charge-induced self-assembly and nanocrystal assisted catalytic graphitization for supercapacitors. Chem. Commun. 2015, 52, 6673–6676.

(5) Zhang, J.; Zhang, C.; Zhao, Y.; Amiunu, I. S.; Zhou, H.; Liu, X.; Tang, Y.; Ma, S. Three dimensional few-layer porous carbon nanosheets towards oxygen reduction. Appl. Catal., B 2017, 211, 148–156.

(6) Xia, J.; Zhang, N.; Chong, S.; Li, D.; Chen, Y.; Sun, C. Three-dimensional porous graphene-like sheets synthesized from biocarbon via low-temperature graphitization for supercapacitor. Green Chem. 2018, 20, 694–700.

(7) Muramatsu, H.; Kim, Y. A.; Yang, K.-S.; Cruz-Silva, R.; Toda, I.; Yamada, T.; Terrones, M.; Endo, M.; Hayashi, T.; Saitoh, H. Rice husk-derived graphene with nano-sized domains and clean edges. Small 2014, 10, 2766–2770.

(8) Chen, C.; Yu, D.; Zhao, G.; Du, B.; Tang, W.; Sun, L.; Sun, Y.; Besenbacher, F.; Yu, M. Three-dimensional scaffolding framework of porous carbon nanosheets derived from plant wastes for high-performance supercapacitors. Nano Energy 2016, 27, 377–389.

(9) Olsson, J. G.; Jaglid, U.; Pettersson, J. B. C.; Hald, P. Alkali metal emission during pyrolysis of biomass. Energy Fuels 1997, 11, 779–784.

(10) Kowalski, T.; Ludwig, C.; Wokaun, A. Qualitative evaluation of alkali release during the pyrolysis of biomass. Energy Fuels 2007, 21, 3017–3022.

(11) Li, C.-Z.; Sathe, C.; Kershaw, J. R.; Pang, Y. Fates and roles of alkali and alkaline earth metals during the pyrolysis of a Victorian brown coal. Fuel 2000, 79, 427–438.

(12) Wang, L.; Sun, F.; Gao, J.; Pi, X.; Pei, T.; Qiu, Z.; Zhao, G.; Qin, Y. A novel melt infiltration method promoting porosity development of low-rank coal derived activated carbon as supercapacitor electrode materials. J. Taiwan Inst. Chem. Eng. 2018, 91, 588–596.

(13) Liu, D.; Xu, B.; Zhu, J.; Tang, S.; Xu, F.; Li, T.; Jia, B.; Chen, G. Preparation of highly porous graphitic activated carbon as electrode materials for supercapacitors by hydrothermal pretreatment-assisted chemical activation. ACS Omega 2020, 5, 11058–11067.

(14) Shi, N.; Liu, Q.; Liu, Y.; Chen, L.; Zhang, H.; Ma, L. Identification of the soluble byproducts formed during the hydrothermal conversion of cellulose catalyzed by solid tungstated alumina. ACS Omega 2020, 5, 19140–19150.

(15) Gala, A.; Schiavo, B.; Antonetti, C.; Galletti, A. M. R.; Interrante, L.; Lessi, M.; Scaldone, O.; Valenti, M. G. Autohydrolysis pretreatment of Arundo donax: a comparison between microwave-assisted batch and fast heating rate flow-through reaction systems. Biotechnol. Biofuels 2015, 8, 218.

(16) Galletti, A. M. R.; Antonetti, C.; Bertoldo, M.; Piccinelli, F. Chitosan as biosupport for the MW-assisted synthesis of palladium catalysts and their use in the hydrogenation of ethyl cinnamate. Appl. Catal., A 2013, 468, 95–101.

(17) Hui, Y.; Cao, L.; Xu, Z.; Huang, J.; Ouyang, H.; Li, J. Mesoporous LiTiO2 nanoparticles synthesized by a microwave-assisted hydrothermal method for high rate lithium-ion batteries. J. Electroanal. Chem. 2016, 763, 45–50.

(18) Pronyk, C.; Mazza, G.; Tamaki, Y. Production of carbohydrates, lignins, and minor components from triticate straw by hydrothermal treatment. Energy Fuels 2011, 59, 3788–3796.

(19) Liu, D. D.; Jia, B. Y.; Li, S.; Dong, L. J.; Gao, J. H.; Qiu, Y. K. Effect of pyrolysis conditions on the improvement of the physicochemical structure of activated carbon obtained from Jixi bituminous coal. Asia-Pac. J. Chem. Eng. 2019, 14, No. e2289.

(20) Yu, Y.; Lei, Z.; Yang, X.; Yang, X.; Huang, W.; Shimizu, K.; Zhang, Z. Hydrothermal carbonization of anaerobic granular sludge: effect of process temperature on nutrients availability and energy gain from produced hydrochar. Appl. Energy 2018, 229, 88–95.

(21) Zhai, Y.; Liu, X.; Zhu, Y.; Peng, C.; Wang, T.; Zhu, L.; Li, C.; Zeng, G. Hydrothermal carbonization of sewage sludge: the effect of feed-water pH on fate and risk of heavy metals in hydrochars. Bioreour. Technol. 2016, 218, 183–188.

(22) Liu, D.; Gao, J.; Wu, S.; Qin, Y. Effect of char structures caused by varying the amount of FeCl3 on the pore development during activation. RSC Adv. 2016, 6, 87478–87485.

(23) Liu, D.; Zhao, X.; Su, R.; Hao, Z.; Jia, B.; Li, S.; Dong, L. Highly porous graphitic activated carbons from lignite via microwave pretreatment and iron-catalyzed graphitization at low-temperature for supercapacitor electrode materials. Processes 2019, 7, 300.

(24) Mori, H.; Asami, K.; Ohtsuka, Y. Role of iron catalyst in fate of fuel nitrogen during coal pyrolysis. Energy Fuels 1996, 10, 1022–1027.

(25) Liu, D.; Gao, J.; Cao, Q.; Wu, S.; Qin, Y. Improvement of activated carbon from Jixi Bituminous coal by air preoxidation. Energy Fuels 2017, 31, 1406–1415.

(26) Liu, D.; Gao, J.; Cao, Q.; Wu, S.; Qin, Y. Effects of oxygen functional groups and FeCl3 on the evolution of physico-chemical structure in activated carbon obtained from Jixi bituminous coal. RSC Adv. 2018, 8, 8569–8579.

(27) Sonibare, O. O.; Haeger, T.; Foley, S. F. Structural characterization of Nigerian coals by X-ray diffraction, Raman and FTIR spectroscopy. Energy 2010, 35, 5347–5353.

(28) Li, Y.-T.; Pi, Y.-T.; Lu, L.-M.; Xu, S.-H.; Ren, T.-Z. Hierarchical porous active carbon from fallen leaves by synergy of K2CO3 and their supercapacitor performance. J. Power Sources 2015, 299, 519–528.

(29) Mahmoudian, L.; Rashidi, A.; Dehghani, H.; Rahigh, R. Single-step scalable synthesis of three-dimensional highly porous graphene with favorable methane adsorption. Chem. Eng. J. 2016, 304, 784–792.

(30) Sevilla, M.; Fuertes, A. B. The production of carbon materials by hydrothermal carbonization of cellulose. Carbon 2009, 47, 2281–2289.

(31) Liu, D.; Su, R.; Hao, Z.; Zhao, X.; Jia, B.; Dong, L. Catalytic effect of NaCl on the improvement of the physicochemical structure of coal-based activated carbon for SO2 adsorption. Processes 2019, 7, 338.

(32) He, C.; Giannis, A.; Wang, J.-Y. Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior. Appl. Energy 2013, 111, 257–266.

(33) Kang, S.; Li, X.; Fan, J.; Chang, J. Characterization of hydrochars produced by hydrothermal carbonization of lignin, cellulose, D-xylose, and wood meal. Ind. Eng. Chem. Res. 2012, 51, 9023–9031.

(34) Yang, K.; Peng, J.; Xia, H.; Zhang, L.; Srivinasakannan, C.; Guo, S. Textural characteristics of activated carbon by single step CO2 activation from coconut shells. J. Taiwan Inst. Chem. Eng. 2010, 41, 367–372.

(35) Pietrzak, R. XPS study and physico-chemical properties of nitrogen-enriched microporous activated carbon from high volatile bituminous coal. Fuel 2009, 88, 1871–1877.

(36) Yi, D.; Cui, X.; Li, N.; Zhang, L.; Yang, D. Enhancement of electrochemical performance of LiFePO4@C by Ga coating. ACS Omega 2020, 5, 9752–9758.