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Early-stage performance evaluation of flowing microbial fuel cells using chemically treated carbon felt and yeast biocatalyst

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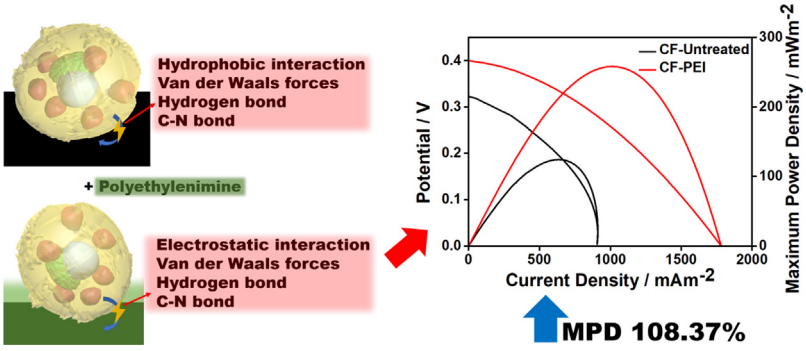
HIGHLIGHTS

- Yeast and chemically treated CF effects on MFC performance are investigated.
- CdbndO/CsbndN dangled on CF-PEI are key bonds for performance enhancement.
- Pi-pi bond conjugation and lone electron pair induce performance enhancement.
- High yeast growth rate and optimal yeast growing time are determined.
- MPD of MFC using CF-PEI is 256.3 mW m^2.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of closed-loop flowing-type microbial fuel cells using differently pretreated carbon felts is measured. Yeast cultivated from *S. cerevisiae* is used as biocatalyst, while glucose is the substrate. For the pretreatment of felt, acetone, nitric acid, and polyethyleneimine are employed. First the optimal conditions for yeast cultivation are quantitatively determined. As a result, a high yeast growth rate (1.083 h^{-1}) and the optimal yeast growing time (48 h) for cell tests are obtained. The differently pretreated felts are analyzed by X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy and optical microscopy. Conductivity, charge transfer resistance, and CdbndO and CsbndN groups dangled on the felt are crucial parameters determining the performance of the microbial fuel cell. Particularly, the conjugation effects of pi-pi bonds and lone pairs facilitating the attachment of yeast to the CdbndO and CsbndN groups on the carbon felt promote (i) mutual adhesion between them and (ii) growth of yeast on CF-PEI. This correlation is confirmed by optical analysis of the felts after the cell tests. To evaluate the early-stage performance of the microbial fuel cells using the different felts, polarization curves are measured. In the measurements, the maximum power density of the cells depends on the superficial state of felts, while the performance of the cell using the PEI-treated felt is best, at 256.3 ± 11.5 mW·m^{-2}. These data match other results attained by pretreatments.

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1. Introduction

Microbial fuel cells (MFCs) are a fascinating technology that can achieve both energy extraction from low-grade biomasses and remediation of wastewaters, derived from a large variety of human and industrial activities [1], and the solid fraction of organic waste [2]. Over the last decade, MFCs have been used to harvest energy not only from derivatives of sugar [3], oilfield waters [4], urban wastewaters [5], and rice mill wastewater [6] but also dairy and slaughterhouse wastewaters [7], swine [8], azo dye residues [9] and composite food waste [10]. Moreover, these bio-electrochemical systems (BESs) can efficiently exploit sunlight [11,12], be incorporated in constructed ecosystems [13] and detect glucose levels [14] due to the strict correlation between their electrochemical and electrical behaviors [15]. An interesting and recent trend is using microbial electrolysis cells (MECs) for biohydrogen generation [16], solid waste valorization [17], bioremediation [4], and production of other valuable chemicals from solid waste and food waste [18–20].

However, in spite of such remarkable progress, there are still limitations to be addressed, such as reproducibility, standardized performance and real economic feasibility [21–24]. Particularly, the economic profitability of MFCs depends on (i) finding cost-effective electrode and membrane materials to promote the generation of electricity without using precious and expensive metals and (ii) minimizing the time-to-power production, i.e., the time required from electrode pretreatments, start-up, to electricity generation. These points play a key role in determining whether the MFCs can replace other competitive wastewater treatment technologies because long-term operations can be achieved by periodic substitution of the substrate and anolyte, but reducing the time-to-power of MFCs is currently underestimated or reported to a limited extend [25,26].

For example, Alatrakcthi et al. [27] achieved a power density of 374.9 $mW{\cdot}m^{-2}$ after two consecutive batch operations of several days using an expensive anode with gold nanoparticles. LaBarge et al. [28] studied the pre-acclimation steps of bog sediments in MECs to produce methane and a useful gas evolution was achieved only after 4–7 cycles (total time of 60–80 days), with granular activated carbon and an expensive ruthenium foil as electrodes. Liang et al. [29] reported power densities of 600–1200 $mW{\cdot}m^{-2}$ when an intermittent switch on/off regulation procedure was applied to the MFCs using a reduced graphene oxide (rGO)/MnO_2 anode and a high concentration of sodium acetate as substrate. Zhang et al. [30] demonstrated that the current obtained at the start-up of their MFC was dependent on even low applied resistances to biofilm formation at an early stage. The time-to-power was always approximately 5–6 days and they did not mention the effects of different anode materials. Later, they [31] reported a similar study using a continuous-flow MFC and various external resistances and concluded that biofilm distribution due to anolyte flow could improve the start-up performance. Recently, Paitier et al. [32] demonstrated that another limiting factor for the start-up and biofilm establishment is the presence of competing microbial communities and with different strains the time-to-stable-power was 10–20 days and power density of these MFCs could be only maintained for a short interval without a fresh substrate.

Therefore, reducing the start-up and acclimation time is required, and the parameters that determine them should be effectively managed to improve the feasibility in real scale applications. To alleviate the slow procurement issue of starting inoculum, yeast can be considered as a fast-growing inoculum. Differently from the bacteria used in the above-mentioned works, yeasts have short growing periods, are time-saving and in dried form can be stored under soft conditions for a very long time. In prospect, for real and large scale applications, this is a competitive advantage because it makes yeasts “ready-to-use”, easy to stock and transport, unlike some bacteria strains, giving to yeasts a high potential for practical exploitation in biotechnology processes [18].

In fact, yeasts have been already used in many real applications as for example in biofuel production from residual biomass [20], bio-hydrogen evolution from fermentation of agro and industrial wastes and sugar oxidation [33–35]. Even for MFCs, yeast has facilitated extracellular electron transfer, and in particular, *Saccharomyces cerevisiae* is a robust, fast-growing, facultative anaerobe, non-pathogen and temperature tolerant biocatalyst that is mainly employed in mediated MFCs [36–39] or membraneless MFCs [40]. It is also notable that in case of oxygen infiltration, biological contamination or accidental increase in temperature, *S. cerevisiae* can survive at a higher rate without sudden stoppage, although it is not the most powerful exo-electrogenic biocatalyst due to its low open circuit voltage (OCV) of approximately 0.3–0.4 V [41]. It is therefore thought that its electron transfer mechanism should be promoted by using genetic engineering [42] or surface modification of electrodes [43], with further improvements in power and electricity production.

Recently, the use of layer-by-layer and physical immobilization techniques of the biocatalyst has been an effective approach to promote the interaction between electrode surface and biocatalyst [44–46]. According to Zhu et al. [47], a multistep CF treatment of 6–7 days was proposed to functionalize carbon felt fibers. Despite the long pretreatment, the start-up data were not clearly mentioned and after the start-up the time needed for acquiring stable power was 200–250 h. Hidalgo et al. [48] proposed two surface modifications based on (i) a nitric acid treatment and (ii) in situ polyaniline deposition. However, even in this case, the benefits attained by the use of nitric acid and polyaniline should be better clarified because the glucose concentration was too high (60 $g{\cdot}L^{-1}$) and the OCV of MFC was still low, and its power density decreased after 24 h. Consequently, electrode modification is another critical factor to improve the early-stage performance of MFCs and carbon felt (CF) is mainly used as a supporting material of the electrode for MFCs, but pretreatments are necessary before use. Therefore, more efforts are required to further develop effective and easy surface modification methods to advance the feasibility and convenience of yeasts as biocatalyst in MFCs.

Unlike the abovementioned studies, in this work, we report a complete analysis including results from preparation of treated felts, physical and chemical characterization using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS), optical contact angle (OCA) measurement, and pH-grow curve of biocatalyst to quantify the optimal conditions for yeast cultivation. Afterward, real application of the proposed treatments is demonstrated with a new closed-loop flowing-type MFC system using the three different one-step pretreated CF electrodes and polarization, power curves, OCV, maximum power density (MPD) are reported to compare the performances. Yeast from *S. cerevisiae* and glucose are the biocatalyst and substrate, respectively. The effects of modifications of the carbon felt electrode on surface chemistry after full cell tests are characterized using XPS and digital optical microscopy (DOM), while the increase in immobilized yeast due to the treatments is measured in terms of dry biomass before and after use in anodes.

2. Materials and methods

2.1. Carbon felt treatments

The carbon felt (XF30A–3.5T) was purchased from Toyobo (Osaka, Japan). Polyethyleneimine (PEI) (50% w/v) was purchased from Sigma Aldrich (St. Louis, USA). Acetone (C_3H_6O, 99.7%) was from Samchun Chemicals (Gyeonggi-do, Korea). Nitric acid (HNO_3, 60% w/v) was purchased from Matsunoen Chemicals (Osaka, Japan).

Three different surface treatments of CF were initially implemented. The CF was modified using acetone, nitric acid, or PEI. An untreated carbon felt was also used as control. The CF samples that had an active area of 2 × 2 cm^2 were immersed in acetone (99.7% w/w), nitric acid (10% v/v), or PEI (5 $mg{\cdot}mL^{-1}$) for 3 h at room temperature. Afterward, all carbon felts were washed with deionized (DI) water until a neutral