



Lowering the potential of electroenzymatic glucose oxidation on redox hydrogel-modified porous carbon electrode



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ABSTRACT

Herein, we demonstrate high current densities per projected surface area for the electroenzymatic oxidation of glucose at low potential using a hierarchically structured electrode based on MgO-templated carbon. The modified electrode was prepared by assembling glucose oxidase (GOx) with an osmium-based redox polymer with a low formal potential (-0.03 V vs. Ag|AgCl), in which Os complexes are tethered to the polymer backbone via a 13-atom alkyl chain and a crosslinker. A glucose oxidation current density of 15 mA cm^{-2} was measured at 0 V vs. Ag|AgCl at 37°C and pH 7, with a plateau value of 50 mA cm^{-2} at 0.3 V. The hydrogel electrodes composed of the same redox polymer and FAD-dependent glucose dehydrogenase delivered only 10% of the current densities obtained with the GOx electrode.

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1. Introduction

We recently reported the development of a glucose-oxidizing electrode using MgO-templated mesoporous carbon (MgOC), with an average pore diameter of 38 nm, as an electrode material. The MgOC was coated with a hydrogel containing a redox polymer, glucose oxidase (GOx), as well as FAD-dependent glucose dehydrogenase (FADGDH) [1,2]. With the objective of improving the mass transfer of fuel and electrolyte ions through the porous carbon layer, porous carbon particles were deposited on a glassy carbon substrate by an electrophoretic technique, to form 10 μm -scale macropores. The hydrogel, composed of a redox polymer, partially quaternized poly(1-vinylimidazole) complexed with [Os(bipyridine)₂Cl] (polymer I, $E^{\circ} = 0.22$ V vs. Ag|AgCl) [3,4], GOx, and a crosslinker, produced glucose oxidation current densities as high as 60 mA cm^{-2} at 0.7 V at 37°C . This current density is 12 times higher than that obtained with the same polymer on a glassy carbon electrode (GC-E). For comparison with other GOx-hydrogel-based electrodes, the effect of the hierarchical structure of the MgOC-based electrode can be elucidated using polymer I, which has been used on other porous carbon materials [4–6]. Similar hydrogel-modified porous carbon electrodes, composed of the same redox polymer and deglycosylated FADGDH, have achieved current densities of 180 mA cm^{-2} at 0.7 V and 37°C , which is 3

times higher than current densities for GOx-based electrodes [2]. However, this electrode system was far from optimum, because the redox mediator potential was too high for use in efficient biosensors and biofuel cells (BFCs) [7]. A redox mediator with a lower potential is required to avoid the electrochemical oxidation of interfering substances, to achieve high accuracy sensors, and to increase the operational voltage of BFCs [8–10]. Mano et al. developed redox polymers with lower redox potentials [11]. The rate of electron transfer from the active center of GOx, FAD, to the Os complex tethered to the polymer backbone was reported to increase as the potential difference between the two species increased. This paper also reported that O₂ can be reduced on these polymers to produce H₂O₂, with an E° value lower than +0.07 V vs. Ag|AgCl; the rate of this reaction increased exponentially with decreasing E° .

Therefore, in this study we selected a redox polymer (polymer II), which consists of poly(vinyl pyridine) complexed with Os(1,1'-dimethyl-2,2'-biimidazole)₂-2-[6-methylpyrid-2-yl]imidazole^{2+/3+} [11–13]. This polymer has a redox potential of -0.03 V vs. Ag|AgCl and allows GOx to produce an efficient glucose oxidation current (2.5 mA cm^{-2}) on a GC-E at 37°C , with a hydrogel loading of $200 \mu\text{g cm}^{-2}$ [12]. To achieve further enhancement in current density, Ketjen Black (KB, a type of carbon black with $800 \text{ m}^2 \text{ g}^{-1}$ of high specific surface area) [12] and a three-dimensional carbonaceous foam [13] were used as potential porous electrode materials in order to increase the efficiency of the enzymatic anode. The KB-modified electrode, with $200 \mu\text{g cm}^{-2}$ of hydrogel loading, produced 8 mA cm^{-2} of catalytic current density at 37°C and

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6000 rpm, while the latter porous carbonaceous electrode, with $1734 \mu\text{g cm}^{-2}$ of hydrogel loading, produced 18 mA cm^{-2} at 37°C and 2000 rpm. However, the enhancement in catalytic current achieved using these porous structured carbon electrodes was quite limited. The past studies of glucose anode based on hydrogel-porous carbon are summarized in Table 1.

To circumvent this limitation, in this study, hydrogels with polymer II and GOx or FADGDH were prepared on hierarchically structured MgOC-based porous electrodes. The present work shows that high catalytic currents at low redox potentials can be obtained for GOx immobilized with a polymer II-based hydrogel matrix, without a significant decrease in electroenzymatic current for glucose oxidation. Surprisingly, although FADGDH has a superior electron exchange ability over GOx toward polymer I [14], polymer II was found not to be able to connect efficiently to FADGDH.

2. Experimental

The MgO-templated carbon-modified electrode (MgOC-E) was fabricated according to our previous papers [1,2]. MgO-templated carbon, with an average pore diameter of 38 nm, was kindly donated by Toyo Tanso (CNovel[®], Osaka, Japan). The mixed biocatalyst solution was composed of enzyme, GOx (from *Aspergillus niger*, Wako Pure Chemical, 40 mg mL^{-1}) or FADGDH (from *Aspergillus terreus*, Ikeda Thoka, 40 mg mL^{-1}), redox polymer II (8 mg mL^{-1}), and a crosslinker, poly(ethylene glycol) diglycidyl ether (PEGDGE, molecular weight 500, Sigma-Aldrich, 8 mg mL^{-1}). The total hydrogel loading on the electrode surface was fixed at $1000 \mu\text{g cm}^{-2}$. The percentage weight of the crosslinker for total hydrogel loading was varied (10, 15, 20, 30% relative to the total hydrogel), while maintaining a constant (1:1) ratio of enzyme to polymer II. This biocatalyst solution was pipetted onto the MgOC-E surface, which was conferred with hydrophilicity by prior plasma oxidation (10 min). After modification, the electrode was dried at 4°C for 18 h. Rotating disc cyclic voltammetry was performed on an electrochemical analyzer (BSA 50 W). The electrode was rotated at 8000 rpm, using a rotator (RDE-2, BAS), to observe the catalytic activity-limited current. Platinum wire counter and Ag|AgCl|sat. KCl reference electrodes were used. All measurements were performed at 37°C in a thermostated water jacket-equipped

electrolysis cell. The electrolysis solution was comprised of 0.1 M phosphate buffer (pH 7) in a total volume of 20 mL.

3. Results and Discussion

Fig. 1A depicts the cyclic voltammograms for the hydrogel electrodes prepared with GOx and polymer II on an MgOC-E (blue curve (a)) or a GC-E (red curve (b)), in the presence and absence (gray curve (c)) of 0.5 M glucose, with a total hydrogel loading of $1000 \mu\text{g cm}^{-2}$ at 37°C . The symmetric voltammogram observed in the absence of glucose (gray dashed-curve (c)) indicates that the formal potential is -0.022 V vs. Ag|AgCl and that the total surface density of the Os complex is $2 \times 10^{-7} \text{ mol cm}^{-2}$, indicating that most of the Os complex applied to the electrode is involved in the surface redox reaction. The onset potential of the glucose oxidation current was observed to be -0.12 V vs. Ag|AgCl, and the current reached a steady state at 0.3 V. The steady-state glucose oxidation current on the MgOC-E was determined to be $45 \pm 7 \text{ mA cm}^{-2}$, which is almost 20 times higher than that for the GC-E (red curve (b), $2.3 \pm 0.1 \text{ mA cm}^{-2}$). The current density at 0 V vs. Ag|AgCl is 15 mA cm^{-2} , while at the same potential, the hydrogel electrode comprising conventional polymer I is not able to produce any current (Table 1) [1,2,4–6].

The steady-state catalytic glucose oxidation process depends on the hydrogel composition, as shown in Fig. 1, panel B. At a constant total hydrogel loading of $1000 \mu\text{g cm}^{-2}$, the highest current densities, 50 ± 8 and $50 \pm 6 \text{ mA cm}^{-2}$, are observed for hydrogel GOx:polymer:crosslinker compositions of 40:40:20 and 42.5:42.5:15 respectively. As the percentage weight of the crosslinker increases from 10% to 15 or 20%, although the content of the biocatalyst decreases, the efficiency of current production increases. The stability of the continuous current response improves as the weight ratio of crosslinker increases [15,16]. In presence of 10 wt% crosslinker, the current density was observed to decrease by 40% after the electrode has rotated at 8000 rpm, at 37°C , for 5 minutes. Under the same operating conditions, almost 90% of the initial current remains for the electrodes made with hydrogel samples containing 15% or 20% crosslinker.

Fig. 2 (panel A) shows the dependence of the glucose oxidation current on hydrogel loading. The catalytic current increases linearly, to a loading of $1000 \mu\text{g cm}^{-2}$, owing to the high surface

Table 1
Comparison of the construction and performance of some recent hydrogel-porous carbon-based glucose electrodes.

Ref. No.	Enzyme	Polymer	Hydrogel loading	Electrode material (carbon)	Buffer (conc., pH, temp.)	Temp.	Glucose conc.	Electrode rotation rate	Onset potential vs. Ag AgCl/V	Current density
[1]	GOx	Polymer I	$1000 \mu\text{g cm}^{-2}$	MgOC on GC	0.1 M PB, pH 7,	37°C	500 mM	8000 rpm	0.05	60 mA cm^{-2} @ 0.7 V
[2]	d-FADGDH	Polymer I	$1600 \mu\text{g cm}^{-2}$	MgOC on GC	1 M PB, pH 7,	37°C	500 mM	9000 rpm	0.05	180 mA cm^{-2} @ 0.7 V
[4]	GOx	Polymer I	$800 \mu\text{g cm}^{-2}$	CNT on CP	PB, pH 7.1,	37.5°C	50 mM	4000 rpm	0.10	22 mA cm^{-2} @ 0.6 V
[6]	GOx	Polymer I	$13 \times 10^{-10} \text{ mol cm}^{-2}$ of Os complex	CNT forest	PB, pH 7	37.5°C	200 mM	Stirring the solution	0.10	25 mA cm^{-2} @ 0.4 V
[12]	GOx	Polymer II	$200 \mu\text{g cm}^{-2}$	Ketjen black on GC	20 mM PB + 140 mM NaCl, pH 7,	37°C	100 mM	6000 rpm	-0.20	8 mA cm^{-2} @ 0.3 V
[13]	GOx	Polymer II	$1734 \mu\text{g cm}^{-2}$	Carbonaceous form	100 mM PB, pH 7.2	37°C	50 mM	2000 rpm	-0.10	18 mA cm^{-2} @ 0.3 V
[14]	d-GOx	Polymer I	$200 \mu\text{g cm}^{-2}$	GC	100 mM PB, pH 7	37°C	200 mM	5000 rpm	0.10	5.4 mA cm^{-2} @ 0.4 V
[14]	d-FADGDH	Polymer I	$200 \mu\text{g cm}^{-2}$	GC	100 mM PB, pH 7	37°C	200 mM	5000 rpm	0.10	7.5 mA cm^{-2} @ 0.4 V
This work	GOx	Polymer II	$1000 \mu\text{g cm}^{-2}$	MgOC on GC	100 mM PB, pH 7	37°C	500 mM	8000 rpm	-0.12	50 mA cm^{-2} @ 0.3 V
	d-FADGDH	Polymer II	$1000 \mu\text{g cm}^{-2}$	MgOC on GC	100 mM PB, pH 7	37°C	500 mM	8000 rpm	-0.05	8 mA cm^{-2} @ 0.3 V

PB: phosphate buffer.

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