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Electrospun carbon nanofibers from polyacrylonitrile blended with activated or graphitized carbonaceous materials for improving anodic bioelectrocatalysis

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HIGHLIGHTS

- Activated carbon or graphite was blended in polyacrylonitrile to prepare carbon nanofibers (CNFs).
- Such blends increased specific surface area and porosity in resulting CNFs.
- Bioelectrocatalytic current generation was improved with these CNF electrodes.
- Using such blends in precursors can be a viable strategy for making efficient CNF electrodes.

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ABSTRACT

The electrospun carbon nanofibers obtained from polyacrylonitrile (PAN) and PAN blends with either activated carbon (PAN-AC) or graphite (PAN-GR) were tested as anodes using *Shewanella oneidensis* MR-1. Extensive physico-chemical and electrochemical characterization confirmed their formation, their fibrous and porous nature, and their suitability as electrodes. N_2 adsorption measurements revealed high specific surface area (229.8, 415.8 and 485.2 $m^2\ g^{-1}$) and porosity (0.142, 0.202 and 0.239 $cm^3 g^{-1}$) for PAN, PAN-AC and PAN-GR, respectively. The chronoamperometric measurements showed a considerable decrease in start-up time and more than a 10-fold increase in the generation of current with these electrodes (115, 139 and 155 μA cm^{-2} for PAN, PAN-AC and PAN-GR, respectively) compared to the graphite electrode (11.5 μA cm^{-2}). These results indicate that the bioelectrocatalysis benefits from the blending of PAN with activated or graphitized carbonaceous materials, presumably due to the increased specific surface area, total pore volume and modification of the carbon microstructure.

1. Introduction

The exploration of microorganisms to enable oxidation and reduction reactions at electrodes has led to the development of highly versatile microbial bioelectrochemical system (BES) technologies that have gained remarkable and widespread attention in recent decades. These systems exploit the extracellular electron transfer (ET) capabilities of microbes at the anode or at the cathode to carry out a particular process (Patil et al., 2012a). Microbial fuel cells (MFCs), the leading example of such systems, principally utilize microorganisms at anodes that oxidize organic substrates to generate electricity (Rabaey et al., 2010). The feasible electrical current driven biochemical or fuel production using either microbial or chemical catalysis at cathodes has further widened the opportunities for such systems (Rabaey and Rozendal, 2010). The BES technologies have been proposed to possess potential for several applications ranging from energy recovery from wastewater, bioremediation, desalination, metal recovery to the production of reduced products, such as multicarbon compounds, hydrogen, and methane (Logan and Rabaey, 2012).

Along with several other parameters, the ability of microbes to respire using anodes, to form biofilms, their metabolism and ET rates at anodes mainly determine the overall performance of BESs like MFCs. New microbial catalysts and enrichment or improvement of microorganisms able to respire at anodes have been extensively tried (Rabaey et al., 2010). Development of biocompatible electrode materials with high surface area and stability that can facilitate the maximum growth of bacteria and enhance the ET rates has been another important strategy to increase the bioelectrocatalytic performance. Several carbon-based materials such as graphite rod, carbon paper, carbon cloth, carbon felt, carbon mesh

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and reticulated vitrified carbon have been used as anodes in MFCs (Zhou et al., 2011). Improvement in MFC performance via altering electrode surface properties by surface treatment procedures, such as ammonia treatment (Cheng and Logan, 2007), heat and acid treatment (Feng et al., 2010), using carbon nanotubes (Peng et al., 2010), or by adding functional groups (Picot et al., 2011; Yuan et al., 2011), or mediated and conductive polymers (Patil et al., 2012b) has been achieved. In addition, the approach of increasing the active surface area by means of using brush (Logan et al., 2007), macroporous sponge (Xie et al., 2012), microchannelled (Katuri et al., 2011) and three-dimensional (3D) fiber (Chen et al., 2011a,b; He et al., 2011; Zhao et al., 2010) electrodes has delivered promising results. Although most of these strategies have resulted in the improvement of microbe–electrode interactions and thus the ET rates, the use of highly porous carbon-based fiber materials has demonstrated the most encouraging results (Chen et al., 2011b). Carbon nanofiber (CNF) materials are of great interest due to their high aspect ratio, large specific surface area, high temperature resistance and good electrical or thermal conductivities, encompassing fascinating properties for catalyst carriers, electrochemical probes, energy storage electrodes, supercapacitors, height temperature filters and adsorbents (Arshad et al., 2011; Ding et al., 2010; Saito et al., 2011). The atomic structure of a carbon fiber is similar to that of graphite, consisting of carbon atom layers (graphene sheets) arranged in a regular hexagonal pattern. Depending on the precursors and the manufacturing processes, the layer planes in the carbon fibers may be either turbostratic, graphitic or of a hybrid structure. Due to the high content of delocalized π electrons and parallel alignment of graphene layers along the fiber axis, carbon fibers show good electrical conductivity in the fiber direction (Huang, 2009).

CNF materials can be produced from a variety of precursors such as polyacrylonitrile (PAN), pitch, rayon, polybenziimidazole and lignin (Huang, 2009). The conventional synthetic strategies for CNF materials, that include the substrate method and vapor growth method, are known to be very complicated and economically the least viable. Comparatively, electrospinning has been shown to be a simple and versatile technique for the preparation of carbon fiber materials. It relies on repulsive electrostatic forces to draw any solution or melt of optimal viscoelasticity into nanofibers (Teo and Ramakrishna, 2006). The continuous nature of nanofibers obtained with electrospinning offer easy handling and a high specific surface area compared to the fibers obtained from a conventional spinning method (Li and Xia, 2004). Due to their conductive, porous and fibrous features, electrospun CNFs are considered as suitable supports for the growth and immobilization of electroactive bacteria. However, quite a few studies have been focused on employing such materials as anodes in MFCs and the influence of using carbonaceous components in precursor solutions while preparing such materials on their characteristics and bioelectrocatalysis has been scarcely reported (Chen et al., 2011b).

It has been generally accepted that the quality of the high performance electrospun CNF mat depends mainly on the composition of the precursors and the processing conditions. However, the physical and chemical structural transformations that take place during heat treatments are extremely complicated. Therefore, it is difficult to predict the way to effectively improve the performance of the resulting carbon fibers. Nevertheless, one approach to address these issues is to use different precursors and to directly compare the evolution of the structural features and the properties of the resulting fiber materials. In this paper, we report the fabrication of carbon fiber materials as a function of precursor solution composition and their use as anodes for BES applications. PAN was chosen as the spinnable polymer for the three precursor solutions (PAN, activated carbon + PAN and graphite powder + PAN) because of its wide use predominantly due to its high carbon yield (Nataraj et al., 2012). Several physico-chemical properties of the resulting fiber materials were analyzed. For investigating the performance of the CNF materials as anodes, a metal-reducing and well-known exoelectrogen bacterium, *Shewanella oneidensis* MR-1 was used as a model microbe in this proof-of concept study. The bioelectrocatalytic performance was monitored with semi-batch, chronoamperometric (CA) experiments and the current was normalized with projected surface area of the respective materials. In addition, scanning electron microscopy (SEM) was used to get insights into the structure and morphology of these materials.

2. Experimental

2.1. General

If not mentioned otherwise, all chemicals with either research or analytical grade were purchased from Sigma–Aldrich and Merck. The microbial growth medium and other aqueous solutions were prepared in water purified and deionized (18 MΩ) with a Milli-Q system (Millipore, Bedford, MA, USA). The potentials provided in this article refer to the Ag|AgCl (sat. KCl) reference electrode. All bioelectrochemical experiments were performed under sterile and anoxic conditions.

2.2. CNF preparation and characterization

PAN (Mw = 150000) purchased from Sigma Aldrich Chemical Co was used as the spinnable polymer for all precursor solutions. Activated carbon (AC) and graphite (GR) were purchased from BDH Chemicals Ltd (Product 33032, Poole, England) and Jencons Scientific Limited (Product H147/2/290, Berdfordshire, England) respectively. Three different precursor solutions – (1) 10 wt.% PAN, (2) 1 wt.% AC + 10 wt.% PAN and (3) 1 wt.% GR + 10 wt.% PAN were prepared in *N*,*N*-dimethylformamide (DMF) to obtain three different carbon fiber materials denominated as PAN, PAN-AC and PAN-GR, respectively. After gentle stirring at room temperature for 24 h, these solutions were loaded into a 25 mL polypropylene syringe equipped with a stainless steel needle that was connected to the anode of a high voltage power supply. The conditions employed for electrospinning were of the order; 20 kV applied voltage, 15 cm tip to collector distance and a flow rate of 0.5 mL h^{-1}. A grounded stainless steel plate wrapped with aluminum foil was employed as the collector. The electrospun nanofibers after collecting for a sufficient time to get a thick sheet (see Fig. S1 in SI) were cut out and sandwiched between two graphite sheets (Fig. S2(A) in SI). They were stabilized in air at 230 °C, carbonized at 500 °C in N_2 and further heated to 1000 °C in N_2 to complete carbonization and initiate activation. The stages involved in the formation of CNFs are shown in Scheme S1 in SI (Nataraj et al., 2012).

The extent of carbonization was determined by investigating the disappearance of the characteristic functional groups of PAN using a Perkin Elmer Spectrum 100 ATR-FTIR (Attenuated total reflectance-Fourier transform infra red) spectrometer (Shelton, Connecticut, USA). The elemental composition was obtained by using a Vario Elementar Microcube EL111 (Hanau, Germany). The specific surface area and porosity of all these materials were determined by N_2 adsorption measurements using an ASAP2400 Micromeritics (Atlanta, GA, USA). Before the measurements, these materials were degassed at 400 °C for 24 h under vacuum. The fiber diameter in resultant electrospun carbon materials was measured using scandium software (Münster, Germany). Cyclic voltammetry (CV) was also recorded to study the electrochemistry of these materials using 5 mM $K_3Fe(CN)_6$ prepared in 100 mM KCl buffer at a scan rate of 50 mV s^{-1}. For SEM details see Section 2.5.