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Short communication

An electrodeposited redox polymer–laccase composite film for highly efficient four-electron oxygen reduction

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HIGHLIGHTS

- ► Thin films of redox polymer–laccase composite are electrodeposited onto carbon electrodes under mild conditions.
- ► The deposited films catalyze the electroreduction of O_2 at an operating potential of 0.58 V (vs. Ag/AgCl).
- ► The deposited films show excellent performance in terms of O_2 electroreduction current density and stability.

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ABSTRACT

In this report, it is shown that novel thin films of $Os(dcbpy)_2$ (dcbpy = 4,4′-dicarboxylic acid-2,2′-bipyridine)-based redox polymer–laccase composite can be electrodeposited onto carbon electrodes under mild conditions. In a nutshell, the exchange of the inner-sphere Cl^- of the $Os(dcbpy)_2Cl^{+/2+}$ complex tethered to partially quaternized poly (4-vinylpyridine) (PVP) by a pyridine ligand of a second PVP chain leads to cross-linking and deposition of the redox polymer. Laccase, which has coordinatively linkable functions of amines and histidines, is readily incorporated in the electrodeposited redox polymer. Because the reaction centers of the co-deposited laccase are electrically connected to the electrode through the deposited redox polymer, the electrodeposited film can catalyze the electroreduction of O_2 at 0.58 V (vs. Ag/AgCl) – the least reducing potential for highly efficient four-electron reduction of O_2 in pH 5.5 0.10 M phosphate buffer solution. Furthermore, the electroreduction of O_2 is found to be O_2 transport-limited when the reduction potential is poised at $\geq$120 mV more reducing than that of the reversible O_2/H_2O couple. This composite film could be an excellent candidate for uses as cathode in enzymatic biofuel cells.

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1. Introduction

Biofuel cells convert the chemical energy of a biofuel into electrical energy by means of biochemical pathways [1–3]. A variety of approaches have been proposed in the operation of the biofuel cells [1–9]. In addition, a number of high energy density biofuels, such as methanol, ethanol, and sugars, have been tested in the biofuel cells. Amongst them, the glucose–O_2 enzymatic biofuel cells, where glucose is electrooxidized to gluconolactone at the anode and O_2 is electroreduced to water at the cathode, are the most studied [1–5,10–12]. Unlike other types of fuel cells, the enzymatic biofuel cells are expected to be operable under mild physiological conditions [6,12]. More importantly, they are highly miniaturizable because they can be operated in a compartmentless manner [13–15]. Although their energy conversion efficiencies are usually not as high as other biofuel/biomass-based energy conversion devices, the enzymatic biofuel cells can potentially be the energy sources of implanted biomedical devices since the biofuels, such as glucose and O_2 required for their operation, can feasibly be drawn from their immediate environment [15]. The first example of the enzymatic biofuel cells, employing glucose oxidase to oxidize glucose at the anode, was constructed in 1962 [16]. Although great progress has been made in the past 20 years, a number of challenges remain to be addressed. These include relatively short lifetime, low power output, and poor biocompatibility. For instance, most of the proposed enzymatic biofuel cells are capable of meeting the demands of implanted medical devices for short term applications of only up to days, whereas lifetime in the order of weeks, months, or even years would be required for powering implanted medical devices [1–5]. The low power output

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is largely due to the fact that in most of the glucose–O_2 biofuel cells, the O_2 cathode is often the limiting factor in determining the current density due to the much lower concentration of O_2 in aqueous solutions and biological fluids. Besides, the turnover rates of the immobilized enzymes are normally lower than those found in their corresponding natural systems [17,18]. To address these problems, wired-enzyme technology, where a mediating species is chemically bound to a polymer backbone (redox polymer) and to the enzyme in a manner that allows close contact between the redox centers of the enzyme, has been developed. By bypassing the natural route, the redox polymer serves to "electronically wire" the enzyme to facilitate a free flow of electrons from the enzyme to the electrode via the mediator [5,19]. On the other hand, the direct adsorption of some enzymes, including laccase, onto the surface of an electrode without their "wiring" also allows flow of electrons [20,21]. Nonetheless, the transfer of electrons from the electrode to the adsorbed enzyme requires the orientation of the active sites of the enzyme to be toward the surface of the electrode. Since only a small fraction (<2%) of one monolayer of the randomly oriented enzyme is appropriately oriented, the current density that is reached does not approach that of the wired-enzyme electrode and this limits the practical value of the biofuel cells employing the adsorbed enzymes. The reason for the much higher current density for the former is that in the redox hydrogel, the enzyme does not need to orientate itself relative to the surface of the electrode; all reaction centers are wired to the electrode through the redox centers of the hydrogel in a three-dimensional manner with its mobile segments approaching the enzyme's reaction centers. Furthermore, not one layer, but multiple layers of enzyme in the three-dimensional volume of a hydrogel are brought into electrical contact with the electrode [19]. A number of enzyme electrodes and biofuel cells have been fabricated based on this technology [1–5]. Both the current density and stability of such devices have been improved substantially. However, an important consideration for the future development of the enzymatic biofuel cells is about developing new immobilization strategies that are appropriate for the construction of highly stable miniature biofuel cells which require the precise control of film deposition on spatially discrete electrode areas. Electrochemical immobilization provides an elegant alternative for the one-step deposition of enzymes on a small-area electrode of defined geometry [22–24]. Such immobilization provides a simple but versatile approach for controlling the amount and spatial distribution of the deposited film and is especially applicable to the construction of micrometer-size biofuel cells. To date, the majority of such studies have focused on the immobilization of enzyme in electrochemically generated conducting polymer matrixes. However, they could pose serious difficulties in practical applications since there is no direct electron transfer between the enzyme and the conducting polymer backbone. Hence, either a mediator or a high potential is needed to monitor the enzymatic reaction.

In this report, we focused on the immobilization and optimization of a laccase-mediator pair to function optimally as an O_2 reduction cathode for the enzymatic biofuel cells. A novel redox polymer containing osmium-4,4′-dicarboxylic acid-2,2′-bipyridine (dcbpy) complex was chosen as the electron mediator (wire). The redox polymer displayed good kinetics and excellent mediating power with respect to laccase. More importantly, this redox polymer and laccase can be electrochemically co-deposited onto a carbon electrode, thus forming an insoluble film with laccase on the carbon electrode via coordinative cross-linking. The resulting redox polymer–laccase composite film showed excellent performance in terms of O_2 electroreduction current density and stability, opening new perspectives for the enzymatic biofuel cells operating at higher current density with better stability.

2. Experimental section

2.1. Reagents and apparatus

$(NH_4)_2OsCl_6$, poly (4-vinylpyridine) (PVP) (M_w 60,000), and laccase were purchased form Sigma–Aldrich (St Louis, MO) and purified following a published procedure [25]. $Os(dcbpy)_2Cl_2$ was synthesized from $(NH_4)_2OsCl_6$ followed the procedure proposed by Lay and co-workers [26]. The redox polymer used in this work was partially quaternized PVP (QPVP) pyridine-complexed with $Os(dcbpy)_2Cl^{+/2+}$ (QPVP-Os). The quaternization is meant to increase its solubility in water and to maximize laccase loading through the formation of additional electrostatic adducts during electrodeposition. Synthesis of the polymer was described elsewhere [27]. The structure of the redox polymer is given in Fig. 1. A 0.10 M phosphate buffer solution was used as the supporting electrolyte for electrochemical tests. The pH of the phosphate buffer was adjusted by adding an appropriate amount of phosphoric acid or sodium hydroxide. All solutions were freshly prepared with ultrapure water and certified analytical reagents from Sigma–Aldrich.

Electrochemical experiments were carried out using a CH Instruments Model 760D electrochemical workstation (CH Instruments, Austin, TX). A three-electrode system, consisted of a carbon working electrode, a BAS micro-Ag/AgCl (KCl saturated) reference electrode (Bioanalytical System, Inc., West Lafayette, IN) and a platinum wire counter electrode, was used in all electrochemical experiments. An analytical rotator (Pine Instrument Company, Grove City, PA) was used to control convection processes when needed. Electrodeposition of the redox polymer–laccase composite film was performed in a home-made small volume (1.0 mL) electrochemical cell. All potentials reported were referred to the Ag/AgCl reference electrode.

2.2. Electrodeposition of redox polymer–laccase composite film on carbon electrode

The electrodeposition of the redox polymer–laccase composite film on a carbon electrode (glassy carbon, screen-printed carbon, wax-impregnated graphite, and carbon cloth) was carried out as previously described with slight modification [23]. Briefly, square waves between −0.2 and 1.2 V were applied to an O_2 plasma-treated carbon electrode in a pH 7.4 0.10 M phosphate buffer containing 1.0 mg mL^{-1} redox polymer and 2.0 mg mL^{-1} laccase under

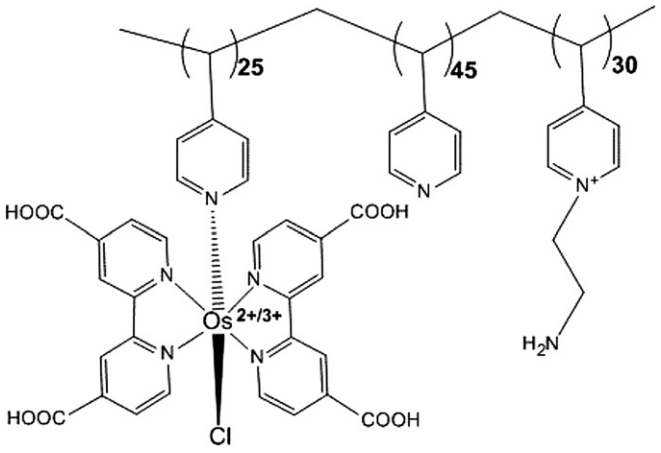

Fig. 1. Chemical structure of the redox polymer used in the preparation of the redox polymer–laccase composite film.

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