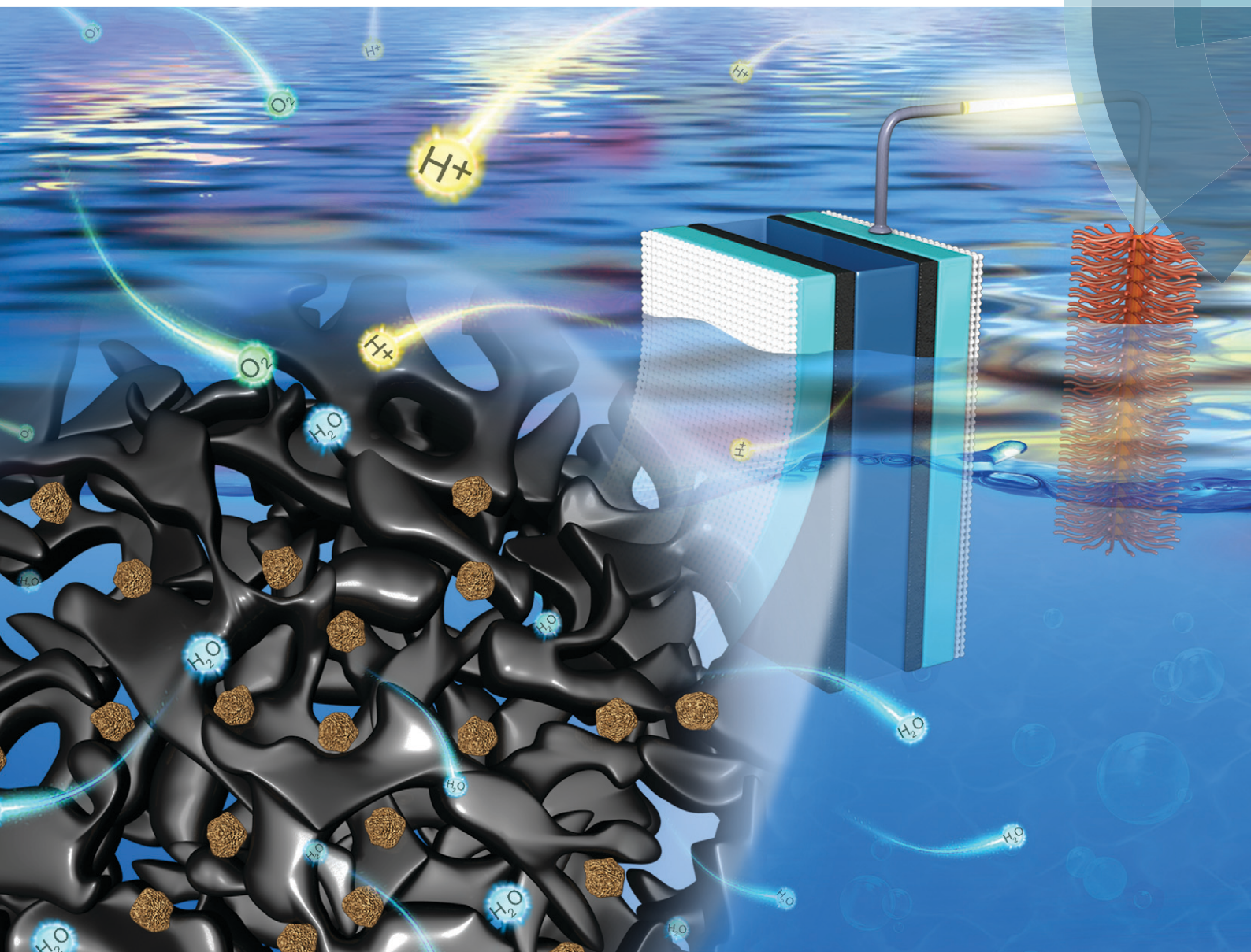


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## COMMUNICATION

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## Addition of conductive particles to improve the performance of activated carbon air-cathodes in microbial fuel cells

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Activated carbon (AC) is an inexpensive and sustainable catalyst for oxygen reduction in air-cathodes of microbial fuel cells (MFCs), but its electrical conductivity is relatively poor. To improve cathode performance, five different more conductive materials were added to AC: three carbon materials (carbon black, mesoporous carbon, and carbon nanotubes), and two metal powders (inexpensive copper and inert gold). Carbon-based particles improved maximum power densities by 6–14% compared to plain AC due to reduced charge transfer resistance. Copper powder had reduced performance, likely due to toxicity effects on the anode bacteria, while gold particles were similar to plain AC. Heat treated AC mixed with carbon black produced the highest power density of  $1900 \pm 76 \text{ mW m}^{-2}$ , 41% higher than the widely used Pt air-cathode ( $1350 \pm 55 \text{ mW m}^{-2}$ ). The use of inexpensive carbon black with heat treatment was therefore the most effective and economical approach for improving cathode performance in MFCs.

### Introduction

Microbial fuel cells (MFCs) are bioelectrochemical systems being developed to convert organic matter in wastewater into electricity, accomplishing simultaneous wastewater treatment and energy production.<sup>1–6</sup> Air-cathodes used in MFCs can enable relatively high power densities from readily available oxygen in air as the electron acceptor, without the need for water aeration.<sup>7,8</sup> Pt is commonly used as a catalyst in lab-scale reactors for oxygen reduction reactions (ORR), but Pt is a precious metal and its catalytic performance rapidly deteriorates

### Water impact

A microbial fuel cell is a sustainable technology for simultaneous wastewater treatment and electricity generation. Practical applications have been limited by cathode performance and cost of materials. Here, the use of several carbon and metals particles was examined to improve performance. Inexpensive carbon black combined with heat treatment produced the most effective activated carbon catalyst for improving cathode performance.

over time due to catalyst poisoning and biofouling.<sup>9,10</sup> Carbon based materials<sup>11–14</sup> have been proposed as alternatives to Pt, among which activated carbon (AC) is one of the most promising catalysts due to its low cost, good performance, and longevity.<sup>9,15</sup>

The performance of different activated carbons for the ORR can depend on the base carbon materials and modifications to the material that can improve performance. Peat- and coal-based AC powders were shown to generate higher power densities than those made from hardwood, coconut shells, or phenolic resins when used in MFC cathodes.<sup>16</sup> Heat treatment can increase the specific surface area of AC, and thus this approach has been used to improve AC performance.<sup>9,17</sup> Incorporating N and/or transition metals into AC can also improve the electrochemical activity for oxygen reduction and increase MFC power densities.<sup>12,18</sup> Modification of the applied AC structure and enhancement of conductivity, by blending 10 wt% carbon black (CB) into the AC, increased MFC maximum power densities by 16% compared to plain AC.<sup>10</sup> However, there have been few studies on the use of other additives with AC, particularly materials that can make AC more electrically conductive. There is great interest in further improving cathode performance, since MFC power densities are mainly limited by oxygen reduction potential and the kinetics at the cathode.<sup>8,19</sup>

In this study, five different conductive particles were individually added to determine their impact on oxygen reduction and MFC performance. Three different carbon materials were used as inexpensive catalyst additives to improve conductivity:

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carbon black ( $2\text{--}12\text{ S cm}^{-1}$ ),<sup>20</sup> mesoporous carbon (graphitized carbon black,  $2\text{--}12\text{ S cm}^{-1}$ ),<sup>20</sup> and carbon nanotubes ( $\sim 1\text{--}10\text{ S cm}^{-1}$ ).<sup>21</sup> Two metal nanoparticles were also examined: copper and gold. Copper was selected as it is one of the most inexpensive metals and it is more electrically conductive (bulk,  $\sim 10^5\text{ S cm}^{-1}$ ) than carbon black. Although gold particles would not be practical for applications in MFCs, gold will not corrode and thus this metal provides a useful comparison to copper, which can form copper oxides in air. These materials were added to AC and systematically compared to plain AC cathodes in MFCs in neutral pH media. The materials were further examined by electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) with a rotating disk electrode (RDE) to test their catalytic rates for ORR. The best performing material was also mixed with heat treated AC to further improve performance. To better understand how heat treatment and the best performing additive impacted the material properties, the conductivity and contact angle of the cathodes were also examined.

## Materials and methods

### Air-cathode materials and their fabrication

Peat-based AC (Norit SX plus, Norit Americas Inc., USA) was selected as the plain AC base material.<sup>16</sup> Five conductive particles were separately blended into AC at a 10 wt% ratio: carbon black (CB, Vulcan XC-72, Cabot Corporation, USA); mesoporous carbon (MC, <500 nm particle size, Sigma-Aldrich, USA); carbon nanotubes (CNT, multiwalled, 8–15 nm diameter, 10–50  $\mu\text{m}$  length, Nanostructure & Amorphous Materials Inc. USA); gold nanoparticles (Au, 99.9% trace metal basis, <100 nm particle size, Sigma-Aldrich, USA); and copper microparticles (Cu, 2–3.5  $\mu\text{m}$  particle size, Alfa Aesar). In addition, CB was blended into heat-treated AC (HT) at 800 °C under Ar gas for 1.5 h. This temperature was chosen based on the optimal temperature for AC synthesis and non-precious metal catalyst pyrolysis in previous reports on ORR.<sup>22,23</sup> All AC-based catalysts were applied at a constant loading of 300 mg per cathode (11  $\text{cm}^2$  total area and 7  $\text{cm}^2$  projected area). Air-cathodes with a polytetrafluoroethylene (PTFE) and CB diffusion layer (PTFE loading of 37.5  $\text{mg cm}^{-2}$  and CB loading of 25  $\text{mg cm}^{-2}$ ) on a stainless steel mesh were fabricated by a recently developed batch press process that showed enhanced performance.<sup>24</sup> Comparisons in performance were benchmarked against widely used platinum air-cathodes (Pt/CC, 5  $\text{mg cm}^{-2}$  10% Pt on Vulcan XC-72 and 5 wt% Nafion binder) with carbon cloth and 4 PTFE diffusion layers fabricated as previously reported.<sup>7</sup>

### Electrochemical analyses, conductivity, and hydrophobicity characterization

Electrochemical tests were conducted using a potentiostat (VMP3, BioLogic Science Instruments, USA). Air-cathodes were examined in an abiotic, cubic shaped electrochemical reactor (4 cm length, 2 cm per chamber) with an anion ex-

change membrane in the middle, a platinum plate (99.99% Pt, 1  $\text{cm}^2$ ) as a counter electrode, and a Ag/AgCl reference electrode placed adjacent to the cathode. The electrolyte was a 50 mM phosphate buffer solution (PBS) that contained: 4.57  $\text{g L}^{-1}$   $\text{Na}_2\text{HPO}_4$ , 2.45  $\text{g L}^{-1}$   $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ , 0.31  $\text{g L}^{-1}$   $\text{NH}_4\text{Cl}$  and 0.13  $\text{g L}^{-1}$  KCl. Chronoamperometry tests conducted by setting the potential in a stepwise manner at potentials of 0.2 V, 0.1 V, 0 V, −0.1 V, −0.2 V and −0.3 V (*versus* Ag/AgCl) for 1 h at each potential.

A 3 electrode RDE setup (MSR rotator, PINE Instruments, USA) was used to evaluate the ORR kinetics of the catalysts (AC, AC-CB, HT-CB, and Pt/C). Catalyst inks were prepared by adding 45 mg of catalyst into a vial with 0.8 mL of isopropyl alcohol and a 0.2 mL 5 wt% Nafion mixture, with ultrasonication for 15 min. The ink suspension ( $\sim 30\text{ }\mu\text{L}$ ) was dropped onto a 1.3 cm diameter graphite carbon disk with an effective area of 0.283  $\text{cm}^2$  (0.6 cm diameter). LSV and EIS were conducted at a rotation rate of 2500 rpm to minimize mass transfer limitations. LSV measurements were carried out at a scan rate of 5  $\text{mV s}^{-1}$ . EIS was conducted at −0.1 V *vs.* Ag/AgCl over a frequency range of 10 000 to 0.002 Hz with a sinusoidal perturbation of 10 mV in amplitude.

The conductivities of the AC, AC-CB, heated AC and HT-CB catalyst layers were measured using a commercial four-probe sheet resistance system (model SX1944, Jiangsu Telecommunication, China). The hydrophobicity of these catalyst layers was measured using an optical contact angle measuring instrument (OCAH200, Dataphysics, Germany).

### MFC experiments

Cubic single-chamber MFCs were constructed (24 mL volume) as previously described.<sup>25</sup> The anode was a graphite fiber brush (2.5 cm in both diameter and length). The air-cathode was placed at the other side of the reactor, with the diffusion layers facing air. MFCs were inoculated with the effluent of the MFCs being operated for over one year. The medium was 1  $\text{g L}^{-1}$  sodium acetate in 50 mM PBS amended with 12.5 mL  $\text{L}^{-1}$  minerals and 5 mL  $\text{L}^{-1}$  vitamins. All the MFCs were operated in batch mode with a 1000  $\Omega$  external resistor (except as noted) at  $30 \pm 1\text{ }^\circ\text{C}$  in a constant temperature room.

Voltages ( $U$ ) were recorded across an external resistance ( $R$ ) every 20 min using a multimeter with a computerized data acquisition system (2700, Keithley Instrument, USA). Polarization curves were obtained using a multi-cycle method, by applying different external resistors from 1000  $\Omega$  to 20  $\Omega$ , with each resistance used for a complete cycle. Current densities ( $j$ ) and power densities ( $P$ ) were normalized with an air-cathode projected area ( $A = 7\text{ cm}^2$ ), using  $j = U/RA$  and  $P = jU$ . Electrode potentials were reported *versus* an Ag/AgCl reference electrode (+0.21 V *versus* a standard hydrogen electrode).

## Results and discussion

### MFC performance of different AC based air-cathodes

All of the carbon based conductive particles (CB, MC and CNT) increased the power densities produced by the MFCs

compared to the plain AC air-cathode or the Pt control (Fig. 1A). Among the three different conductive particles (no heat treatment), CB and MC produced similar maximum power densities of  $1840 \pm 20 \text{ mW m}^{-2}$  (AC-CB) and  $1830 \pm 60 \text{ mW m}^{-2}$  (AC-MC), which were higher than all other cathodes and were 35% higher than the widely used Pt/C carbon cloth air-cathode control ( $1350 \pm 50 \text{ mW m}^{-2}$ ). The power densities for AC and MC were slightly higher than that of AC-CNT ( $1710 \pm 10 \text{ mW m}^{-2}$ ) and 14% higher than that of plain AC ( $1610 \pm 50 \text{ mW m}^{-2}$ ) (Fig. 1A). The anode potentials were essentially the same at the same current densities in all the MFCs, indicating that the cathode potentials were responsible for the differences in power generation (Fig. 1B).

The three carbon based conductive additives also outperformed the Cu and Au metal additives. The power density for the CB and MC cathodes was 15% higher than AC-Au ( $1600 \pm 76 \text{ mW m}^{-2}$ ) (Fig. 1A). Polarization data could not be obtained for cathodes with Cu powder due to failure of these reactors. During acclimation of the reactors using the Cu cathodes, the voltage produced by the MFCs ( $1000 \Omega$ ) decreased from 570 mV to <200 mV after only 3 cycles of operation, due to its rapidly decreased anode performance. Copper is known to be toxic to bacteria, and previous tests with copper anodes have shown that the use of copper in these systems produces much less power than Cu-free electrodes.<sup>26</sup> However, there had not been previous reports using copper particles in cathodes.

Based on the results of these tests, the addition of CB produced the best results compared to the other cathode addi-

tives. Therefore, additional tests were conducted using heat treated AC. Heat treated AC mixed with CB (HT-CB) produced even higher power densities of  $1900 \pm 70 \text{ mW m}^{-2}$ , which was 41% higher than the Pt control (Fig. 1A). This power density was also higher than that obtained using many other materials in a similar reactor, including N-doped graphene ( $1470 \text{ mW m}^{-2}$ ),<sup>27</sup> and N-doped carbon nanotubes ( $1600 \text{ mW m}^{-2}$ ).<sup>11</sup> It was also higher than a Co-based catalyst derived from a metal-organic-framework ( $1660 \text{ mW m}^{-2}$ ),<sup>28</sup> a Fe-based catalyst derived from iron and aminoantipyrene ( $1660 \text{ mW m}^{-2}$ ),<sup>29</sup> and a nano Fe-based catalyst on AC ( $1430 \text{ mW m}^{-2}$ ).<sup>18</sup> However, this power density for the HT-CB was less than that obtained using an Fe- and 1,10-phenanthroline-based metal organic framework AC cathode ( $2600 \text{ mW m}^{-2}$ ) made without CB.<sup>30</sup> This suggests that the higher power densities might be further improved by adding MOFs to the cathodes prepared using CB.

### Conductivity and hydrophobicity characteristics

Among the electrical conductivity measurements, the AC-CB catalyst layer had the highest conductivity of  $0.59 \text{ S cm}^{-1}$ , compared to  $0.40 \text{ S cm}^{-1}$  for the plain AC layer. The heat-treated AC layer had a lower conductivity of  $0.37 \text{ S cm}^{-1}$ . Heat treatment is known to increase the total AC surface area, as shown in a previous study where a larger BET surface area of  $922 \pm 6 \text{ m}^2 \text{ g}^{-1}$  was obtained for heat treated AC compared to the original AC ( $883 \pm 5 \text{ m}^2 \text{ g}^{-1}$ ).<sup>17</sup> The BET surface area of CB was  $234 \pm 5 \text{ m}^2 \text{ g}^{-1}$ . Adding CB into the heated AC would therefore not increase further the BET surface area, but it did increase the conductivity by 16% to  $0.43 \text{ S cm}^{-1}$ . Thus, the overall ORR performance enhancement of HT-CB likely resulted from both the increase in surface area by heat treatment and the conductivity increase due to CB addition. The hydrophobicity was also altered by these different additives. HT-CB was much more hydrophobic than the other materials, with a contact angle of  $96^\circ$ , which was over twice that of plain AC ( $46^\circ$ ), and slightly higher than AC-CB ( $91^\circ$ ). This increase in hydrophobicity might be helpful in creating three-phase interfaces and thus contribute to improved ORR kinetics.

### Electrochemical performance

Based on chronoamperometry tests, HT-CB achieved the highest performance among all the air-cathodes, with relatively similar performances obtained for the other AC cathodes consistent with the results in the MFC tests (Fig. 2). At a potential of  $-0.3 \text{ V vs. Ag/AgCl}$ , the CB additive had the highest current among the non-heat treated cathodes, with a current density of  $17.7 \text{ A m}^{-2}$  compared to  $15.9 \text{ A m}^{-2}$  for plain AC, and  $12.1 \text{ A m}^{-2}$  for the Pt control. The heat-treated AC and CB cathode (HT-CB) produced the highest current density of  $20.8 \text{ A m}^{-2}$  (Fig. 2), consistent with the MFC test results.

The differences in performance of these cathodes were due to both kinetics and mass transfer, which is expected as

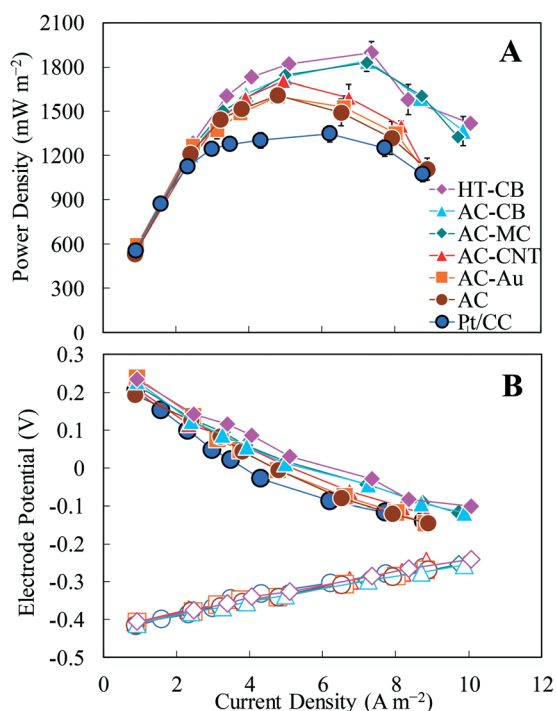


Fig. 1 (A) Power density and (B) electrode potential (solid symbol: cathode potential; open symbol: anode potential) as a function of current density in the MFCs with different cathodes.

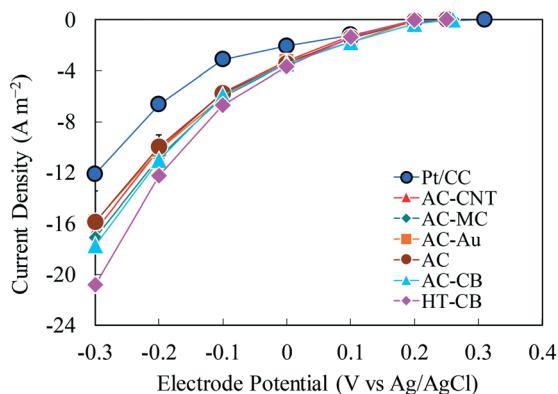


Fig. 2 Current-potential curves of different cathodes obtained in a biotic electrochemical cell by chronoamperometry tests.

the AC-based cathodes have relatively thick catalytic layers relative to the thin Pt-catalyst layer. To further examine the performance of the cathodes with minimal mass transfer resistance, four cathode materials (HT-CB, AC-CB, AC and Pt) were examined using a RDE. In RDE-based LSV tests with the inks, there was greater variability among the scans, likely due to the electrode capacitance, compared to chronoamperometry tests with whole cathodes. At  $-0.1$  V vs. Ag/AgCl, the HT-CB ink had the highest current density of  $1.91 \text{ mA cm}^{-2}$ , which was 29% higher than the Pt/C ink ( $1.48 \text{ mA cm}^{-2}$ ), and higher than the AC-CB ( $0.99 \text{ mA cm}^{-2}$ ) and AC ( $0.60 \text{ mA cm}^{-2}$ ) inks (Fig. 3A).

Larger differences were observed among the materials based on EIS tests, showing that the differences among the materials were primarily due to the reduction in the charge transfer resistance upon adding the conductive materials. Plain AC had the largest charge transfer resistance of  $1120 \Omega$  (Fig. 3B). Adding CB decreased the charge transfer resistance by 33% to  $820 \Omega$  (AC-CB), and heat treatment further reduced this to  $683 \Omega$  (HT-CB). Pt/C had the lowest charge transfer resistance of  $212 \Omega$  due to its high ORR activity when mass transfer resistances are minimized (Fig. 3B). These results demonstrated as expected that Pt has high ORR activity with minimized mass transfer resistances, but the thicker catalytic layer of AC helped improve the performance. Thus, adding the conductive CB material combined with heat-treatment on AC was the most effective catalytic strategy among those tested here in large part due to the reduced charge transfer resistance.

### Cost analysis and implications

Both AC and CB cost  $\sim \$1$  per kg (www.alibaba.com) and therefore are inexpensive. Heat-treatment is similar to the carbonization process used for AC production, and thus a heat-treatment process may be conducted during AC manufacturing or later as a separate process. The extra cost for heat-treatment is estimated to be only  $\sim \$0.02$  per kg AC (the cost may vary depending on the oven and operation conditions) not including the cost for the inert gas, assuming an

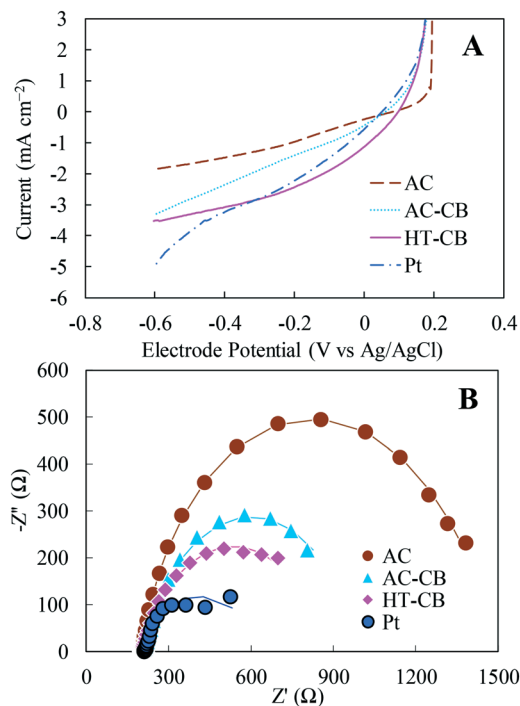


Fig. 3 (A) LSV and (B) Nyquist plots using different catalyst inks at a rotation rate of 2500 rpm in RDE tests.

electricity price of  $\sim \$0.1 \text{ kW h}^{-1}$ . Based on these assumptions, the cost of heat-treated AC with 10% CB is only  $\sim \$0.3$  per  $1 \text{ m}^2$  cathode based on a catalyst loading of  $0.27 \text{ kg m}^{-2}$ . Thus, conductive CB addition combined with heat-treatment of AC should be a simple and cost-efficient method for improving the cathode performance even for large-scale cathode fabrication.

## Conclusions

Carbon-based conductive particle additives for AC air-cathodes, including CB, MC and CNT, enhanced the MFC power density by 6–14% compared with plain AC. They also outperformed the conductive metal particles (Au and Cu powders). CB achieved the highest performance among these additives, and heat-treated AC with CB reached the highest maximum power densities of  $1900 \pm 76 \text{ mW m}^{-2}$ , 41% higher than the widely used Pt/C air-cathode and 18% higher than plain AC, due to decreased charge transfer resistance and increased hydrophobicity. Thus, CB additive combined with heat-treatment on AC is a cost-efficient and useful strategy to enhance AC-based air-cathode performance of MFCs.

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