

Polyelectrolyte–single wall carbon nanotube composite as an effective cathode catalyst for air-cathode microbial fuel cells

Huanan Wu, Min Lu, Lin Guo, Leonard Guan Hong Bay, Zheng Zhang and Sam Fong Yau Li

ABSTRACT

Polyelectrolyte–single wall carbon nanotube (SCNT) composites are prepared by a solution-based method and used as metal-free cathode catalysts for oxygen reduction reaction (ORR) in air-cathode microbial fuel cells (MFCs). In this study, two types of polyelectrolytes, polydiallyldimethylammonium chloride (PDDA) and poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] (PEPU) are applied to decorate the SCNTs and the resulting catalysts exhibit remarkable catalytic ability toward ORR in MFC applications. The enhanced catalytic ability could be attributed to the positively charged quaternary ammonium sites of polyelectrolytes, which increase the oxygen affinity of SCNTs and reduce activation energy in the oxygen reduction process. It is also found that PEPU–SCNT composite-based MFCs show efficient performance with maximum power density of 270.1 mW m^{-2} , comparable to MFCs with the benchmark Pt/C catalyst (375.3 mW m^{-2}), while PDDA–SCNT composite-based MFCs produce 188.9 mW m^{-2} . These results indicate that PEPU–SCNT and PDDA–SCNT catalysts are promising candidates as metal-free cathode catalysts for ORR in MFCs and could facilitate MFC scaling up and commercialization.

Key words | cathode catalyst, microbial fuel cells, oxygen reduction reaction, polyelectrolyte

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INTRODUCTION

The microbial fuel cell (MFC), a device utilizing bacteria to harvest electricity from organic matter in wastewater, has received increasing attention due to its great promise in wastewater treatment. It has been considered as an attractive future option for organic waste decomposition and bioenergy harvesting from wastewater. In a typical MFC, electrons and protons are generated on the anode through the degradation of organic matter by exoelectrogenic bacteria. Subsequently, the electrons and protons migrate through the external circuit and solution, respectively, toward the cathode for a reduction reaction, forming a complete electrical circuit with electricity generation (Logan 2008). Recently, MFCs utilizing air as the cathode have been rapidly developed owing to the easy access of air. However, many factors, such as MFC configuration, exoelectrogenic bacteria and substrates, still retard the further development of the air–cathode MFC (Liu & Logan

2004; Liu *et al.* 2005; Cheng *et al.* 2006a; Jong *et al.* 2006). One of the most important factors is the cathode performance which limits the energy production because of the slow kinetics of oxygen reduction (Gil *et al.* 2003; Jang *et al.* 2004). Although platinum (Pt) has been the most commonly used catalyst in MFCs to accelerate the oxygen reduction reaction (ORR) (Logan *et al.* 2006), the high cost and limited reserve hinder its use in MFCs.

To reduce the cathode cost while sacrificing the performance to a small extent, some non-precious metal containing catalysts such as metal macrocycles (Zhao *et al.* 2005) and manganese oxide (Li *et al.* 2010) as well as metal-free catalysts (Tepper *et al.* 2009; Kjaergaard *et al.* 2010) have been explored as alternatives to Pt. Metal macrocycles presented good performance in terms of power generation; however, they suffer from poor stability. Pyrolysis could help to some

extent but improvements are still needed. Among metal-free catalysts, nitrogen-doped carbon materials show good ORR activity. For example, nitrogen-doped carbon nanotubes (Chen *et al.* 2009; Fujigaya *et al.* 2011), nanofibers (Matter *et al.* 2006; Liu *et al.* 2010), layered nanosheets (Luo *et al.* 2011; Wang *et al.* 2011a), nanocapsules (Shanmugam & Osaka 2011) and xerogels (Jin *et al.* 2011) show remarkable ORR catalytic activity. However, nitrogen-doped carbon materials are mostly prepared at high temperature and inert environments, which would be complex, cost-ineffective and time-consuming. The catalytic activity of electroconductive polymers and more interestingly biocatalysts have also been proved. However, further optimization studies are still needed, as discussed in a recent review (Liew *et al.* 2014). Interestingly, carbon nanotubes functionalized with polyquaternium, which contains positively charged ammonium sites, have been found to possess good catalytic ability for ORR (Wang *et al.* 2011b). Interaction between the carbon support and quaternary ammonium-containing polyelectrolyte increases oxygen affinity and thus accelerates ORR (Figure 1). Inspired by these studies, we here employ two polyelectrolytes, namely polydiallyldimethylammonium chloride (PDDA) and poly[bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea] (PEPU), to functionalize polyelectrolyte-single wall carbon nanotubes (SCNTs) for the enhancement of air-cathode MFCs. It is found that both of the two polyelectrolytes can be well decorated onto the SCNTs. The resultant polyelectrolyte-SCNT catalysts show remarkable electrocatalytic capabilities toward ORR in MFCs. It is believed that this type of metal-free catalyst will lead to a promising direction for MFC improvement due to the low cost, easy preparation and excellent catalytic abilities.

METHODS

Synthesis of polyelectrolyte-SCNT composite catalyst

PDDA-SCNT and PEPU-SCNT composites were prepared using a solution-based method (Wang *et al.* 2011b). In each case, 100 mg SCNTs were dispersed in 400 mL aqueous solution of 5 wt% (wt% represents 'weight percentage') polyelectrolyte. The suspension was ultrasonicated until it was clear and particle-free, and then stirred overnight at room temperature for uniform dispersion. The products were then filtered, washed and dried in a vacuum oven at 70 °C for 24 h.

The N content of these composites was determined by elemental analysis (Elementar Vario Micro Cube), while surface N atoms were examined by X-ray photoelectron spectroscopy (XPS Thermo Scientific Theta Probe) for their interaction with adjacent groups. Morphological characterization of these catalysts as well as bare SCNTs (B-SCNT) was conducted using a field-emission scanning electron microscope (FESEM, JEOL JSM-6701F) at the acceleration voltage of 5.0 kV. The prepared composites were ground in an agate mortar before each test. All the chemical reagents were analytical pure and used without further purification unless otherwise specified.

Electrochemical measurement

Electrodes for electrochemical measurements were fabricated according to the procedure reported previously (Lu *et al.* 2011). PDDA-SCNT or PEPU-SCNT catalyst and polyvinylidene fluoride binder were mixed at a certain

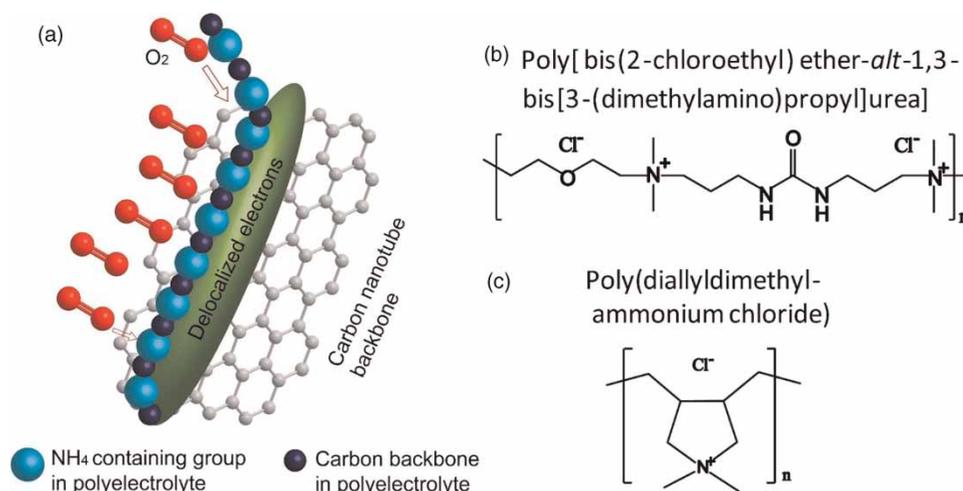


Figure 1 | Illustration of the proposed catalytic mechanism (a). Interaction between O_2 and composite catalysts. Polyelectrolytes used are (b) PDDA and (c) PEPU.

weight ratio in N-methyl-2-pyrrolidone solvent and well dispersed to form slurry. A small volume of slurry was spread onto the surface of a glass carbon electrode (GCE with 3.0 mm diameter) with a micropipette. The GCEs were dried at 70 °C in a vacuum oven for 1 h to remove the solvent. The commercially available Pt/C catalyst (45.6% Pt) was utilized as the benchmark material for comparison, and Pt/C-modified GCE was fabricated with 5% Nafion solution as binder.

Cyclic voltammetry (CV) was carried out on an electrochemical workstation (IviumStat) to examine the catalytic capability of each catalyst. A three-electrode system was employed with catalyst-coated GCE serving as the working electrode, Ag/AgCl/KCl (3 M) as the reference electrode and Pt gauze as the counter electrode. All the measurements were carried out in 0.2 mol/L NaCl electrolyte at a scan rate of 50 mV s⁻¹ over the range of 0.2 to -1.0 V. The solution was bubbled with O₂ or N₂ for 30 min before each scan series, and for 3 min between every two scans to establish an aerobic or anaerobic environment.

MFC setup and operation

The MFCs were set up with the same configuration as previously reported (Lu *et al.* 2011). Generally, acrylic single-chamber MFC reactors with the anodic chamber of Φ 6 cm \times 1 cm (28.3 mL) were assembled. Non-wet-proof carbon cloth (E-TEK) was used directly as the anode, and also as the cathode with further modification, where the carbon cloth was coated firstly with carbon base layer, and subsequently catalyst layer at the inner side and then hot pressed together with the proton exchange membrane (Nafion 117) as a membrane-cathode-assembly (Cheng *et al.* 2006b). The cathode catalysts were applied by spraying the mixed slurries onto the carbon cloth and dried at room temperature. Cathode catalysts with different loadings, Pt/C (0.5 mg Pt cm⁻²), PDDA-SCNT (3 mg cm⁻²) and PEPU-SCNT (3 mg cm⁻²), were used for MFC duplicates.

Activated sludge (Ulu pandan water reclamation plant, Singapore) was used as inoculum. Artificial wastewater (~1 g L⁻¹ sodium acetate in 30 mmol/L phosphate saline buffer with mineral and vitamins solution (Lovley & Phillips 1988)) was applied as anolyte, fed continuously at a flow rate of 1.3 mL min⁻¹ after successful inoculation. A 10 Ω resistor was connected to each MFC, and the voltage across the resistor was constantly monitored and recorded at a fixed interval by a home-made data acquisition system. Voltages across different resistors were measured to obtain electric currents used for the polarization curve. All MFCs were continuously monitored under identical conditions for 2 months. Initially in the inoculation stage, we used a Pt-based cathode for starting up; after the anode reached stabilization, we changed to the polyelectrolyte-SCNT cathode for the long-term test. Data obtained were measurements over 2 months after stabilization. Within these 2 months, there have been fluctuations within an acceptable range (10%) in terms of power density.

RESULTS AND DISCUSSION

Characterization of polyelectrolyte-SCNT composite catalysts

To directly compare the polyelectrolyte-modified SCNTs with B-SCNT, morphologies are observed under FESEM (Figure 2). As shown in Figure 2, no obvious morphology change was observed after the formation of polyelectrolyte-modified SCNTs. Fine nanoparticles appear in Figures 2(a) and 2(b), indicating the uniform dispersion of polyelectrolyte with no aggregation.

Considering the N content is an indicating parameter for polyelectrolyte loading, we further studied the polyelectrolyte-SCNT composites by elemental analysis. The results of N

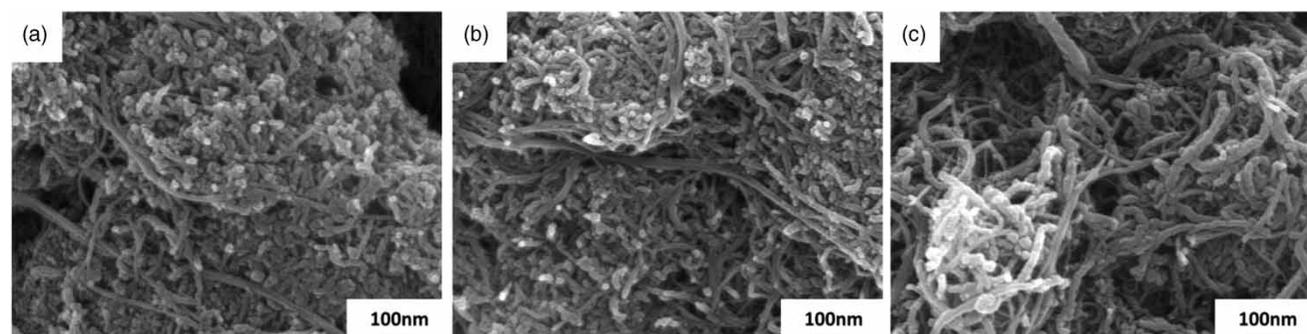


Figure 2 | Field-emission scanning electron microscope images of PDDA-SCNT (a), PEPU-SCNT (b) and B-SCNT (c).

content by elemental analysis are summarized in Table 1. It demonstrates the successful polyelectrolyte incorporation with 24 and 11 wt% polyelectrolytes in the PDDA-SCNT and PEPU-SCNT composites, respectively.

Catalytic capability toward ORR with polyelectrolyte-SCNT composites

We further examined the catalytic capability of the polyelectrolyte-SCNT composites in neutral media by CV (Figure 3). The benchmark Pt/C catalyst yielded a broad ORR peak from -0.1 to -0.7 V in aerated electrolyte. Similarly, both PDDA-SCNT and PEPU-SCNT catalysts showed peaks from -0.1 to -0.4 V under aerobic conditions, but no such peaks under anaerobic conditions, which implies that this peak is attributed to the ORR process. Compared with B-SCNT, the ORR peak intensities increase for both composites with polyelectrolyte incorporation, indicating enhanced catalytic capability. These results indicate the important role of polyelectrolytes during the process of ORR.

Table 1 | Elemental contents of different composites

Sample	C/wt%	N/wt%
PDDA-SCNT	78.82	2.04
PEPU-SCNT	87.89	1.61
B-SCNT	93.24	N.A.

N.A. represents 'not applicable'.

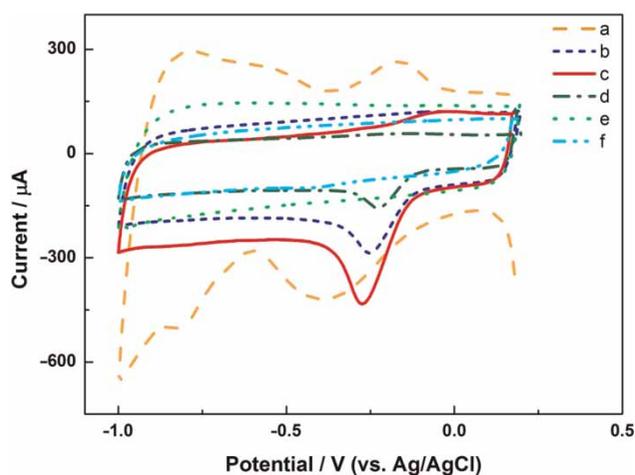


Figure 3 | Cyclic voltammograms for ORR with different catalysts and conditions. (a) Pt/C $0.5 \text{ mg Pt cm}^{-2}$; (b) and (e) PDDA-SCNT 3 mg cm^{-2} ; (c) and (f) PEPU-SCNT 3 mg cm^{-2} ; (d) B-SCNT 3 mg cm^{-2} ; (a)-(d) in aerobic conditions; (e), (f) in anaerobic conditions.

To further investigate the catalytic mechanism of these polyelectrolyte-SCNT composites, the interaction between carbon nanotubes and polyelectrolyte is investigated by XPS. In previous studies, the binding energy for N atoms was found to be negatively shifted. Therefore, Wang *et al.* described the intermolecular interaction theory, in which electron transfer occurs between quaternary N and C in the SCNT backbone thus improving oxygen affinity (Wang *et al.* 2011b). However, as shown in Figure 4 and Table 2, the binding energy of N atoms in pure polyelectrolyte and in polyelectrolyte-SCNT composite does not vary, which indicates no obvious direct electron transfer between the C backbone and N atom in the quaternary ammonium group. Therefore, we believe that the catalytic activity is due to the increased oxygen affinity at positive quaternary ammonium sites. In the meanwhile, the delocalized electrons of the adjacent carbon backbone in SCNTs are responsible for the enhanced electron transfer from the catalyst to the adsorbed oxygen with weakened O-O covalent bond (Li *et al.* 2012; Sharifi *et al.* 2012). In previous studies, it was found that more positively charged quaternary nitrogen valley sites ($\text{N-Q}_{\text{valley}}$) are the more active sites for ORR in nitrogen-doped carbon nanotubes compared with less negatively charged quaternary nitrogen center sites ($\text{N-Q}_{\text{center}}$) (Sharifi *et al.* 2012). Furthermore, it has been reported that enhanced catalytic activity of metal-free nitrogen-doped hollow carbon spheres for ORR arose from the doping of nitrogen in the form of quaternary nitrogen (Li *et al.* 2012). The synergetic effect between quaternary ammonium and delocalized electrons on the carbon backbone promotes the catalytic efficiency of the polyelectrolyte-SCNT composites. Moreover, the better performance of PEPU-SCNT could be due to the longer linear chain structure, which allows a higher degree of freedom, leading to stronger interaction between PEPU and SCNT, while the five-member-ring structure of PDDA causes the steric hindrance on contact with SCNT (Lin *et al.* 2011).

Catalyst performance and cost

To further evaluate the catalytic capabilities of these polyelectrolyte-SCNT composites in the air-cathode MFC systems, MFCs equipped with PDDA-SCNT, PEPU-SCNT and Pt/C individually applied as cathode catalyst were investigated and compared. Performances of these MFCs are summarized in Table 3 and the polarization and power curves are presented in Figure 5. Open circuit voltages were obtained as 0.617 V for PEPU-SCNT-based MFCs.

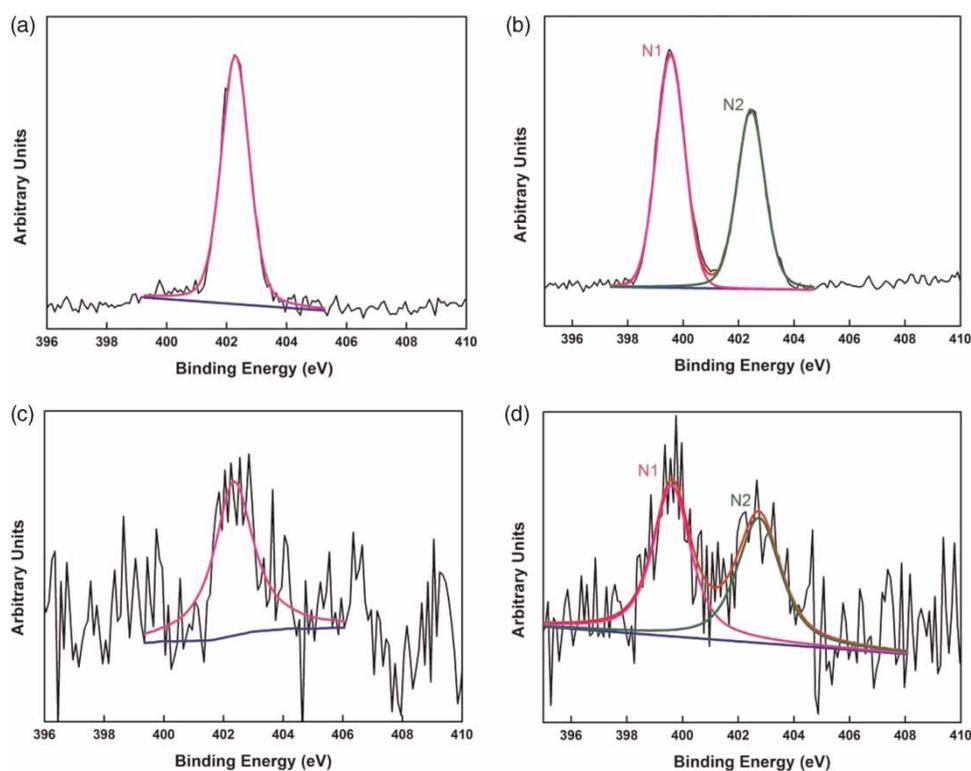


Figure 4 | XPS spectra of N1s for (a) PDDA, (b) PEPU, (c) PDDA-SCNT and (d) PEPU-SCNT. N 1s in (a) and (c) is assigned to quaternary N species, while N1 and N2 in (b) and (d) to urea N and quaternary N, respectively.

Table 2 | Detailed breakdown of N1s signal with peak position and relative composition of different nitrogen groups

	PDDA		PDDA-SCNT		PEPU		PEPU-SCNT	
	Pk (eV)	At. %	Pk (eV)	At. %	Pk (eV)	At. %	Pk (eV)	At. %
Quaternary N	402.28	7.2	402.35	0.5	399.55	7.3	399.62	0.7
Urea N	–	–	–	–	402.44	9.5	402.35	0.8

Pk represents 'peak position'; At. % represents 'atomic percentage'.

Table 3 | Performance of air-cathode MFCs based on different cathode catalysts

Catalysts	Electromotive force/V	Open circuit voltage/V	Internal resistance/ Ω	Maximum power/mW	Maximum power density/mW m ⁻²
PDDA-SCNT	0.399	0.543	73.3	0.534	188.9
PEPU-SCNT	0.459	0.617	69.7	0.763	270.1
Pt/C	0.531	0.641	67.1	1.061	375.3

This value is higher than that of PDPA-SCNT-based MFCs (0.543 V) and approaching that of Pt/C-based MFCs (0.641 V). The internal resistances, calculated from the slope of polarization curves, were 73.3 Ω (PDPA-SCNT) and 69.7 Ω (PEPU-SCNT), respectively. Importantly, in the presence of PEPU-SCNT catalyst, the MFCs generate

a maximum power density of 270.1 mW m⁻², reaching over 70% of Pt/C-based MFC (375.3 mW m⁻²). Slightly lower power density was observed for the MFC with PDPA-SCNT catalyst (188.9 mW m⁻²), which is consistent with the CV results. Moreover, these data presented were collected 2 months after the initial inoculation stage.

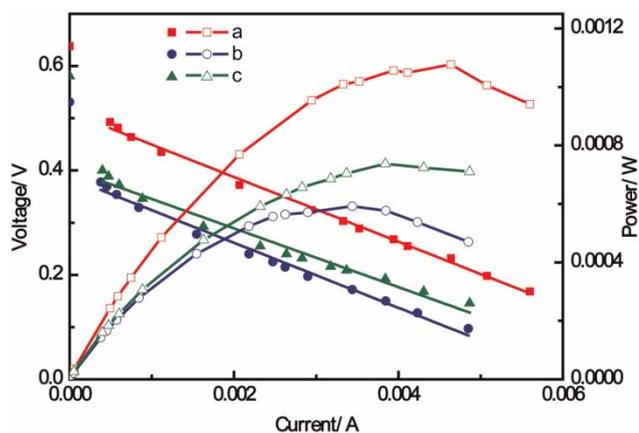


Figure 5 | Polarization and power curves for air-cathode MFCs. (a) PDDA-SCNT 3 mg cm⁻²; (b) PEPUSCNT 3 mg cm⁻²; (c) Pt/C 0.5 mg Pt cm⁻².

Within these 2 months, MFC performance fluctuated in the normal range (10%) in terms of power density. Taken together, the results obtained in the MFCs strongly indicate that PDDA-SCNT and PEPUSCNT could be effective MFC cathode catalysts. Similar to other metal-free carbon-based catalysts such as nitrogen-doped carbon nanotubes and graphene (Liew *et al.* 2014), the polyelectrolyte-SCNT catalysts have demonstrated electrocatalytic activity comparable to Pt/C catalysts, although some catalysts prepared at high temperature have outperformed Pt/C in terms of power density (Liu *et al.* 2014; Wen *et al.* 2014).

Considering the overall cost, the price of commercial Pt/C catalyst is around \$150/g, which is limited by the price of Pt. In contrast, SCNT costs around \$1/g, and incorporated with PDDA or PEPUSCNT would not affect the cost significantly due to the even lower prices of these polyelectrolytes and the simple preparation procedures. Moreover, because of the limited reserves of Pt, the price of Pt catalyst will keep increasing, while polyelectrolyte-SCNT composite catalysts will be more cost-effective with scaled up production. Furthermore, the composite catalysts were prepared using non-toxic polyelectrolytes through environmentally friendly methods under mild conditions, compared to the doped carbon nanostructures (Chen *et al.* 2009; Fujigaya *et al.* 2011). Meanwhile, these catalysts are also entirely metal-free, making themselves more competitive in MFC practical applications.

CONCLUSION

In this study, two kinds of polyelectrolyte-SCNT composites, PDDA-SCNT and PEPUSCNT, were prepared by a simple

solution-based method. The resulting nanocomposites were further studied by CV. The results demonstrate that both of them have good catalytic capability toward ORR in neutral media. When applied in MFCs, the performances of PDDA-SCNT and PEPUSCNT were quite comparable to Pt/C. Noticeably, PEPUSCNT-based MFCs produced 72% as much power as that of Pt-based MFCs. With simple preparation, low cost and good catalytic capability, we believe that the polyelectrolyte-SCNT composite will be a promising category of MFC cathode catalysts that are worthy of further investigation.

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