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Inherently Catalyzed Boudouard Reaction of Bamboo Biochar for Solid Oxide Fuel Cells with Improved Performance

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ABSTRACT: The feasibility of direct utilization of bamboo biochar (BC) as a fuel for solid oxide fuel cells (SOFCs) is studied by comparing BC to de-ashed BC (DC) and activated BC (AC) in terms of Boudouard reactivity and the performance of the fuel cell. The CO partial pressures in the carbon dioxide temperature-programmed oxidation profiles of BC and DC are 3.18×10^{-8} and 1.04×10^{-8} Torr at 850 °C, respectively, which indicates that BC has superior Boudouard reactivity compared to DC. The peak power densities (PPDs) of the cells fueled with BC and DC are 121 and 73 mW cm⁻² at 850 °C, respectively. The inherent metal elements in BC, mainly K of 33.88 mg g^{-1} and Ca of 2.06 mg g^{-1} , play a key role in boosting its Boudouard reactivity and the performance of the cell. In addition, the loading of artificial catalysts to BC can noticeably enhance its Boudouard reactivity and gain a higher power output of the cell fed with it. The PPD of catalyst-loaded BC achieves approximately 191 mW cm⁻² at 850 °C. This study reveals that BC is a promising carbon-neutral fuel for SOFCs and provides an efficient alternative to use this renewable resource in sustainable power generation.

1. INTRODUCTION

Biomass has received growing attention in the last few decades as a renewable and carbon-neutral energy source for the development of a sustainable energy portfolio. Plants and other organisms convert around 105×10^9 metric tons of carbon into biomass per year by photosynthesis, with the energy scale of approximately 130 terawatts globally.¹ As one of the fastest growing plants on the earth, bamboo is one of the most important biomass resources, with high productivity and wide distribution. Besides many value-added utilization channels for bamboo resources, recently, bamboo waste has been used for electricity generation in China to meet the rapidly expanding energy demand.

As a clean alternative for the conventional combustion-based power generation technology, fuel cells electrochemically carry out the conversion of chemical energy stored in fuel to electric power in the manner of high efficiency and low emissions.^{2–4} Solid oxide fuel cells (SOFCs) are a type of fuel cell based on a solid oxide electrolyte, normally running at 700–1000 °C.⁵ The high operating temperatures make SOFCs possess the capability to use a broad spectrum of fuels.⁴⁻⁶ Besides hydrogen, more accessible carbon-containing substances, such as hydrocarbons, carbon monoxide, coal, and biochar, are all potential fuels for SOFCs.⁷⁻¹¹ Solid carbon as fuel not only has a much higher energy density (20 kWh L^{-1}) than H₂ (2.4 kWh L^{-1}) but also has more safety and convenience for storage and transportation than gaseous and liquid fuels without any change in the current infrastructure.⁵ In comparison to the direct carbon fuel cells (DCFCs) with hydroxide or molten carbonate electrolytes, SOFCs avoid the problems of electrolyte

degradation, leakage, and corrosion.¹²⁻¹⁶ In addition, the electrical conductivity of carbon fuels is no longer regarded as a key factor influencing the performance of SOFCs, where solid carbons just serve as a fuel rather than a current collector.

Recently, a series of studies have revealed that the Boudouard gasification of carbon (eq 1) overcomes the so-called primary challenge for direct carbon-solid oxide fuel cells (DC-SOFCs), that is, the interface contact problem of the solid carbonaceous fuel to the solid cermet anode, which greatly limits the triple-phase boundary (TPB) and power output.¹⁵⁻¹ Carbon monoxide (CO) produced from eq 1 subsequently diffuses upon the anode surface and is electrochemically oxidized with electron release (eq 2).

 $C + CO_2 \leftrightarrow 2CO$ (1)

$$CO + O^{2-} \rightarrow CO_2 + 2e^-$$
(2)

However, the Boudouard reaction is a strong endothermic reaction ($\Delta H_{298 \text{ K}}^{\circ}$ = +171 kJ mol⁻¹), which thermodynamically favors the formation of CO at elevated temperatures.^{6,7} The CO concentration reaches nearly 70 vol % in the equilibrium system at 727 °C.⁶ Besides elevating the reaction temperature, the use of catalyst is another effective way to accelerate the

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reaction and decrease the reaction temperature.^{19–22} The elements of transition, alkali, and alkaline earth metals, such as iron (Fe), potassium (K), and calcium (Ca), are well-recognized as effective catalysts to promote the Boudouard reaction of various carbon fuels.^{21–26}

One of the interesting features of biochar is the biologically assembled metal elements, which homogeneously disperse among the carbon matrix and normally have catalytic activity for the Boudouard reaction. Some metal elements, including K, Ca, Mg, and Fe, are essential for plant photosynthesis and other metabolism processes. In general, K is the most abundant metal element in plants, which is involved in the working of more than 60 enzymes. Ca not only plays many crucial physiological functions but is also a part of the architecture of cell walls and membranes. Recently, the effects of these essential metal elements in biomass on the Boudouard reactivity of biochar and the electrochemical performance of the cell fed with biochar have drawn much attention. A SOFC fueled with the biochar prepared from the leaves of an orchid tree exhibited higher power generation performance than that of cells using an activated carbon with an iron-based catalyst, which is attributed to the porous structure of the char and the uniformly distributed metal elements with catalytic activity in it.² However, biomass and its derived biochar are diverse.²⁸ There is large room to explore suitable biochar fuels for DCFCs.

This present work focuses on the feasibility of direct use of bamboo biochar (BC) as fuel for SOFCs. De-ashed BC (DC) and activated BC (AC) are prepared as contrasts. On the basis of the microstructure and the metal element analyses of these carbon samples, the catalytic effect of the inherent metal elements in BC on the Boudouard reactivity and cell performance is discussed in detail. In addition, the comparative experiments of catalyst-loaded AC and DC to catalyst-loaded BC are also performed to examine the influences of the carbon microstructure on the catalyst loading efficiency and the Boudouard reactivity of these carbon fuels.

2. EXPERIMENTAL SECTION

2.1. Preparation of Carbon Fuels. Figure 1 shows the BC-derived carbon fuels and the related processes. The detailed preparation processes are described as follows:



Figure 1. Schematic diagram of the carbon fuels derived from BC and the related processes: ① de-ashing of BC to prepare DC, ② structure modification of BC to prepare AC, and loading of catalyst to ③ BC, ④ AC, and ⑤ DC to prepare catalyst-loaded BC, AC, and DC, respectively.

2.1.1. BC. Bamboo debris was cleaned and heated in a N₂ atmosphere with an increasing temperature evenly to 700 °C within 135 min in a quartz tube furnace and then held 700 °C for 120 min. After returning back to the ambient temperature, obtained BC with the yield of approximately 29% on a dry basis was ground in an agate motor and further sieved to <75 μ m for further use.

2.1.2. Process ^① To Prepare DC. The BC powder was immersed in 6 mol L⁻¹ HCl solutions for 24 h, and then it was treated thoroughly by distilled water to remove residual HCl and the soluble salts. The elimination of Cl⁻ was examined by dropping saturated AgNO₃ solution into the washing wastewater. Obtained DC was dried at 110 °C, ground, and sieved to the particle sizes of <75 μ m for further use.

2.1.3. Process ⁽²⁾ To Prepare AC. The BC powder was treated with a potassium hydroxide solution (19.6 mol L⁻¹) with the ratio of BC/KOH of 1:4 by weight.²⁹ The slurry was heated at 110 °C and held for 720 min; then in the N₂ atmosphere, the temperature was evenly increased to 400 °C within 58 min and held for 60 min; and then the temperature further rose to 800 °C with the same increasing rate of the temperature and held at 800 °C for 60 min. The obtained sample was washed first with hydrochloric acid (1 mol L⁻¹) and subsequently using distilled water to wash until pH ≈ 7.0. Finally, AC was dried in an oven at 110 °C, then ground, and sieved to the particle sizes of <75 μ m for further use.

2.1.4. Processes (3-(5)) To Prepare Catalyst-Loaded Carbon Fuels. A Boudouard reaction catalyst, $Fe_mO_n-M_xO$ (M = Li, K, and Ca), was used to enhance the CO₂ gasification reactivity of the samples of BC, AC, and DC. The ingredients of the catalyst are the nitrates of iron, lithium, potassium, and calcium with the weight ratio of 20:1.6:3.8:1.²⁴ The loading method followed that reported in the literature elsewhere.²⁴

2.2. Evaluation of Boudouard Reactivity of Carbon Fuels.³⁰ The Boudouard reactivity of the solid carbon was evaluated by the CO_2 temperature-programmed oxidation (CO_2 -TPO) method.³⁰ Carbon of 30 mg or carbon with a catalyst of 35 mg was introduced into a U-shaped tube-type reactor. To remove adsorbed water, the temperature of the sample was increased to 200 °C and stayed for 60 min. Then, a stream of CO_2 at a rate of 15 mL min⁻¹ flowed over the sample. The temperature was further increased evenly to 1000 °C within 80 min. The partial pressure of CO was monitored by a Hiden QIC-20 mass spectrometer. The temperature was held at 1000 °C until the CO signal returned to the baseline.

2.3. Fabrication of SOFCs. The SOFC was constructed by the porous cermet anode layer, the dense and thin electrolyte layer, and the porous cathode layer according to the reported procedure elsewhere.³¹ The nickle-yttrium-stabilized zirconia (Ni-YSZ) anode layer is the thickest layer, which serves as the support of the cell. The YSZ electrolyte layer is a thin layer for reducing the ionic transfer resistance. The cathode material is La_{0.8}Sr_{0.2}MnO₃ (LSM). The cell was assembled with a quartz tube using silver sealing adhesives. The solid carbon fuel of 0.1 g was set into the anode chamber and closely contacted with the surface of the anode. Two quartz tubes were positioned beneath the asbestos: one is to feed in $H_2/Ar/CO_2$, and the other is to release the reaction products $(CO + CO_2)$. The electrochemical performance of the above-mentioned cells fed with different fuels was tested by the cell testing system (shown in Figure 2). The cathode was directly exposed to ambient air. The electrochemical performance of fuel cells, including current-voltage (I-V) or electrochemical impedance spectrum (EIS) data, was investigated using the electrochemical instrument (Iviumstat, Ivium Technologies, Netherlands) by four-terminal configuration. The conversion efficiency tests for ~ 0.04 g of BC and BC with the catalyst were performed at 825 °C.

2.4. Characterization of Carbon Fuels. The graphitic structures of BC, AC, and DC were analyzed using the X-ray diffraction (XRD) method (D8 diffractometer, Bruker, Germany, operated at 40 kV and 100 mA, with Cu K α radiation) over a range of 10–90° and Raman spectroscopy (Jobin Yvon Labram HR800, France, with exciting wavelength $\lambda = 5145$ Å) between 800 and 2400 cm⁻¹. The texture properties of samples were examined using nitrogen physisorption via an adsorption analyzer (ASAP 2020, Micromeritics, Norcross, GA, U.S.A.). The Brunauer–Emmett–Teller (BET) method was applied to calculate the specific surface areas of samples. The information on pore volumes and pore sizes of samples was obtained via the Barrett–Joyner–Halenda (BJH) method. The chemical functional groups on the surface of BC, AC, or DC were determined by a Fourier transform



Figure 2. Schematic diagram of the fuel cell test setup.

infrared (FTIR) spectrometer (Vertex 70, Bruker, Germany). The morphologies of the samples were observed using scanning electron microscopy (SEM, JSM-7001F, JEOL, Japan). The metal element composition analyses of samples were performed using energy-dispersive X-ray spectroscopy (EDX, QX200, Bruker, Germany). The metal element contents of samples were determined using inductively coupled plasma mass spectrometry (ICP–MS, NexION 350, PerkinElmer, Waltham, MA, U.S.A.). The sample of 0.025 g was thoroughly digested by a microwave using 8 mL of guaranteed reagent of HNO₃ (37 wt %) for 80 min.

3. RESULTS AND DISCUSSION

3.1. Evaluation of Boudouard Reactivity. CO_2 -TPO is a very effective technology to evaluate the Boudouard reactivity of carbon samples. To examine the intrinsic Boudouard reactivity of BC and the influences of the inherent metal elements and the carbon microstructures on it, DC and AC were taken as contrasts. In addition, the effects of the carbon microstructure on the catalyst loading efficiency and further on the Boudouard reactivities of catalyst-loaded BC, AC, and DC were also evaluated. Figure 3 depicts the CO partial pressure profiles of BC, AC, and DC and those of them loaded with the catalyst from the CO_2 -TPO measurements. The detailed information extracted from Figure 3 is summarized in Table 1, including the CO partial pressures at certain temperatures and the amount of CO generated within a certain period (the integrated values of CO peak areas).

As shown in Figure 3a, the CO partial pressures for both BC and AC are higher than that for DC before 980 °C (approximately 2.36×10^{-7} Torr versus 6.89×10^{-8} Torr at 980 °C). The CO partial pressures of BC and AC are approximately 3 times that of DC from 800 to 900 °C. Among the full temperature range, i.e., 600–1000 °C, the Boudouard reactivities of these samples can be generally ranked in the order of BC \geq AC > DC based on their CO partial pressures, except for the case at temperatures below 840 °C, where the Boudouard reactivity of BC is lower to a certain extent than that of AC. In addition, the same trend was followed by the CO integral peak areas within 38 min for BC, AC, and DC (Table 1), which represent the produced CO quantities. In brief, Figure 3a reveals that BC and AC have nearly the same intrinsic Boudouard reactivity, which is 3 times that of DC.

Figure 3b depicts that the Boudouard reactivities of catalystloaded BC, AC, and DC are improved significantly. The improvement of Boudouard reactivity of catalyst-loaded DC is the most, which narrows the gap between catalyst-loaded DC and the other two samples greatly. The CO partial pressures of the BC, AC, and DC with the catalyst are 3.918×10^{-7} , $4.308 \times$ 10^{-7} , and 3.594×10^{-7} Torr at 900 °C, respectively, which are approximately 4, 7, and 17 times those of BC, AC, and DC without the catalyst. However, the rank order of the Boudouard reactivities of these samples changes to AC + catalyst > BC + catalyst > DC + catalyst at temperatures from 790 to 920 °C, although the gap between one another is limited. At temperatures below 790 °C, the rank order remains as the case without the catalyst; however, the gap of DC to the others is significantly narrowed. In addition, the initial reaction temperatures of DC, BC, and AC with the catalyst decrease from approximately 800, 730, and 660 °C to 670, 605, and 610 °C, respectively. As shown in Table 1, CO produced (the integrated value of CO peak areas) within 33 min of DC, BC, and AC with the catalyst is 6.8, 1.9, and 2.3 times that of DC, BC, and AC without the catalyst within 38 min, respectively. Figure 3b indicates that the Boudouard reaction catalyst shows a strong influence on the Boudouard reactivity of all carbon samples and can markedly narrow the difference of the samples without the catalyst. In short, the catalysts, either existing intrinsically or loaded externally, have the capability to significantly improve the Boudouard reactivity of these carbon samples.

3.2. Electrochemical Performance of the Fuel Cell. Figure 4 shows the EIS profiles of the cells operating on BC and BC with the catalyst at various temperatures. In general, the total resistance (R_v , the low-frequency intercept on the real axis) of a SOFC consists of the ohmic resistance (R_o , the high-frequency intercept) and the polarization resistance (R_p); i.e., $R_t = R_o + R_p$. R_o mainly reflects the resistances from the electrolyte



Figure 3. CO_2 -TPO profiles of BC, DC, and AC: (a) without catalyst and (b) with catalyst.

Table 1. Boudouard Reaction Information from the CO₂-TPO Experiments

	CO partial pressure (×10 ⁻⁸ , Torr)			integration of CO peak area ($\times 10^{-5}$, Torr min)		
fuel	800 °C	850 °C	900 °C	value	temperature (°C)	
BC	1.18	3.18	9.42	1.91	600-980	
AC	1.89	3.10	6.12	1.79		
DC	0.40	1.04	2.12	0.47		
BC + catalyst	11.01	20.57	39.18	3.59	600-930	
AC + catalyst	11.90	26.03	43.08	4.08		
DC + catalyst	10.07	18.57	35.94	3.20		

and the current collectors and related contact interfaces. As shown in panels a and b of Figure 4, with the temperature decreasing, the R_p values increase significantly with a slight increase of R_o values. In particular, the low-frequency arcs expand themselves larger and larger, yet the high-frequency arcs keep almost no change and superpose one another. The resistance arcs in the high- and low-frequency ranges are normally assigned to the overpotentials related to the



Figure 4. Electrochemical impedance spectra of SOFCs operated on (a) BC and (b) BC with the catalyst at open circuit voltage and 775, 800, 825, and 850 $^\circ$ C.

electrochemical reactions and mass transport processes, respectively. In brief, Figure 4 illustrates that the production of CO was reduced with a decreasing temperature, which resulted in the decrease of CO partial pressures and the increase of low-frequency resistances.

By a comparison of the spans of the impedance arcs in the low-frequency range in Figure 4a to those in Figure 4b at the corresponding temperature, it can be seen that every former is always greater than every corresponding later, which indicates that the concentration polarization in Figure 4a is higher than that in Figure 4b. According to a model study for the anode-supported SOFCs, the partial pressure of the gaseous fuel at the TPB determines the diffusion resistance of fuel (or concentration polarization) in the anode chamber.³² Catalyst-loaded BC had a higher CO producing rate than BC itself, resulting in a higher CO partial pressure in the anode and, thus, lower gas diffusion resistances in Figure 4b. The EIS features of catalyst-loaded AC/DC are similar compared to those of AC/DC.

Table 2 gives the electrochemical performance data when using various carbon fuels in 775–850 °C. Figure 5 shows the I-V and I-P curves for the cell using BC fuel as an example.

The following points can be drawn from the data in Table 2: (1) The PPD of the cell using BC fuel is at least 1.5 times that of the cell using DC at the corresponding temperature. The PPDs of the cells using BC, AC, or DC as fuel can be ranked in

Table 2. Electrochemical Performance of the Fuel Cells

		850) °C	825	°C	800	°C	775	°C
fuel	performance	C ^a	N/C ^b	С	N/C	С	N/C	С	N/C
BC	OCV (V)	1.10	0.94	0.99	0.86	0.95	0.85	0.94	0.82
	PPD (mW cm^{-2})	191	121	161	84	113	64	77	47
AC	OCV (V)	1.05	0.92	0.97	0.88	0.94	0.86	0.92	0.85
	PPD (mW cm^{-2})	227	110	170	62	117	40	80	31
DC	OCV (V)	1.02	0.95	0.97	0.86	0.94	0.83	0.89	0.82
	PPD (mW cm^{-2})	182	73	155	54	98	33	65	26
	1								

 ${}^{a}C$ = carbon fuels with the catalyst. ${}^{b}N/C$ = carbon fuels without the catalyst.



Figure 5. I-V and I-P curves for the cells fueled with (a) BC and (b) BC with the catalyst.

the order of BC > AC > DC, which is consistent with the result of CO_2 -TPO experiments. (2) Loading catalyst to BC, AC, or DC can significantly improve the performance of the cells using them as fuel. In particular, the PPDs of the cells using catalystloaded DC/AC as fuel are at least 2.5 times that of the cells fed with DC/AC at the corresponding temperature. However, the PPDs of the cells using catalyst-loaded BC as fuel are less than 2 times those of the cells fed with BC at the corresponding temperature. The PPDs for these catalyst-loaded fuels have the rank order of AC + catalyst > BC + catalyst > DC + catalyst. The difference between the PPDs for DC + catalyst and BC + catalyst is significantly narrowed in comparison to that between the PPDs for DC and BC. Again, the results indicate that the loading catalyst can narrow the difference of the gasification reactivity of the carbon fuel, as shown in the CO₂-TPO experiments. (3) The PPDs dropped sharply with a decreasing temperature for any of the fuels, which can be understood as follows. First, both R_o and R_p of the cell increase with a decreasing temperature. Second, the decrease of the temperature makes the Boudouard gasification rate slow down, leading to the CO supply being insufficient. Under the condition without using appropriate catalysts, an elevated reaction temperature, usually 800–1000 °C, is needed to maintain a usable Boudouard reaction rate.

3.3. Conversion Efficiency. The conversion efficiency (eq 3) is one of the important parameters to evaluate the practicability of the carbon fuel

$$\eta = \frac{C_{\text{elec}}}{C_{\text{ld}}} \times 100\% \tag{3}$$

where C_{elec} and C_{ld} denote the masses of electrochemically oxidized carbon and the fed carbon fuel, respectively.

The results of the conversion efficiency tests are shown in Figure 6. As seen in Table 3, the conversion efficiencies of BC



Elapsed time (h)

Figure 6. Conversion efficiency test for the cells fueled with BC and BC with the catalyst at 50 mA cm⁻² and 825 °C under ambient air as an oxidant.

and catalyst-loaded BC are 46.74 and 45.29%, respectively, indicating that BC without the catalyst might be a more feasible fuel for DC–SOFCs. However, there is large room to improve the conversion efficiency of BC or bamboo biomass. Recently, it was reported that a molten hydroxide fuel cell using the biochar of apple tree origin achieved a fuel conversion efficiency of 95%.³³ A SOFC directly using waste coffee grounds as fuel indicated that the heteroatoms and hydrogen contained in the biomass produced gaseous compounds by *in situ* gasification, which highly enhanced the cell performance.³⁴

Table 3. Conversion Efficiency of BC and BC with the Catalyst

sample	discharge time (h)	electric quantity (C)	carbon converted (g)	carbon loaded (g)	conversion efficiency (%)
BC	3.48	300.64	0.01870	0.04000	46.74
BC + catalyst	3.37	291.33	0.01812	0.04000	45.29

3.4. Properties. Carbon crystallinity, surface area, surface chemistry, mineral inclusions, and particle size of carbon fuels are identified as important factors influencing their Boudouard reactivity.^{35–38}

3.4.1. Crystalline Property. As shown in Figure 7a, an intense broaden peak of BC appears at approximately $2\theta = 24^\circ$,



Figure 7. (a) XRD and (b) Raman patterns of BC, AC, and DC.

which corresponds to the (002) basal plane reflection of graphite. The weak broaden peak of BC at approximately $2\theta = 44^{\circ}$ is assigned to the (100) lattice plane reflection of graphite. In particular, BC has many small but sharp diffraction peaks in its XRD pattern, which may be ascribed to the inclusion of inorganic minerals in its carbon matrix. In comparison to the XRD pattern of BC, the (002) reflection peak of AC left shifts

at around $2\theta = 20^{\circ}$ with a decreased weak peak intensity and the (100) reflection peak is observed at approximately $2\theta = 43^{\circ}$ with an increased strong peak intensity. The results suggest that the restructuring of AC crystallinity has occurred. The crystallization seems to be improved at the (100) crystal face direction. On the contrary, at the (002) crystalline direction, the structure changes to a more turbostratic state. For the XRD pattern of DC, the profile has a shape similar to that of BC but is evidently smoother than that of BC.

To compare BC to AC and DC in terms of crystalline property, their carbon crystalline parameters are calculated by eq 4 and the Scherrer equation (eq 5) based on their diffraction peaks of the (002) and (100) crystalline planes^{29,30}

$$d_{002} = \frac{\lambda}{2\sin(\theta_{002})} \tag{4}$$

$$L = \frac{K\lambda}{\beta\cos\theta} \tag{5}$$

where λ represents the X-ray wavelength, θ represents the diffraction angle, θ_{002} represents the diffraction angle of the (002) peak, d_{002} represents the crystalline interplanar spacing, K (shape factor) is 0.89 for L_c and 1.84 for L_a , β represents the peak width at the half-maximum intensity of the diffraction peak, L_c represents the crystalline size perpendicular to the basal plane based on the (002) reflection, and L_a represents the crystalline size parallel to the basal plane based on the (100) reflection. The calculated crystalline parameters are listed in Table 4.

Table 4. Crystamme Tarameters of the Tuer Samples	Table 4.	Crystalline	Parameters	of the	Fuel	Samples
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sample	<i>d</i> ₀₀₂ (nm)	$L_{\rm c}~({\rm nm})$	$L_{\rm a}~({\rm nm})$
BC	0.381(1)	1.022(1)	2.205(5)
AC	0.449(5)	1.180(1)	2.608(1)
DC	0.384(2)	1.061(3)	2.273(3)

According to the data in Table 4, it can be found that BC and DC are similar in terms of the carbon crystalline structure. However, it is distinct for AC. On the one hand, AC has a larger interplanar spacing (~0.449 nm) than BC (~0.381 nm), which suggests that AC has a looser stacking of carbon layers than BC. The looser stacking might lead to the higher stacking height of AC (~1.180 nm) than that of BC (~1.022 nm). On the other hand, AC has larger graphitization carbon layers (~2.608 nm) than BC (~2.205 nm). This can be understood from the chemical bonds or interaction potentials existing in the carbon structures. The stacking of the graphitization carbon layers is driven by van der Waals forces, and the carbon atoms in the graphitization carbon layers are constrained by covalent bonds along with delocalized π electrons. The covalent bonds are far stronger than the van der Waals forces, leading to the much stabler graphitization carbon layers than the stacking of them. Therefore, under the condition of activated treatment, the stacking of the graphitization carbon layers are easily disassembled, but it is hard to destruct themselves. In addition,

Energy & Fuels

the treatment temperature of 800 $^{\circ}\mathrm{C}$ might be high enough to promote the condensation polymerization of carbon atoms.

Figure 7b shows the Raman spectra of BC, DC, and AC with the G (graphite) and D (disorder) bands at approximately 1580 and 1340 cm⁻¹, respectively. The G band reflects the phonon vibration of the aromatic carbon atoms in graphitic carbon structures. The D band results from the phonon vibration of the carbon atoms with non-saturated bonds in disordered carbon structures.^{35,36} The ratio of integral intensity (I_D/I_G) correlates strongly with the graphitization degree of carbon. A greater value of I_D/I_G normally means a lower graphitization degree of the carbon materials.^{35,36} The I_D/I_G values of BC, DC, and AC are estimated to be 2.76, 2.83, and 3.02, respectively, which indicate that their graphitization degree should be ranked in the order of BC > DC > AC.

3.4.2. Textural Property. The Boudouard reactivities of solid carbons are in close relation to their textural properties.^{37–43} Nitrogen physisorption at 77 K is usually used to characterize the carbon textural property. Table 5 summarizes the results

Table 5. Specific Surface Areas and Pore Parameters of the Carbon Samples

	BC	AC	DC
BET surface area (m ² g ⁻¹)	55.0	1538.7	785.4
BJH pore volume (cm ³ g ⁻¹)	0.012	0.29	0.18
BJH pore size (nm)	9.6	2.6	5.5

obtained from the nitrogen adsorption measurement, including the surface areas, pore volume, and pore size of these samples. AC has the maximum BET surface area among the three samples, which is approximately 27-fold greater than that of BC. The surface area of DC is also enlarged to approximately 14-fold that of BC. The textural properties of AC and DC should greatly favor their Boudouard reaction. In addition, the textural properties of carbon materials have significant effects on their catalyst loading efficiency and further on their Boudouard reactivities, which can be seen in Figure 3, where the rank order of the Boudouard reactivities of catalyst-loaded BC, AC, and DC is AC + catalyst \geq BC + catalyst > DC + catalyst.

The specific surface area of BC is nearly 40 times that of a coal char sample (\sim 1.4 m² g⁻¹).³⁰ This large gap should result from their unique texture structures. Figure 8a shows the SEM image of the pristine bamboo, where bunches of fibrils and sponge-like structures interweave together. After carbonization to BC, the texture structure of the raw bamboo evolves into a loose structure with many crevices and holes, as shown in Figure 8b. However, the particles of BC in the micrometer level are still compact (Figure 8c). Until activation by chemicals to AC, substantial numbers of micropores formed among the bulk (Figure 8d).

3.4.3. Surface Chemistry. In general, the carbon atoms on the surface or in the alkyl chains of carbon materials and those directly bonding to the functional groups containing oxygen atoms show high Boudouard reactivity. The surface functional group information on solid carbons is usually measured by FTIR methods. As presented in Figure 9, although the carbonization process makes the raw bamboo lose most of its oxygen-containing functional groups, some important functional groups still remain in BC, DC, and AC, such as the hydroxyl groups (~3420 cm⁻¹), the carboxyl groups bonded with aromatic carbon atoms or the aromatic groups (~1570 Article



Figure 8. SEM micrographs of (a) raw bamboo, (b) BC, (c) BC powder, and (d) AC powder.



Figure 9. FTIR spectra of BC, DC, and AC.

cm⁻¹), the C–O groups in the structures of ether, alcohol, or phenol (~1100 cm⁻¹), and the CH₂ and CH₃ groups in alkyl chains (2920 and 2850 cm⁻¹).

Although the spectrum profiles of BC, DC, and AC are similar, the changes of their surface chemistry can be analyzed by comparing the areas of corresponding peaks, which correlates to the relative proportion of the functional group in the sample. According to the method reported in the literature, herein, we take the band at 1570 cm⁻¹ as the benchmark. First, the peak areas of the stretching vibrations of OH, CH₂, CH₃, and C–O functional groups are calculated. Second, the ratios of these peak areas to that of the benchmark are calculated and accumulated.⁴⁴ The total peak area ratios (TPAR) for AC, DC, and BC are 9.3, 8.6, and 8.5, respectively. The greater the TPAR, the more the active carbon atoms. Therefore, AC with the greatest ratio value should have the most active carbon atoms participating in the Boudouard gasification reaction.

3.4.4. Inherent Metal Elements. Figure 10 provides the EDX elemental distribution mapping of BC. As seen, the metal elements are all uniformly distributed on the carbon background, regardless of whether their contents are high or low. In fact, the content of K is much higher than that of every other metal. An ICP–MS analysis of BC gives the content information on these elements (Table 6). It was reported



Figure 10. (a) SEM micrograph, (b–f) surface element distribution maps, and (g) surface element distribution diagram of BC.

Table 6. Metal Element Contents in BC. AC. and	DC
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element	BC (mg/g)	AC (mg/g)	DC (mg/g)
K	33.88	0.53	1.40
Ca	2.06	0.31	0.74
Mg	0.97	0.18	0.32
Fe	0.36	0.08	0.19

that the element K exhibited a higher catalytic effect on Boudouard gasification than Ca.²³ On the other hand, a biochar with biologically accumulated Ca showed a better catalytic activity for the Boudouard reaction than carbon added with Ca salts by mechanical mixing.²⁷ The distribution of metal elements in BC is the result of a biological self-assembly process of essential metals, which should be a more homogeneous distribution among the carbon matrix than that of an artificial catalyst loaded by chemical or mechanical methods. This may be the reason why a very limited amount of biometals (K, Ca, Mg, and Fe) has a significant impact on the gasification reactivity of BC (see Figure 3a). In short, the

$$\operatorname{Fe}_{m}\operatorname{O}_{n+1} + \operatorname{C} \to \operatorname{Fe}_{m}\operatorname{O}_{n} + \operatorname{CO}$$
 (6)

$$\operatorname{Fe}_{m}O_{n} + \operatorname{CO}_{2} \to \operatorname{Fe}_{m}O_{n+1} + \operatorname{CO}$$
 (7)

$$CaCO_3 + C \rightarrow CaO + 2CO$$
 (8)

$$CaO + CO_2 \rightarrow CaCO_3$$
 (9)

$$K_2 CO_3 + 2C \rightarrow 2K + 3CO \tag{10}$$

$$2K + CO_2 \rightarrow K_2O + CO \tag{11}$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \tag{12}$$

As shown in Figure 11, there are traces of metal elements existing in AC and DC. Considering that EDX typically



Figure 11. Surface element distribution maps of (a) AC and (B) DC.

provides the local element concentrations of the surface of the sample, ICP–MS analyses were also performed. The data in Table 6 indicate that AC has less amount of residual metal elements than DC and the removal efficiencies of these metal elements can be ranked in the order of K > Ca and Mg > Fe. These data confirm that the metal elements in AC and DC were almost removed and their catalytic effects on the Boudouard gasification of AC and DC should be very limited.

4. CONCLUSION

The feasibility of direct utilization of BC as a fuel for SOFCs is examined in this paper. BC has noticeably higher Boudouard reactivity than DC. The performance of the cell when using BC fuel is markedly superior to that using DC under the same conditions. The inherent metal elements in BC play a crucial role in enhancing its Boudouard reactivity. The comparative experiments of catalyst-loaded AC and DC to catalyst-loaded BC reveal that the microstructure of carbon is an important factor impacting its catalyst-loaded BC has an improved gasification reactivity, and the PPD of the related cells reaches approximately 191 mW cm⁻² at 850 °C. In short, this work demonstrates that the combination of SOFCs with BC promises an efficient alternative to use this renewable resource in sustainable power generation.

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Notes

The authors declare no competing financial interest.

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