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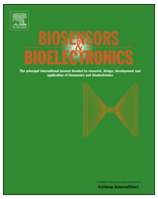

Manganese cobaltite/polypyrrole nanocomposite-based air-cathode for sustainable power generation in the single-chambered microbial fuel cells☆

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ABSTRACT

Manganese cobaltite nanorods ($MnCo_2O_4$ NRs) were prepared and tested as potential air-cathode catalyst for the single-chambered microbial fuel cells (sMFC). The power generation of sMFC increases with $MnCo_2O_4$ NRs loading to the cathode. The Polypyrrole (PPy) and Vulcan XC were used as conducting support to the $MnCo_2O_4$ NRs to form composites either by *in situ* or by mechanical mixing in the cathode fabrication. The cyclic voltammetry, linear sweep voltammetry and electrochemical impedance studies reveal that the *in situ*-$MnCo_2O_4$ NRs/PPy composite has higher catalytic activity than that of mechanically mixed-$MnCo_2O_4$NRs/PPy composite because of higher interfacial contact between $MnCo_2O_4$ NRs and PPy. The maximum volumetric power density with *in situ*-$MnCo_2O_4$ NRs/PPy, mechanically mixed-$MnCo_2O_4$ NRs/PPy, $MnCo_2O_4$ NRs/Vulcan XC and catalyst-free (only Vulcan XC) cathode was measured to be 6.11, 5.05, 4.22, and 1.77 W/m^3, respectively, in the sMFC. This suggests that PPy is not only a better conducting support than that of conventionally used Vulcan XC but also the cathode composite fabrication process is important for enhanced performance. The synergetic effect of $MnCo_2O_4$ NRs and PPy was found to play an important role for the improved energy recovery and it could be applied as an efficient and inexpensive cathode catalyst for the sMFC.

1. Introduction

Air-cathode microbial fuel cells (MFC) draw much attention of researchers in recent years for the sustainable electricity generation from biodegradable wastes by utilizing electrochemically active bacteria (EAB) (Sevda et al., 2013; Raghavulu et al., 2012). A notable progress has been made on air-cathode MFC design with various engineering approaches (Sevda et al., 2013; Zhang et al., 2011). In order to minimize the internal resistance of air-cathode MFC, various membrane/cloth cathode assemblies (MCAs/CCAs) were developed (Li et al., 2011; Luo et al., 2013). However it has been observed that the performance of MFC is majorly limited by the cathode. Thus the cathode materials and their design are the most challenging aspects for developing an efficient MFC (Pandit et al., 2012). The sluggish oxygen reduction reaction (ORR), increased internal resistance due to hot-pressing of MCAs, and expensive manufacturing costs of MCAs are the important factors which restrict the practical application of MFC (Kim et al., 2007; Rismani-Yazdi et al., 2008). In order to accelerate ORR, a number of electroactive catalysts have been employed. The incorporation of noble metals catalysts such as Pt, Pd, Au, and Ag on cathode considerably decreases the activation energy barrier and improve the ORR kinetics (Zhou et al., 2011; Carpenter et al., 2012; Guo and Sun, 2012). However, the high cost and catalyst poisoning restrict their commercialization. The transition metals, metal oxides and metal complexes were tested as alternate low-cost ORR catalyst to Pt with limited success (Zhou et al., 2011; Ahmed et al., 2012; Wang, L. et al., 2011; Wang, S. et al., 2011; Roche et al., 2009; Zhao et al., 2005).

Further to avoid the bottlenecks associated with hot-pressing process, researchers have employed different means of fabricating MCAs. In particular, Zuo et al. developed a tubular MCA by coating a tubular ultrafiltration membrane with graphite paint and non-precious metal (Zuo et al., 2007). Zhuang et al. constructed a low-cost membrane-less CCA by coating a canvas cloth with nickel-based or graphite-based paint and MnO_2 (Zhuang et al., 2009). Recently, mixed valence transition metal oxides with spinel structures of formula AB_2O_4 attract attention as electrocatalysts for ORR due to their conducting/semiconducting nature (Xu et al., 2012;

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Wu et al., 2012). The spinels with two different 3d-metal ions at A and B are reported to show improved catalytic activity, selectivity, stability and resistance to poisoning in a number of catalytic/electrocatalytic processes, such as ORR, and oxidation of CO and hydrocarbons (Hamdani et al., 2010; Liang et al., 2012). Among the transition metal spinels, partially substituted cobalt spinel has been studied extensively as electrocatalyst because of its low cost, simple preparation and high stability. Manganese cobaltite ($Mn_xCo_{3-x}O_4$) has been used as ORR catalyst because of its ability to provide donor–acceptor chemisorption sites for the reversible adsorption of oxygen for ORR (Restovic et al., 2002). But poor electrical conductivity is a major drawback of spinel which reduces the electrochemical performance. Therefore, conducting support such as activated carbon has been used to improve its electrochemical activity. Polypyrrole (PPy) is a well-known conducting polymer with good conductivity and stability along with easy preparation (Yuan et al., 2013). Recently, PPy has been used as efficient catalyst support in several electrochemical processes (Mohana Reddy et al., 2008). The unique electronic structure of PPy reduces the ORR activation energy by enhancing oxygen adsorption on its surface (Khomenko et al., 2005). Thus the combination of manganese cobaltite and PPy can be a better performing ORR catalyst for the MFC.

In the present study, we focused on three important aspects of the air-cathode electrode. First, the as-synthesized manganese cobaltite nanorods ($MnCo_2O_4$ NRs) supported on PPy matrix has been evaluated as potential cathode material for the sMFC and its performance is compared with benchmark Pt/C. Second, the role of PPy as a catalyst support is compared with traditional Vulcan XC in the sMFC. Finally, the effect of blending technique (mechanical mixing *vs. in situ* blending) of catalyst dispersion in the PPy support matrix is studied.

2. Material and methods

2.1. Chemicals

Pyrrole (99%) was obtained from Sigma Aldrich. Manganese chloride ($MnCl_2 \cdot 4H_2O$), cobalt chloride ($CoCl_2 \cdot 6H_2O$), hydrochloric acid (HCl) (35% v/v), ammonium fluoride (NH_4F), urea ($CO(NH_2)_2$), ammonium persulfate ($(NH_4)_2S_2O_8$), cetyltrimethylammonium bromide (CTAB) and all other required chemicals were purchased from Merck (India) and used without further purification.

2.2. Synthesis of $MnCo_2O_4$ NRs and PPy

$MnCo_2O_4$ NRs were synthesized using a simple template-free hydrothermal process followed by calcination. In a typical synthesis, 10 mL of each 0.1 M $MnCl_2 \cdot 4H_2O$, 0.2 M $CoCl_2 \cdot 6H_2O$, 0.6 M $CO(NH_2)_2$ and 0.2 M NH_4F solutions were mixed one by one with continuous stirring. The resulting mixture was then transferred to a 50 mL Teflon-lined stainless steel autoclave and heated at 130 °C for 6 h in a muffle furnace. Subsequently the furnace was cooled to room temperature naturally and precipitate formed inside the container was collected by centrifuge. The precipitate was first washed with distilled water several times followed by ethanol and dried at 70 °C for 6 h. The dried precipitate was calcined at 400 °C in air for 2 h.

PPy was synthesized by oxidative polymerization of pyrrole at room temperature. In a typical polymerization, 364 mg CTAB was dispersed in 80 mL 1 M HCl by sonication. Then 0.14 mL of pyrrole monomer was added to the solution with constant stirring. Polymerization was initiated by adding 20 mL 1 M HCl containing 570 mg $(NH_4)_2S_2O_8$. The resulting mixture was stirred for 12 h. The product formed was centrifuged and washed with 1 M HCl, distilled water and ethanol. Finally, washed precipitate was dried at 60 °C for 6 h.

2.3. Synthesis of $MnCo_2O_4$ NRs/PPy and $MnCo_2O_4$ NRs/Vulcan XC composite

$MnCo_2O_4$ NRs/PPy composite was synthesized either *in situ* or by mechanical mixing. The *in situ*-$MnCo_2O_4$ NRs/PPy was synthesized by polymerization of pyrrole in presence of $MnCo_2O_4$ NRs. 100 mg of $MnCo_2O_4$ NRs was dispersed in 80 mL 1 M HCl and sonicated for 20 min. Then 0.14 mL monomer solution was added and stirred for another 30 min. Rest of the procedure remain same as the PPy synthesis. The mechanically mixed $MnCo_2O_4$ NRs/PPy (m-$MnCo_2O_4$ NRs/PPy) composite was prepared by ultrasonically mixing $MnCo_2O_4$ NRs (100 mg) with PPy (150 mg) in acetone and 10 wt% Nafion™ suspensions (Aldrich). The $MnCo_2O_4$ NRs/Vulcan XC composite was prepared in the same way as that of m-$MnCo_2O_4$ NRs/PPy by replacing PPy with Vulcan XC.

The details on catalyst characterization, MCA preparation, and MFC operation are presented in the Supplementary material (SI).

3. Results and discussion

3.1. Morphology and crystal structure of the catalysts

The surface morphology of the as-synthesized samples was analyzed by the field emission scanning electron microscope (FE-SEM) and shown in Fig. 1. Fig. 1(a) shows the flower-like spherical structures with diameter 3–6.5 μm. The magnified FE-SEM image [inset Fig. 1(a)] clearly indicates that these flower-like structures are assembled of $MnCo_2O_4$ NRs with an average diameter of ~65 nm and length 0.6–1 μm. The magnified images reveal that $MnCo_2O_4$ NRs are consisted of interlinked particles forming one-dimensional nanostructure, as confirmed by transmission electron microscopy (TEM). The FE-SEM image [Fig. 1(b)] of as-synthesized PPy shows 80–160 nm diameter agglomerated particles.

Microstructural analysis of as-synthesized samples was carried out by the TEM. Fig. 1(c) represents a TEM image of $MnCo_2O_4$ NRs with 30–80 nm diameter matching FE-SEM result. It clearly reveals that NRs are formed by regular interconnection of nanoparticles of size < 50 nm. A lattice resolved high-resolution TEM (HRTEM) image [inset Fig. 1(c)] shows an average d-spacing of 0.465 nm corresponding to (111) planes and crystalline nature of particles. Fig. 1(d) displays a TEM image of as-synthesized PPy showing agglomeration of spherical particles of size 90–200 nm. The TEM images of *in situ*-$MnCo_2O_4$ NRs/PPy composite [Fig. 1(e)] show the uniform distribution of $MnCo_2O_4$ NRs in the PPy matrix and $MnCo_2O_4$ NRs are coated well with PPy. However, such well dispersion of $MnCo_2O_4$ NRs in the PPy matrix was not found in the m-$MnCo_2O_4$ NRs/PPy composite as shown in Fig. 1(f). The crystal structure of as-synthesized $MnCo_2O_4$ NRs, PPy and their composites was further analyzed by X-ray diffraction and presented in Fig. S1 of Supporting material (SI).

3.2. Electrochemical ORR activity and charge transport property of composite electrodes

Electrocatalytic activity towards ORR was evaluated by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Two different intercompeting mechanisms were proposed for ORR (Lu et al., 2011). Molecular oxygen can be directly reduced to hydroxyl ion by an efficient 4-electron reduction path (Eq. (1)). However the less efficient 2-electron reduction path involves two steps and produced hydrogen peroxide ion (HO_2^-) as an intermediate (Eq. (2))