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A Study on Nanocomposites for Biofuel Cell in Surface Engineering

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Abstract—A novel strategy of surface functionalization and immobilization for EBFC applications using electropolymerized polypyrrole thin film, and demonstrate the advantages of the electropolymerized pyrrole immobilized enzyme/graphene sheet composite electrodes for EBFC application. A membrane less enzymatic glucose/oxygen biofuel cell applications is described using surface Engineering. The biofuel cell employs the gold plate electrodes modified by specific graphene-enzyme conjugations, which are immobilized by electrochemical deposition of the conducting polypyrrole polymer. The electrochemical activity of these electrodes is superior to the electrodes immobilized with sol-gel. Such enhancements can be attributed to the excellent electrical property and enzymeloading capability of the polypyrrole material. The power output and the biostability of the integrated biofuel cell can be also improved.

Keywords—Graphene nanosheets, Polypyrrole, surface engineering, Biofuel cell, enzymatic fuel cell

I. INTRODUCTION

Biofuel cells are electrochemical power generators that are able to convert chemical energy into electrical energy through redox reactions. In recent years, the development of enzymatic biofuel cells (EBFC) is likely to have a significant impact on homeland security, aerospace, and healthcare industries as the EBFCs can produce higher power output than other types of biofuel cells [1]–[4]. The output power of such EBFCs is well sufficient to supply some microscale electronic systems, such as cameras for remote surveillance, transmitters, actuators, or even wireless sensor networks, which paves the path for the U.S. Army's goal to eliminate all army military batteries or at least reduce the frequency of replacing batteries, thus to realize integrated soldier sensor suites as envisioned in the war fighter concept. Considerable efforts of researchers are also given to explore the potential of EBFCs for long-term space mission applications [5].

Current technologies, including solar and nuclear energies are either excessively expensive or dangerous, which motivates scientists to develop an alternative portable energy source. However, due to the poor stability caused by enzyme denaturation, the EBFCs have not been successful in practical applications. Currently, how to improve the stability and to fabricate practical EBFC devices out of theoretical concepts [6]–[10] is a key challenge. Among others, covalent binding and physical entrapment are the two main strategies for stability enhancement. In this paper, a simple, practical EBFC system based on electropolymerized pyrrole immobilized enzyme/graphene sheets composite electrodes is used. Among different enzyme immobilization methods studied so far, encapsulating enzymes in polypyrrole film offers a facile strategy for the fabrication of EBFCs, since the process only includes the application of a fixed potential between the working electrode and the reference electrode in a solution containing the pyrrole monomer and enzymes. This technique is especially attractive for the enzymatic functionalization of EBFC electrodes, because we can estimate the amount of the immobilized enzyme and the thickness of the growing polymer film easily by measuring the charge passed through the electrode. Moreover, earlier studies on the microstructure and the conductivity of polypyrrole [11] showed that polypyrrole is a porous polymer with high conductivity and surface-to-volume ratio.

These properties inspired us to examine the performance of polypyrrole as a diffusion and electron transfer medium and also as a protection of enzymes. Besides the physical encapsulation of polypyrrole, graphene nanosheet material has also been employed to construct covalent linkage between the enzymes and the electrodes. As a novel carbon allotrope, graphene possesses a very large surface area, which is about $2630 \text{ m}^2 \cdot \text{g}^{-1}$ [12]. The electrons on the graphene surface move ballistically over the sheet without any collisions with mobilities as high as $10\,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at room temperature [13]–[16]. Recently, graphene exhibits a larger ID/IG ratio relative to single-walled carbon nanotube, which is an indication of greater sp^2 character [17]. Note that though with high purity, the chemically converted graphene (from graphene oxide) used in our experiments possesses a number of surface active functional moieties, such as carboxylic and ketonic groups, which are reactive and can easily bind covalently with enzymes [18].

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The presence of C=C conjugation in graphene is also expected to boost the electron transfer rate, which significantly enhances the power output of the EBFCs [19]. More recently, graphene and sol-gel, another common immobilization method for biofuel cell assembly are employed. However, the power output and the stability were unsatisfied for future security and space applications [20]. In this paper, a novel strategy of surface functionalization and immobilization for EBFC applications using electropolymerized polypyrrole thin film, and demonstrated the advantages of the electropolymerized pyrrole immobilized enzyme/graphene sheet composite electrodes for EBFC application is studied.

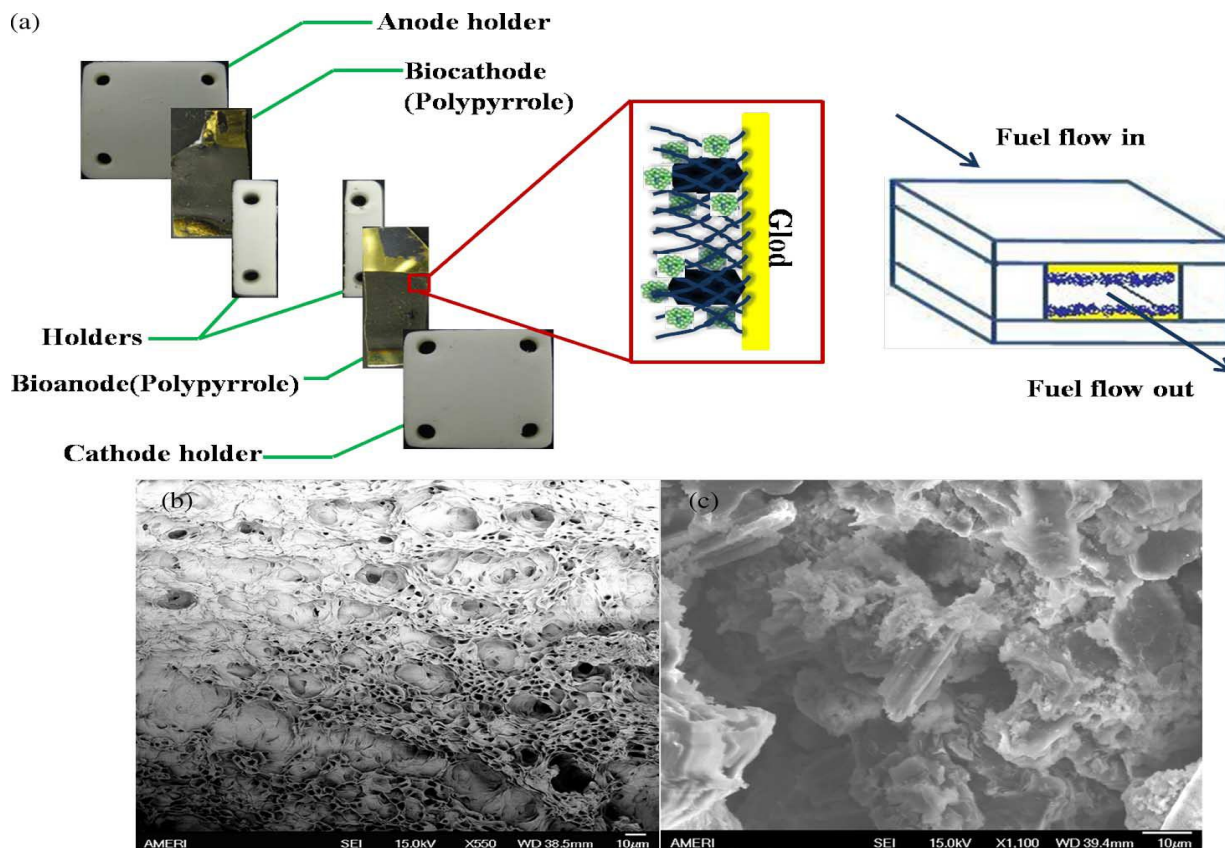


Fig. 1. (a) Polypyrrole-based electrodes microstructure and EBFC assembly diagrams. (b) SEM image of the porous structure of the polypyrrole thin film. (c) SEM image of the porous structure of silica sol-gel matrices.

II. EXPERIMENTAL ANALYSIS

Chang Liu, Zhongfang Chen, and Chen-Zhong Li has undergone the following experiments which are as follows. The bioelectrode is fabricated by coimmobilization of enzyme and graphene using electro generated polypyrrole film. The bioanode was prepared as follows: 10 mg of chemically coated graphene was mixed with 1 mL of dimethylformamide (DMF) and ultrasonicated for 10 h to yield a uniform suspension, then 50 μL of this solution was placed on a gold plate electrode surface (0.5 cm \times 2 cm) and dried under IR lamp for 5 h. Afterward, 100 μL of 8 mM ferrocenemethanol (FM) phosphate buffered saline (PBS, pH 7.4) solution containing 2.5 mg glucose oxidase (E. C. 1.1.3.4, from *Aspergillus niger*; GOD) was deposited on the graphene modified electrode. After incubated for 10 h at 4 $^{\circ}\text{C}$, the electrode was then dipped into 0.02M pyrrole monomer and 0.1M NaClO₄ PBS solution right before the electropolymerization process. Electropolymerization and electrochemical measurement were carried out using a CHI-630 A electrochemical analyzer (CH Instruments, Inc.) with a conventional three electrode setup consisting of a modified gold electrode as the working electrode, an Ag|AgCl reference electrode (3 M KCl) and a platinum counter electrode. Polypyrrole thin layer was deposited at +0.85 V versus Ag|AgCl after 4 C electrical charge (q) passed. The film thickness (s) was estimated to be approximately 2.8 μm by Faraday's law: $s = qM/\rho AzF$, where M is the molar mass of the polymer, ρ is the density of the polymer, z is the number of electrons involved, and F is the Faraday constant. 1.5 g \cdot cm⁻³ was used as the nominal density of the polypyrrole films (ρ)

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and an electron loss z of 2.25 was considered [21]. Finally, the polypyrrole immobilized graphene-enzyme composite electrode was stored in $1 \times$ PBS (pH 7.4) solution at 4°C before test. Similarly, the biocathode was fabricated using the same strategy except the enzyme used was 2.5 mg bilirubin oxidase (E. C.1.3.3.5, from *Myrothecium verrucaria*; BOD) and the redox mediator was 2-azinobis (3-ethylbenzothiazoline-6-sulfonic acid)diammonium salt (ABTS) [see Fig. 1(a)].

III. CONCLUSION

In this paper, a study on novel strategy of surface functionalization and immobilization for EBFC applications using electro polymerized polypyrrole thin film is done. Initially, the surface characteristics of polypyrrole were evaluated by SEM imaging, which indicated a highly porous structure of this material. Moreover, cyclic voltammetry results indicated polypyrrole-based electrodes possess better electron transfer and diffusion properties in comparison with sol-gel immobilization-based electrodes. Finally the power output and life time of the assembled EBFCs are measured. In all experiments, polypyrrole exhibited a better surface immobilization performance than the sol-gel. The observed marked performance of the polypyrrole electrode is mainly due to the porous surface structure and excellent conductivity of the polypyrrole material. As future enhancement the EBFC packaging using low-temperature cofired ceramic (LTCC) for *in vivo* application will be conducted.

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