

## **Calculation of removal efficiency and coulombic efficiency**

 Chemical oxygen demand (COD) removal efficiency (RE) of the system was calculated as

$$
RE = (Cin-Cend)/Cin \times 100\%
$$
 (S1)

30 where  $C_{in}$  is the initial COD concentration in each fed-batch cycle and  $C_{end}$  is the COD concentration at the end of each fed-batch cycle.

 The coulombic efficiency (CE) was defined as the ratio of total recovered coulombs by integrating the current over time to the theoretical charge generated if the substrate was completely converted to electricity. It was calculated as

$$
CE = C_p/C_T \times 100\% \tag{S2}
$$

36 where  $C_p$  is the total Coulombs obtained by integrating the current over time, 37 calculated as  $C_p$ =∫Idt, and  $C_T$  is the theoretical amount of Coulombs that can be produced from acetate, calculated as

$$
C_T = nF(C_{in} - C_{end})V/M
$$
 (S3)

 where F is Faraday's constant (96485 C mol-1 electrons), n the number of moles of electrons produced per mole of substrate (n=8), V the liquid volume of the MFCs, and M=82 the molecular weight of sodium acetate. The COD concentration of the analyte was measured using fast digestion spectrophotometric with a COD digester and photometer (Lianhua 5B–3C, China).





Fig. S1 Picture of the BC (a) and Pt/C (b) cathode supported by the perforated PVC tube.



 Fig. S2. Equivalent circuits for the Pt/C cathode (a) and the BC and BCT cathode (b). The components of Ro, Rin, Rct, Cdl, Cad and W in equivalent circuits representing the ohmic res istance, the interface ohmic resistance, the charge transfer resistance, the double layer capacitance, the pore adsorption capacitance, and the Warburg impedance, respectively.

## **Physical characterization of the catalysts**





Fig. S3 XPS spectra (a) and deconvolution of the N1s (b) and P2p (c) spectra of BC.

 XPS measurements (Fig. S3) are conducted to characterize the chemical composition of the BCT. The full XPS scan of the sample is shown in Fig. S3a. The signals of C1s, O1s, N1s and P2p were detected to confirm the existence of N and P in the sample. To elucidate the property of N and P bonding to the carbon atoms, the high resolution XPS spectrum of N1s and P2p was recorded (Fig. S 3b-c). As shown in Fig. S 3b, the deconvolution of the N1s spectrum revealed that the N-containing 63 species, including graphitic-N ( $\sim$ 401.0 eV), pyrrolic-N ( $\sim$  400.1 eV) and pyridinic-N 64 ( $\sim$  398.3 eV), were found for the cathode (Pels et al., 1995). According to the results, the relative ratio of graphitic-N and pyridinic-N in BC was 36.8 % and 39.9 %, respectively. Previous studies have indicated that the graphitic-N and pyridinic-N play a crucial role in enhancing the ORR activity of carbon-based materials. Lai et al. has demonstrated that graphitic-N and pyridinic-N can greatly increase the limiting current density and the onset potentials respectively (Lai et al., 2012). Similarly, the deconvolution of P2p for BC demonstrated three prominent peaks assigned as P-C (~132.5 eV), P-N (~133.2 eV) and C-O-PO3 (~134.1 eV), as shown in Fig. S 3c. The element P had similar non-metallic characteristics as element N, and the catalytic mechanism of P-doped carbon catalyst in MFCs could be explained using the research of N-doped carbon catalysts (Chen et al., 2014). Razmjooei et al. suggested that P-N 75 and  $C-O-PO_3$  were highly reactive and stable active centers for ORR (Razmjooei et al.,  2015). Chen et al. also reported an excellent ORR characteristic of N and P dual-77 doped carbon catalyst in MFCs with an average electron transfer number of  $\sim 3.5$  (Chen et al., 2014). With the abundant N and P self-doping in BCT, a good ORR property can be expected.

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81 **Table S1 Component analysis of the internal resistance of the different air** 82 **cathodes.**

	Pt/C	<b>BC</b>	<b>BCT</b>
$R_o(\Omega)$	1.52	1.71	1.46
$\text{CPE}_{\text{dl}}\left(\text{F}\cdot\text{s}^{(\text{n-1})}\right)$	$1.04 \times 10^{-4}$	$1.30\times10^{-4}$	$4.03 \times 10^{-5}$
$N_1$	0.74	0.96	0.90
$R_{in}(\Omega)$		0.31	2.15
$CPE_{ad}$		$2.16 \times 10^{-4}$	$1.02 \times 10^{-2}$
$N_2$		0.89	0.58
$R_{ct}$	2.69	4.02	1.74
$W(\Omega \cdot s^{-1/2})$	1.64	$3.19 \times 10^{-3}$	$1.46 \times 10^{-14}$
$R_t(\Omega)$	5.85	6.04	5.35

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## 84 **References:**

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