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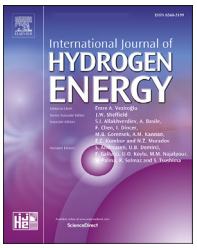

Short Communication

Boosting power density of microfluidic biofuel cell with porous three-dimensional graphene@nickel foam as flow-through anode

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ABSTRACT

Microfluidic microbial fuel cells (μMFC) combine the microfluidic technology and bio-catalysts anchored at the electrode, representing an emerging bio-power generator. However, a major challenge towards further development is their low bio-catalysts loading on the electrodes. Previous researches have revealed the bio-electrode structure and nutrient-feeding type play a significant role in the power generation of μMFC. In this study, we fabricate a membrane-free μMFC with a piece of graphene-decorated nickel mesh as bio-anode, which is fed in a flow-through manner. The scanning electron microscopy and pore-distribution variation analysis show the mixed bacteria grow densely on the surface of the electrode. Benefited from the enriched bacterial colonization and sufficient nutrient supply, the μMFC produces a remarkably high areal power density of 1.11 W m^{-2} at a current density of 2.15 A m^{-2}. These values are substantially higher than those of conventional two-dimensional electrodes and flow-over architectures measured under the same condition.

Introduction

Numerous investigations have resulted in some novel micro-electro-mechanical systems (MEMS) and applications based on micro-scale energy harvesting accessories; examples include piezoelectric, electrostatic and electromagnetic micro harvesters, micro batteries, super capacitors and fuel cells [1–4]. Among the increasing number of studies on micro-scale energy harvesters, several research groups have made tremendous efforts in developing biofuel cells at the micro-scale, such as miniature microbial fuel cells and enzymatic fuel cells [5–8].

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Micro-sized biofuel cells exploit pure enzyme or electrochemically active bacteria (EAB) as catalysts to oxidize the fuel, and deliver the electrons stored in organic matters. Commonly-utilized biocatalyst in these devices include glucose oxidase (GO_x) [9], lactate oxidase (LO_x), *Geobacter sulfurreducens* [10], *Shewanella oneidensis* [11], *Escherichia coli* and mixed communities (*e.g.*, activated sludge) having two or more exoelectrogenic bacteria [5,12]. Compared to noble metal catalysts (*e.g.*, Pd, Pt), biocatalysts served in biofuel cells show a superiorly economic competitiveness and an ultrahigh selectivity at ambient temperature [13]. Since the first demonstration of microchip-based biofuel cell in 2005 [14], it has successfully achieved a prolonged working time and substantially high cell performance [15]. Nevertheless, the low biocatalysts loading onto the electrodes and sluggish substrate transportation interior the electrodes are two major issues that obstruct micro-sized biofuel cells to compete with other miniature power sources [16].

Recently, developing of functional bio-electrodes and novel reactant flow pattern that could facilitate biocatalyst attachment are closely tied to enhance the power output of micro-sized biofuel cells. For example, Yang et al. proposed a micro-channel with multiple anolyte inlets to decrease the distance that the reactant transfers [12]. Benefitting to a sufficient substrate supply, the microfluidic flow channel equipped with multi-inlet allowed the growth of more uniform and denser bacterial communities across the whole anode surface. In another case, the bio-hazardous catholyte will unfavorably contact the bio-catalysts due to the improper structure design, decreasing or even suppressing the bio-catalytic activity. A diverging channel was constructed to ease the issue of catholyte poisoning to the biofilm due to the broadened crossing-over distance. It observed an enhanced bio-communities distribution at the mid-posterior ports, and obtained a 24% enhancement in power density output [17]. Besides actively dealing with the reactant flow pattern, three-dimensional (3D) architecture providing large amount of macro-pores is another efficient approach to facilitate the biocatalysts attachment and substrate transportation interior the electrode. For example, a porous nickel plate housed *Escherichia coli* to decompose the human excreta for power generation. The plate was manufactured to 1 mm in width, 50 mm in length and 0.5 mm in thickness, and glued to the anode chamber. The open-porous structure supplied express panels for the transportation of electron shuttles and even ions. A maximum power density of 104 W m^{-3} was observed under a continuous feeding mode [18]. In this view, nanomaterials like carbon nanotubes (CNTs) and graphene have been recently explored to decorate the 3D electrodes. The use of nanomaterials is hopeful to increase the accessible area for electron/ion transfer between biocatalysts and electrodes. In a previous work, we introduced the 3D nickel foam by coating with graphene monolayers, and demonstrated the electrode was amenable to mixed bacteria colonization [5]. Ren et al., also fabricated a similar 3D graphene scaffold by chemical vapor deposition (CVD) on a nickel template, but further etched the nickel metal to form a fully carbonaceous structure [19]. The bioanode showed a gradient pore-distribution, and could accommodate large amounts of bio-catalysts and enhance the mass transfer compared to those of flat structures (*i.e.* two-dimensional electrodes such as carbon paper, carbon cloth and graphite plate). The μMFC equipped with this anode delivered a record power density of 11,220 W m^{-3} and current density of 31,040 A m^{-3}. Therefore, clever design of porous anode structure and advanced fluid control give it many advantages to improve the power output.

In this work, we fabricated a membrane-free μMFC with a piece of graphene-decorated nickel mesh (denoted as rGO@Ni) as bio-anode. The membrane-free design removed the capital cost, internal resistance and unsuitable pH gradient related to the physical membrane. The mixed bacteria grew densely on the surface of the rGO@Ni, and the nutrient was continuously fed in a flow-through manner (denoted as 3D-FT@μMFC). The type of fuel cell produced a remarkably high areal power density of 1.11 W m^{-2} at a current density of 2.15 A m^{-2}, calculated based on the electrode surface area. The cell performance is substantially enhanced compared to those of flat electrodes and flow-over architectures measured under the same condition.

Materials and methods

We fabricated a membrane-free μMFC with a piece of graphene-decorated nickel mesh (denoted as rGO@Ni) as bio-anode (see the details in the ESI†). The fabrication process of rGO@Ni was prepared as the previous procedure [20,21]. The mixed bacteria grew on the surface of the rGO@Ni, and the nutrient was continuously fed in a flow-through manner (denoted as 3D-FT@μMFC), as showed in Fig. 1. Detailed materials and methods could be found in the electronic supporting information (ESI†).

Results and discussion

The 3D-FT@μMFC was inoculated with mixed bacteria in a continuous feeding mode. The current across the external resistance was collected to monitor the bacterial growth during the inoculation process, *i.e.* growth curve. Two parallel inoculation processes for 3D-FT@μMFC were showed in Fig. 2. A lag phase lasted for 12–15 h followed by a drastic increasing of current output was observed for the two inoculation processes. The exponential time for the 1st trial began from 15.5 h

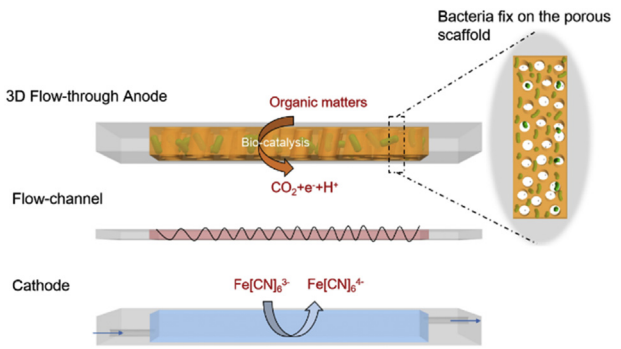

Fig. 1 – Schematic illustration of working principles of 3D-FT@μMFC.

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