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# Boosting current generation in microbial fuel cells by an order of magnitude by coating an ionic liquid polymer on carbon anodes

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ABSTRACT

Microbial fuel cells (MFCs) have attracted great attentions due to their great application potentials, but the relatively low power densities of MFCs still hinder their widespread practical applications. Herein, we report that the current generation in MFCs can be boosted by an order of magnitude, simply by coating a hydrophilic and positively charged ionic liquid polymer (ILP) on carbon cloth (CC) or carbon felt (CF). The ILP coating not only can increase the bacterial loading capacity due to the electrostatic interactions between ILP and bacterial cells, but also can improve the mediated extracellular electron transfer between the electrode and the cytochrome proteins on the outer membrane of *Shewanella putrefaciens* cells. As a result, the maximum power density of a MFC equipped with the CF-ILP bioanode is as high as 4400 ± 170 mW $m^{-2}$, which is amongst the highest values reported to date. This work demonstrates a new strategy for greatly boosting the current generation in MFCs.

## 1. Introduction

Microbial fuel cells (MFCs) are capable of generating electrical energy from organic matters by capitalizing on the metabolic and respiratory processes of special microbial species on electrodes (Logan, 2009; Logan et al., 2006; Tender et al., 2002; Xie et al., 2015; Zhao et al., 2009). MFCs have great application potentials in the fields of energy, environment, medicine, and sensor (Bond et al., 2002; Forrestal et al., 2012; Liu et al., 2004; Lovley, 2006; Yang et al., 2015a). Currently, the relatively low power densities of MFCs still hinder the widespread practical applications. Generally, the power density of a MFC is strongly dependent on the current generation of the bioanode. The bacterial loading capacity and extracellular electron transfer at the bioanode play important roles in the performance of the bioanode (Qiao et al., 2010). To increase the bacterial loading capacity, various three-dimensional (3D) macroporous materials, including 3D graphene-based electrodes, carbon foams, macroporous stainless steel, titanium-based ceramics electrode, and 3D conductive polymer film, have been fabricated and employed as anodes in MFCs (Chen et al., 2012; Massazza et al., 2015; Pocaznoi et al., 2012; Wang et al., 2015a; Xie et al., 2012a, 2012b; Yang et al., 2015b; Yong et al., 2012; Zhao et al., 2015). To improve the extracellular electron transfer between the attached microbes and the electrodes, various conductive polymers and nanomaterials have been modified on electrodes (Feng et al., 2010; Schroder et al., 2003; Tao et al., 2015; Zhang et al., 2015; Zhao et al., 2013a, 2010). Despite the great progress made in the past few years, the power densities of the reported MFCs are typically lower than 3000 mW $cm^{-2}$. Obviously, it is being a challenging task to efficiently boost the current density of the anode for improving MFC performance.

Ionic liquids have been modified on carbon nanotubes and graphene and used for MFC construction, but the power densities of these MFCs are still lower than 1100 mW $cm^{-2}$ (Wei et al., 2016; Zhao et al., 2013b). Ionic liquid polymers (ILPs) as a new type of polymer material can not only display the excellent properties of ionic liquids but also show the advantages of macromolecular architectures (Armand et al., 2009; Le Bideau et al., 2011; Yang et al., 2014). Recently, ILPs have been widely used as polymer electrolytes in electrochemical devices including supercapacitors and lithium ion batteries (Armand et al., 2009; Le Bideau et al., 2011; Yang et al., 2014). Although ILPs may provide a new opportunity to construct MFCs with high power densities, ILPs have not been used in the MFCs to date. Owing to the π-π stacking interaction between ILPs and carbon materials, ILPs can be facilely deposited on the surfaces of carbon materials during polymerization processes (Feng et al., 2013; Wu et al., 2009). Moreover, the process of ILP modification on the surfaces of carbon

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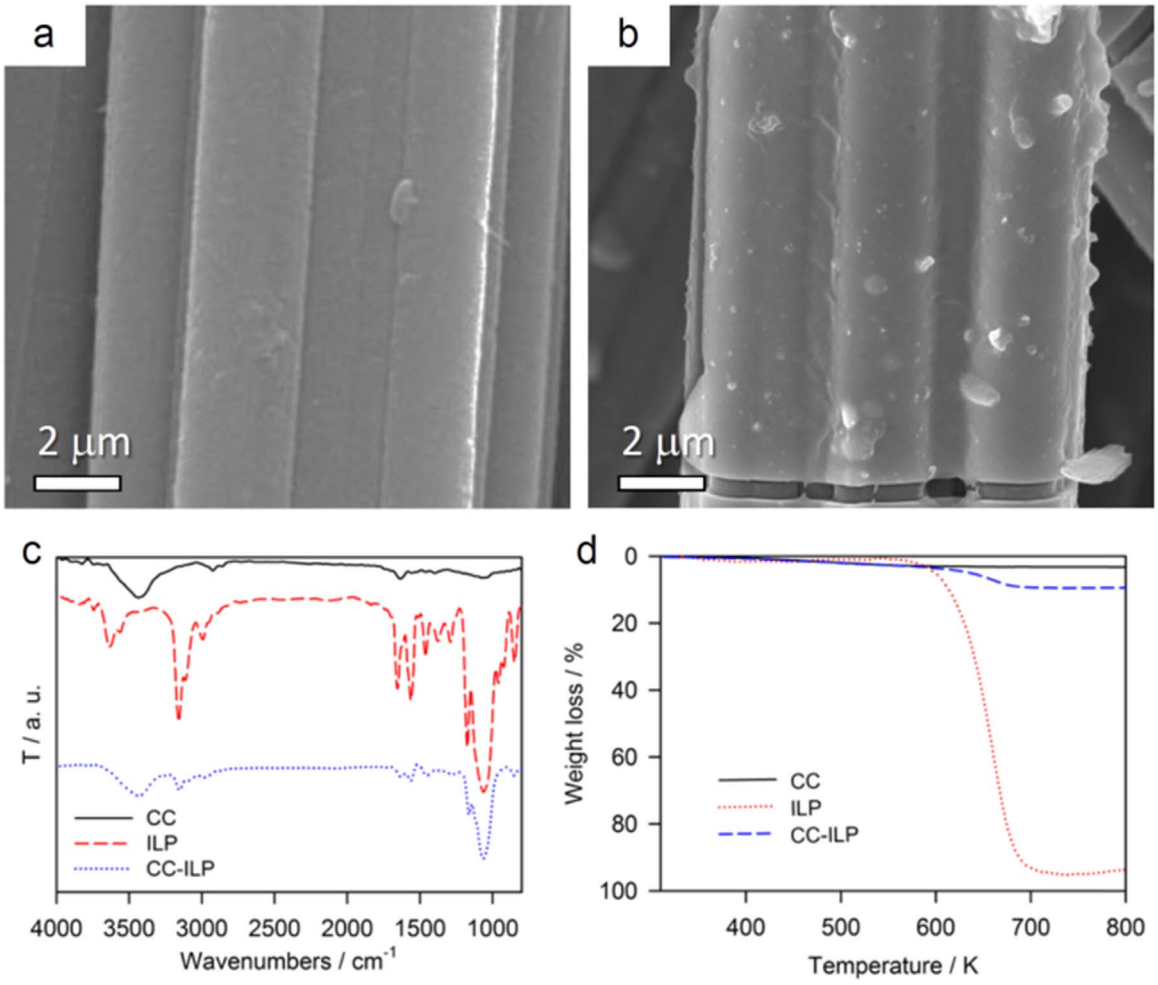


**Fig. 1.** SEM images of CC before (a) and after (b) ILP modification. FT-IR spectra (c) and TGA curves (d) of triturated CC, ILP, and CC-ILP.

materials was mild and environmental friendly, resulting in no structural damage to carbon materials (Wang et al., 2015b).

Herein, we report that the current generation in MFCs can be boosted by an order of magnitude, simply by coating an ILP on carbon anodes. Two base anode materials of different structural configurations were selected here, namely carbon cloth (CC) and carbon felt (CF). The ILP-functionalized carbon electrodes were prepared by one-step thermal-initiation free radical polymerization of 3-ethyl-1-vinylimidazolium tetrafluoroborate ([VEIM]$BF_4$) on CC and CF (Scheme S1). Water contact angle goniometry and Zeta potential measurement indicate the formation of a hydrophilic and positively charged ILP on electrode surfaces. The hydrophilic and positively charged electrode surfaces can increase the bacterial loading capacity due to the electrostatic interactions between ILP and bacterial cells. Moreover, the ILP coated on the carbon electrodes can greatly improve the mediated extracellular electron transfer between the electrodes and the cytochrome proteins on the outer membrane (OMCs) of *Shewanella putrefaciens* cells. As far as we are aware, it is the first example that the efficiency for the extracellular electron transfer is improved by coating a non-electrically conductive polymer on the anode, which is helpful for understanding the extracellular electron transfer in MFCs. Accordingly, the current generation at ILP-based biofilm electrodes (bacterial film modified electrodes) can be boosted by an order of magnitude. Structural configuration of electrode materials is also found to play a vital role in determining the system efficiency. Due to the synergetic effect of ILP coating and electrode structure, the current generation at CF-ILP bioanode is much higher than those at CC, CF, and CC-ILP bioanodes. The maximum power density of a MFC equipped with the CF-ILP bioanode is as high as $4400 \pm 170$ mW $m^{-2}$, which is amongst the highest values reported to date.

## 2. Experimental

### 2.1. Preparation of ILP-based electrodes

CC and CF were cut into designed shapes with length×width×thickness of 1 cm×1 cm×0.04 cm and 1 cm×1 cm×0.3 cm, respectively. Pieces of CC and CF were soaked in 25.0 mL absolute methanol containing 200.0 mg [VEIM]$BF_4$ and 6.9 mg 2,2′-azobisisobutyronitrile (AIBN). The mixture was transferred to a 50.0-mL round-bottomed flask equipped with a condenser and magnetic stirrer. Then, the above mixture was refluxed under vigorous stirring in $N_2$ atmosphere at 353 K for 12 h. The obtained CC-ILP or CF-ILP electrode was washed with acetone and water, and finally dried at 50 °C in a vacuum drying oven. Here the concentration of ionic liquid monomer and polymerization time were optimal to achieve the best electrochemical performance in MFC application.

### 2.2. Preparation of biofilm electrodes

Growth of the bacterial cells on the CC, CC-ILP, CF, and CF-ILP electrodes took place using an applied potential of 0 V in a three-electrode configuration in a M9 buffer solution (pH 7.2) containing lactate (18 mM) and *Shewanella putrefaciens* suspension with $N_2$ bubbling (Carbajosa et al., 2010). In the three-electrode configuration, the CC, CC-ILP, CF, or CF-ILP served as the working electrode, a