Potential of biochar derived from three biomass wastes as an electrode catalyzing oxygen reduction reaction

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ABSTRACT
Biochar is a porous carbonaceous material containing abundant redox functional groups and inorganic minerals, making it a potential electrode material. Nine electrodes were prepared with biochar produced from three different feedstocks at three pyrolysis temperatures, and their oxygen reduction reaction (ORR) activity and electrochemical impedance spectroscopy (EIS) were investigated. The results showed that all biochar electrodes had certain electrocatalytic activity as their current density ranged from 0.26 to 2.17 mA cm⁻², half-wave potential at 0.24–0.41 V, electron transfer number at 2.1–3.9, Rₛ at 9.2–61.2 Ω, and Cₛₛ at 1.1 × 10⁻⁶–2.2 × 10⁻⁴ F. For most biochar electrodes, the current density and half-wave potential increased as the pyrolysis temperature increased from 500°C to 700°C, which was closely related to the increase in aromatization degree (H/C) of biochar. Dairy manure biochar showed much lower current density and half-wave potential than sewage sludge biochar and wood chip biochar, probably due to its relatively smaller surface area. This study indicated that biochars could be converted to carbon electrodes, and both feedstock and pyrolysis temperature could influence the ORR activity of biochar electrodes.

1. Introduction
Biochar is a carbon-rich material produced through pyrolysis of waste biomass, such as wood, manure, and crop residues for the aim of carbon sequestration [1,2]. It has been proven that biochar has many additional environmental benefits, including enhancing soil fertility, immobilizing contaminants or serving as an adsorbent for water purification [3–5]. Recently, biochar has demonstrated promising potential in the field of electrochemical applications. Abundant pores and relatively great specific surface area in biochar potentially provide a large number of sites and reaction interface for oxygen reduction reaction [6]. Furthermore, biochar has abundant minerals such as transition metal elements including Fe, Mn, Co, Ni, et al., which have high catalytic activity for redox reactions [7]. Some minerals (Na, K, P, Si, Ca, et al.) exist as soluble or insoluble salts, forming the type of ionic conductive, then therefore featuring biochar with properties of impurity semiconductor with higher electrical conductivity.

The graphic degree and surface area had a significant effect on the oxygen reduction reaction (ORR) activity of carbon electrodes, and higher graphic degree and surface area resulted in higher ORR activity [8]. Huggins et al. prepared some kinds of wood biochars with higher specific surface areas via gasifier at high temperature of 1000°C for microbial fuel cells, and the optimal output power achieved 532 ± 18 mW m⁻² [9]. The transition metals also played an important role in the ORR. Yuan et al. produced Fe-rich sewage sludge biochar as potential air cathode materials for microbial fuel cells with a higher output power of 500 ± 17 mW m⁻² [10]. They attributed the high efficiency to the high content of ferric oxide and nitrogen-containing compound in sewage sludge biochar. Additionally, biochar (BC) as a cost-effective electrode modifier for sensitive electrochemical determination of organic compounds [11,12].

A series of modified biochars have been studied concerning their electrochemical properties. Graphene-coated pyrogenic carbon with large storage capacity to lithium as the anode of lithium-ion batteries was successfully prepared, and proved the unique electric properties of the graphene “skin” on the pyrogenic carbon [13]. In addition, graphitic biochar produced with high temperature (1000°C) gasification as a support of manganese oxide was prepared and evaluated its ability as a microbial fuel cell air cathode [10]. What’s more, plasma oxidation technology was applied to biochar electrode, and the capacitance could achieve...
171.4 F g⁻¹ for a 5-min oxygen plasma activation, superior to the conventional chemical treated 99.5 F g⁻¹ and the untreated biochar 60.4 F g⁻¹ [14]. Previous studies have implied that the electrochemical activity of biochars was closely related to the specific surface area, pore structure, degree of graphitization, and minerals. Notably, all these properties were mainly determined by the following two factors: pyrolysis temperature and feedstock source. However, influence of pyrolysis temperature and biomass types on the electrocatalytic activity of biochar, which make the correlation between these two factors and ORR of biochars remain unclear.

In this study, nine electrodes were prepared with biochar produced from three different feedstock (sewage sludge, wood chip and dairy manure) at three pyrolysis temperatures (500, 600 and 700°C), and their ORR activity and electrochemical impedance spectroscopy were investigated. We aimed at demonstrating that biochar is a potential electrode material for catalyzing ORR, as well as the influence of biomass properties and pyrolysis temperature.

2. Materials and methods

2.1 Biomass and biochar preparation

The dairy manure (DM), sewage sludge (SS) and wood chip (WC) were collected from a dairy farm in Baoshan district, Minhang Sewage Treatment Plant, and a wood processing factory, Shanghai, China, respectively. The biomass were air-dried and ground into a particle size of 2 mm and then heat-treated under N₂ atmosphere at the desired temperature for 2 h. The details of the biochar production have been described previously [15]. Biochars were produced at three temperatures of 500°C, 600°C, and 700°C were referred to as DM500, DM600, DM700, SS500, SS600, SS700, WC500, WC600, and WC700, respectively. As-prepared biochar were then ball-milled for 2 h before subjected to the following experiment. The metal concentrations in biochar were measured using the inductively coupled plasma (ICP-AES, ICP6000 Radial, Thermo, England), following biochar digestion using the USEPA method 3050B [16]. Ash content was determined according to standard ASTM methods, where the biochars were heated at 550°C under air atmosphere to ensure the completely removal of organic matters [17–19]. Specific surface area and pore size distribution of biochars were determined using a BET-N₂ Quantachrome NOVA 2200e nitrogen adsorption system (Quantachrome Instruments, Boynton Beach, FL).

2.2 Preparation of biochar electrode

The electrode was constructed according to Dong (et al., 2012), which consisted of a biochar layer with the stainless steel mesh as the matrix and the polytetrafluoroethylene (PTFE) as the binder [20]. First, 4 g of biochar powder mixed with 30-mL ethyl alcohol was placed in a 200-mL beaker, then the blend was subject to ultrasonic agitation for 30 min at room temperature, followed by dripping 60 wt% PTFE suspensions (60 wt%, 3 F New Materials Co, Shanghai, China) slowly. After another 30 min, the blend was stirred and dried at 80°C bath to give a dough-like paste. The paste was rolled on one side of the stainless steel mesh to make a circular flat sheet of 0.4-mm thickness with diameter of 3.0 mm. The sheet was then sintered for 25 min at 340°C to melt the PTFE in order to form the fibrous three-dimensional structure for gas transport.

2.3 Measurement of electrochemical properties

All the electrochemical measurements were performed in a standard three-electrode cell with a biochar electrode as the working electrode, a Pt wire as the counter electrode and a saturated calomel electrode as the reference electrode, respectively (0.653 V vs. RHE in 0.5 M Na₂SO₄ at 25°C). All the potential values in this work are present with the reversible hydrogen electrode (RHE). Cyclic voltammogram experiments were conducted in 0.5 M Na₂SO₄ solution saturated with oxygen for ORR at 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was carried out on a potentiostat (Autolab, Mechohm) in 0.5 M Na₂SO₄ solution saturated with oxygen from 0.1 Hz to 10.0 KHz. The rotating disk electrode (RDE) experiment was performed using a disk electrode (8 mm of disk outer diameter, ATA-1B, Jiangsu Jiangfen Electroanalytical Instrument Co.) and a potentiostat (Autolab, Mechohm). The electron number (n) transferred in ORR process was calculated using the Koutecky-Levich equation:

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{\omega B (Dω^{1/2})} \]

where \( j_k \) is the kinetic current density and B is related to the diffusional current density. \( ω \) is the rotate speed of rotating disk electrode. B is related to the diffusion-limiting current density expressed using the following expression:

\[
B = 0.62 n F D^{2/3} v^{-1/6} Co \]

where \( v \) represents the kinematic viscosity of the electrolyte (1.13 × 10⁻² cm² s⁻¹); \( n \) is the electron number exchanged during ORR process; the Faraday constant is represented by \( F \) (96,485 C mol⁻¹); \( Co \) is the concentration of oxygen (1.2 × 10⁻³ mol L⁻¹); \( D \) is the oxygen diffusion coefficient (1.9 × 10⁻⁵ cm² s⁻¹).
3. Results and discussion

3.1 Physicochemical properties of the biochars

The physicochemical properties of the biochars have been found to be strongly related to pyrolysis temperature and original biomass [21]. Table 1 shows the elements content of the nine biochars. Carbon contents were about 50% for the DM biochars, 20% for the SS biochars and 70% for the WC biochars. The carbon content in SS biochar decreased with the increase of pyrolysis temperature due to the enrichment of minerals. These results were consistent with previous researches [22,23]. With the pyrolysis temperature increasing from 500 to 700°C, the contents of N in the biochars decreased from 2.88 to 1.51% for SS biochars and from 1.97 to 1.70% for DM biochars, while the N contents for WC biochars changed slightly [24]. Pyrolysis increased the S content in all the nine biochars and the more the pyrolysis temperature increased, the higher S content in the biochars (Table 1). The ratio of molar H/C (molar ratio of hydrogen to carbon) is an important parameter of aromatization degree referring to degree of graphitization of the biochar [25,26]. The H/C ratio decreased from 0.477 to 0.281 for DM biochars, 0.666 to 0.357 for SS biochars and 0.397 to 0.214 for WC biochars as the pyrolysis temperature increased from 500 to 700°C. The decline in H/C ratio indicates that original biomass is highly carbonized into biochar with a highly aromatic structure as the temperature increased [27,28]. The observed ash content increased with the increase of pyrolytic temperature. The SS and DM biochars have higher ash content than the WC biochars, and the SS biochars have more transition metals (Cu, Zn, Fe, Mn, Ni, Co) than the DM biochars (Table 1). It has been proved that transition metals are the active sites for ORR [29]. The transition metal elements especially Fe in SS biochars were higher than the other two, which might be favorable to the ORR performance.

Higher pyrolysis temperature led to higher specific surface area (SSA) of biochars, which have been also proven by many previous studies [21,24,30]. As shown in Table 2, specific surface area (SSA), total pore volume (TPV) and micropore volume (MV) of the DM biochars increased gradually from 37.60 m² g⁻¹, 0.028 cm³ g⁻¹ and 0.008 cm³ g⁻¹ to 47.00 m² g⁻¹, 0.034 cm³ g⁻¹ and 0.012 cm³ g⁻¹ respectively, with the rise of the pyrolysis temperature from 500°C to 700°C. The changing trends of SSA, TPV, and MV for SS biochars are similar to that in DM biochars. However, the WC biochars are different from the two above, the SSA increased with the pyrolysis temperature increased from 500 to 600°C, but as the pyrolysis temperature increased continually to 700°C, the SSA decreased dramatically. The increase of SSA in higher temperature were caused by the increase of aromatization degree of biochar, forming micro structures

### Table 1. Selected physicochemical properties of dairy manure (DM), sewage sludge (SS) and wood chip (WC) biochars.

| Biochar | C (wt%) | H (wt%) | N (wt%) | S (wt%) | H/C | N/C | Cu (mg g⁻¹) | Zn (mg g⁻¹) | Fe (mg g⁻¹) | Mn (mg g⁻¹) | Ni (mg g⁻¹) | Co (mg g⁻¹) | Ash content (%) |
|---------|---------|---------|---------|---------|------|-----|-----------|-----------|-----------|------------|------------|-----------|----------------|
| DM500   | 50.53   | 2.009   | 1.970   | 0.409   | 0.477| 0.033| 0.110      | 0.602      | 5.730      | 0.420      | 0.021      | 0.007      | 38.20         |
| DM600   | 51.42   | 2.243   | 1.730   | 0.475   | 0.332| 0.029| 0.112      | 0.614      | 5.840      | 0.428      | 0.021      | 0.007      | 38.93         |
| DM700   | 51.01   | 1.994   | 1.700   | 0.546   | 0.281| 0.029| 0.122      | 0.665      | 6.330      | 0.464      | 0.023      | 0.008      | 42.20         |
| SS500   | 21.57   | 1.198   | 2.880   | 0.818   | 0.666| 0.114| 0.326      | 1.585      | 41.245     | 1.223      | 0.087      | 0.025      | 72.36         |
| SS600   | 21.52   | 0.891   | 2.480   | 0.845   | 0.443| 0.099| 0.335      | 1.632      | 42.488     | 1.260      | 0.089      | 0.026      | 74.54         |
| SS700   | 21.20   | 0.631   | 1.510   | 0.929   | 0.357| 0.061| 0.350      | 1.705      | 44.374     | 1.316      | 0.093      | 0.027      | 77.85         |
| WC500   | 70.50   | 2.331   | 0.490   | 0.065   | 0.397| 0.006| 0.012      | 0.089      | 5.382      | 0.157      | 0.007      | 0.004      | 20.31         |
| WC600   | 72.38   | 1.807   | 0.430   | 0.073   | 0.030| 0.005| 0.014      | 0.099      | 5.973      | 0.175      | 0.008      | 0.004      | 22.54         |
| WC700   | 73.83   | 1.315   | 0.460   | 0.087   | 0.214| 0.005| 0.014      | 0.099      | 5.989      | 0.175      | 0.008      | 0.004      | 22.60         |

*H/C: atomic ratio of hydrogen to carbon.
*N/C: atomic ratio of nitrogen to carbon.

### Table 2. Pore structure characteristics of the nine biochars.

| Biochar | SSA (m² g⁻¹) | TPV (cm³ g⁻¹) | Micro pore volume (cm³ g⁻¹) | Meso pore volume (cm³ g⁻¹) | Macro pore volume (cm³ g⁻¹) | % of V_microm | % of V_meso | % of V_macro | APD (nm) |
|---------|--------------|--------------|-----------------------------|---------------------------|----------------------------|---------------|------------|-------------|----------|
| DM500   | 37.6         | 0.028        | 0.008                       | 0.016                     | 0.004                      | 28.6          | 57.1       | 14.3        | 2.98     |
| DM600   | 42.1         | 0.031        | 0.010                       | 0.015                     | 0.006                      | 32.3          | 48.4       | 19.3        | 2.95     |
| DM700   | 47.0         | 0.034        | 0.012                       | 0.014                     | 0.008                      | 35.3          | 41.2       | 23.5        | 2.90     |
| SS500   | 35.8         | 0.052        | 0.012                       | 0.021                     | 0.019                      | 23.1          | 40.4       | 36.5        | 3.73     |
| SS600   | 61.0         | 0.053        | 0.014                       | 0.019                     | 0.020                      | 26.4          | 35.9       | 37.7        | 3.48     |
| SS700   | 67.4         | 0.059        | 0.017                       | 0.018                     | 0.024                      | 28.8          | 30.5       | 40.7        | 3.50     |
| WC500   | 232.9        | 0.115        | 0.071                       | 0.038                     | 0.006                      | 61.7          | 33.0       | 5.3         | 1.98     |
| WC600   | 300.2        | 0.125        | 0.107                       | 0.012                     | 0.006                      | 85.6          | 9.6        | 4.8         | 1.67     |
| WC700   | 261.3        | 0.116        | 0.091                       | 0.020                     | 0.005                      | 78.4          | 17.2       | 4.4         | 1.78     |

*SSA: specific surface area.
*TPV: total pore volume.
*V_microm: percentages of micropore volume.
*V_meso: percentages of mesopore volume.
*V_macro: percentages of macro pore volume.
*APD: average pore diameter.
with a higher SSA [28]. However, if the temperature increased above a certain temperature (perhaps 600°C), some pores would be sealed off as a result of sintering, leading to reduction of the corresponding biochar specific surface area [28,31].

The SSA of biochars is also affected by their biomass sources [21,31]. Biochars derived from the wood chips showed the highest SSA, which was 233–300 m² g⁻¹. The SSA of sewage sludge biochars was in the range of 55.8–67.4 m² g⁻¹, slightly higher than biochars derived from dairy manure (37.6–47.0 m² g⁻¹). Most of the pores in the DM and SS biochars were mesopores and macropores, while the pores in the WC biochars were mainly micropores (Table 2). The average pore diameter of DM, SS, and WC biochars were in the range of 2.90–2.98 nm, 3.48–3.73 nm, and 1.67–1.98 nm, respectively. In conclusion, the physical and chemical properties of biochar were related to its origin and pyrolysis temperature, and might influence the electrochemical catalytic activity for ORR.

### 3.2 Electrochemical oxygen reduction reaction (ORR) of various biochar electrodes

The electrocatalytic activity of biochar electrode for ORR was determined by the linear sweep voltammetry (LSV) and Cyclic voltammetry (CV), which were measured using rotating disk electrode (RDE) in N₂-saturated and O₂-saturated 0.5 M Na₂SO₄ solutions at a scan rate of 100 mV s⁻¹ for CV and 5 mV s⁻¹ for LSV. Figures 1 and 2 showed that all the biochar electrodes had no obvious limiting diffusion current, especially the biochars produced at the temperature of 600°C. This phenomenon were similar to many porous carbon materials [32,33]. The pyrolysis temperature and biomass sources have an important influence on ORR catalytic activity (Figure 2). At low pyrolysis temperature of 500°C, the current densities of these biochar electrodes were very small, being in the range of 0.26–1.26 mA cm⁻² at 0.15 V. It was possibly caused by low degree of aromatization at low pyrolysis temperature which was represented by the atomic ratio of hydrogen to carbon (H/C) in Table 1. The DM500 sample has the lowest current density value that was merely 0.26 mA cm⁻² at 0.15 V, the possible reason was that the specific surface area and transition metal content of DM500 are both relatively small. At middle pyrolysis temperature of 600°C, the current densities increased, due to the increasing aromatic structure and specific surface area which are beneficial to the electrocatalytic activity. The current densities of DM, SS and WC biochar electrodes at 600°C were improved to 0.77–1.54 mA cm⁻². Noted that compared with 500°C, the current densities at 600°C for DM and SS biochar electrodes were significantly increased. For WC biochar electrodes, the current density at 600°C was comparable with the value of WC500. At high pyrolysis temperature of 700°C, the current densities of DM, SS, and WC biochar electrodes further increased and reached the maximum values of 1.82–2.17 mA cm⁻². The SSA of carbonaceous materials plays an important role in determining the surface reactivity of the materials [34]. High surface area and nanoporous size of biochars would benefit the ORR because this high electrode–electrolyte contact area will facilitate O₂ diffusion and expose more catalytic active sites. Meanwhile, the pore size is also crucial, e.g. the mesoporous structure promotes ORR by transporting oxygen gas, and the micropore structure provides active sites to facilitate catalytic activity. Thus, an appropriate combination of micropore and mesoporous would improve the electrochemical performance of carbon materials. Structure of higher specific surface area and mean pore diameter were proved to be optimum for higher ORR [8,35]. Eventually, the current densities have reached 1.88, 2.17, and 1.82 mA cm⁻² for DM, SS and WC biochar electrodes at 700°C, respectively. The biomass sources also had a significant effect on the current density of the biochar electrodes. Generally, the SS biochar electrodes have higher current density than DM and WC biochar electrodes (Table 3 and Figure 2).

The current density at 0.15 V vs. RHE, half-wave potential (E½) vs. RHE, and onset potential (Eonset) vs. RHE of nine biochar electrodes were presented in Table 3 and Figure 2d. The results showed that SS700 biochar electrode had the best electrochemical catalytic

![Figure 1. Cyclic voltammetry curves of dairy manure (DM), sewage sludge (SS), and wood chip (WC) biochars in O₂-saturated 0.5 M Na₂SO₄ solution at 100 mV s⁻¹.](image-url)
activity, with highest current density (2.17 mA cm\(^{-2}\)), onset potential (0.59 V) and half-wave potential (0.41 V) among all nine biochars. In comparison, as the pyrolysis temperature increased, the current density and half-wave potential of biochar electrodes increased, and the SS and WC biochar electrodes had larger current density which possible on account of high mineral content and specific surface area, respectively [22,36]. It has been proved that transition metals are the active sites for ORR [29]. The concentrations of transition metal elements especially Fe in SS biochars are all higher than the other two biochars. Therefore, it is predictable that the transition metals of SS biochars would catalyze the ORR, especially for metals like Fe with high content in biochars. The physical and chemical properties of biochar (e.g. SSA, TPV, H/C), transition metal content were correlated with the ORR performance of biochar electrode, the results were showed in Figure 3. As predicted, the specific surface area, aromatization degree and transition metal content have positive effects on ORR performance, especially macro-pore volume, aromatization degree, and iron content. Additionally, Fig. S1 showed the XPS test of N\(_1s\) spectra of sewage sludge biochar (SS500, SS600, and SS700). Analysis shows that sewage sludge biochar has various nitrogen doping, forming pyridine nitrogen, pyrrole nitrogen and ammonia nitrogen. The Lorentz-Gauss peak fitting method was used for the N\(_1s\) spectra of each sample, and the peak fitting was performed for the presence of three types of N, namely, pyridine nitrogen (398 ± 0.1 eV), pyrrole nitrogen (399.4 ± 0.1 eV) and graphitized nitrogen (401 ± 0.1 eV). In the pyrolysis process, nitrogen atoms enter the graphite-like structure framework and form nitrogen deficient active sites, and both pyridine nitrogen and graphite-nitrogen can promote the catalytic ORR activity of biochar.

Table 3. Onset potential (E\(_{onset}\)) vs. RHE, half-wave potential (E\(_{1/2}\)) vs. RHE and current density at 0.15 V vs. RHE of DM, SS, and WC biochars.

|          | DM500 | DM600 | DM700 | SS500 | SS600 | SS700 | WC500 | WC600 | WC700 |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| E\(_{onset}\)(V) | 0.25  | 0.43  | 0.57  | 0.41  | 0.49  | 0.59  | 0.42  | 0.42  | 0.50  |
| E\(_{1/2}\)(V) | 0.24  | 0.30  | 0.40  | 0.31  | 0.32  | 0.41  | 0.32  | 0.30  | 0.37  |
| JmA cm\(^{-2}\) @0.15 V | 0.26  | 0.77  | 1.88  | 1.17  | 1.54  | 2.17  | 1.26  | 1.17  | 1.82  |
| n value @ 0.25 V | -     | -     | 2.1   | -     | -     | 3.9   | -     | -     | 3.4   |

Figure 2. The linear sweep voltammetry (LSV) curves of the dairy manure (DM), sewage sludge (SS), and wood chip (WC) biochars produced at 500°C (a), 600°C (b), 700°C (c) in O\(_2\)-saturated 0.5 M Na\(_2\)SO\(_4\) solution at 5 mV s\(^{-1}\) and the current density at 0.15 V vs. RHE and half-wave potential vs. RHE of nine biochars (d).
The electrochemical catalytic activity of DM, SS, and WC biochar electrodes for ORR was further investigated by the LSVs at different rotation rates, as shown in Figure 2. The increase of rotation rate was accompanied with the increase of the diffusion current density for the three kinds of biochar electrodes (Figure 4a,c,e). The Koutecky-Levich plots (J⁻¹ vs. ω⁻¹/2) at different potentials showed good linearity (Figure 4b,d,f). The data in

Figure 3. The association analysis of physical and chemical properties, transition metal content of biochar with the ORR performance of biochar electrode. Red indicates positive correlations while blue indicates negative. SSA: specific surface area; TPV: total pore volume; MiPV: Micro pore volume; MePV: Meso pore volume; MaPV: Macro pore volume; H/C: atomic ratio of hydrogen to carbon; N/C: atomic ratio of nitrogen to carbon.

Figure 4. The linear sweep voltammetry (LSV) curves at different rotation rates recorded for ORR at nine biochars in oxygen-saturated 0.5 M Na₂SO₄ solution at 5 mV s⁻¹ (a, c, e). Koutecky-Levich plots for nine biochars at different potentials (b, d, f).
Table 3 exhibited the dependence of electron transfer number \( n \) on potential at three kinds of biochar electrodes. The calculated value of \( n \) was 2.1, 3.9 and 3.4 for DM700, SS700 and WC700, respectively, at 0.25 V according to the slopes of Koutecky-Levich plots in Figure 4(b,d,f). The \( n \) value indicated the ORR process follows mainly 2 electron process for DM700 biochar electrode and 4 electron process for SS700 and WC700 biochar electrodes. This result suggested the SS700 and WC700 biochar electrodes showed higher electrochemical catalytic activity for ORR.

### 3.3 Characterization of electrochemical impedance spectroscopy (EIS) of various biochar electrodes

Electrochemical impedance spectroscopy (EIS) of an electrode material is now well established as a powerful tool for investigating the mechanisms of electrochemical reactions, measuring the dielectric, and transport properties of materials, exploring the properties of porous electrodes, as well as investigating passive surfaces [37]. In this study, the EIS complex plane plots were obtained in the frequency range of 1 Hz to 0.1 MHz, with the same conditions as those in Figure 4. The double layer capacitance \( (C_{dl}) \) and charge transfer resistance \( (R_{ct}) \) are related to the dielectric and insulating features at the electrode/electrolyte interface, they can reflect the features of biochar electrode surface.

The EIS complex plane plots \((-Z_\text{r} \text{ vs. } Z_\text{z})\), fitting curve, and equivalent circuit diagram were shown in Figure 5. The parameters derived from fitting of these plots into modified Randles’ circuit were shown in Table 4. The impedance locus at high frequency displayed a depressed semicircle, but as the frequency was lowered the locus turned upwards becomes a sloped line (Figure 5(a,b,c)). The impedance spectra were fitted to a modified Randles equivalent electrical circuit including a solution resistance, \( R_s \), a constant phase element, CPE, and a charge transfer resistance, \( R_{ct} \), as shown in Figure 5d. \( R_s \) is mainly dependent on the resistance associated with the solution and connectivity of particles to the current collector; where, \( R_{ct} \) is related to the ionic transfer resistance into the pores of electrode [38]. For all these biochars, the angle of the sloped line at low frequency (<45°) decreased with the increase of the pyrolysis temperature from 500°C to 700°C, which may be caused by the decrease of the rate of mesoporous and macroporous (Table 2) [39]. However, the angle of the sloped line at low frequency for DM, SS, and WC biochar electrodes were different. The slopes of SS500 biochar electrodes were greater than 45°, showed the characteristics of capacitance with high double layer capacitance \( (C_{dl}) \) in the range of \( 6.8 \times 10^{-5} – 2.2 \times 10^{-4} \) F (Table 4). While the slopes of DM and WC biochar electrodes were less than 45° with lower double layer capacitance \( (C_{dl}) \). The higher rate of mesoporous and macroporous and more mineral content of SS500 biochar electrodes might resulted in its higher high double layer capacitance [39,40].

![Figure 5](image-url) Nyquist curve, fitting curve of the nine biochars (a, b, c) and Randles’ circuit diagram (d).
The $R_{ct}$ of the biochar electrodes also varied greatly among these nine biochars. As the pyrolysis temperature increased from 500 to 700°C, the $R_{ct}$ of SS biochar electrodes decreased from 31 to 15.5 Ω, however the DM biochar electrodes increased from 25.0 to 53.9 Ω, and the WC biochar electrodes increased from 9.2 (500°C) to 61.2 Ω (600°C) and then decreased to 29.8 Ω (700°C). The changes of $R_{ct}$ was due to the changes of pores structure and the mineral content of the biochar electrodes when the pyrolysis temperature increased from 500 to 700°C. The micropore increased with the rise of the pyrolysis temperature (Table 2), leading to the larger $R_{ct}$ for DM biochar electrodes. The $R_{ct}$ of WC biochar electrodes was also related to the volume of micropores and mesopores. Previous study showed that mesopores were beneficial to the electron transport while micropores would hinder it [39,40]. The $R_{ct}$ of SS biochar electrodes was different from the above two, possibly influenced by the mineral and the degree of graphitization but not the change of pores. However, the DM and WC biochar electrodes were largely influenced by the pore structure. In conclusion, the SS700 biochar electrode has a small $R_{ct}$ of 15.5 Ω and a large $C_{dl}$ of 2.2 × 10⁻⁴ F.

The current density at 0.15 V vs. RHE is 1.88, 2.17, and 1.82 mA cm⁻² for DM700, SS700, and WC700, respectively, meanwhile SS700 biochar electrode has a small $R_{ct}$ of 15.5 Ω and a large $C_{dl}$ of 2.2 × 10⁻⁴ F, slightly lower than 4.5 mA cm⁻² (J) of Pt/C and other materials like N-C and Co₃O₄/Co₉MnO₄ [41–43]. Nonetheless, they can still be used as potential electrode materials.

Table 4. Electrochemical parameters of DM, SS, and WC biochar electrodes in in O₂-saturated 0.5 M Na₂SO₄ solution.

|        | DM500 | DM600 | DM700 | SS500 | SS600 | SS700 | WC500 | WC600 | WC700 |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $R_{ct}$ (Ω) | 23.1  | 20.9  | 27.8  | 34.0  | 18.6  | 20.8  | 48.9  | 50.6  | 43.6  |
| $C_{dl}$ (F) | 5.6 × 10⁻⁵ | 9.2 × 10⁻⁵ | 7.8 × 10⁻⁵ | 6.8 × 10⁻⁵ | 1.5 × 10⁻⁴ | 2.2 × 10⁻⁴ | 1.1 × 10⁻⁶ | 7.9 × 10⁻⁵ | 3.6 × 10⁻⁵ |
| $R_{ct}$ (Ω) | 25.0  | 25.8  | 53.9  | 31.0  | 23.7  | 15.5  | 9.2   | 61.2  | 29.8  |
| $R_{ct}$ (Ω) | 1.3 × 10⁻⁴ | 6.4 × 10⁻⁴ | 5.4 × 10⁻⁴ | 3.6 × 10⁻⁴ | 6.8 × 10⁻⁵ | 2.4 × 10⁻⁵ | 5.9 × 10⁻⁴ | 5.6 × 10⁻⁴ | 8.5 × 10⁻⁴ |

ORR activity of biochar electrodes, and more efficient electrodes could be designed based on the consideration of feedback composition and production parameters.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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