The Mechanism of Electro-Catalytic Oxidation of Glucose on Manganese Dioxide Electrode Used for Amperometric Glucose Detection

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Electrolytic manganese dioxide (EMD) is applied as a non-enzymatic glucose-oxidizing electrode catalyst. To elucidate the electrochemical oxidation mechanism of glucose, the catalytic activity of EMD is examined in a phosphate buffer solution by comparing electro-catalytic decomposition behaviors of four saccharides, glucose, deoxyglucose, ribose, and deoxyribose, with consideration of equilibration of their molecular transformation. We find that anodic decomposition of glucose and ribose is catalyzed at the EMD electrode, however no catalytic behaviors of deoxyglucose and deoxyribose are observed. The catalytic activity is influenced by pH and temperature conditions. Form these observations, it is believed that the anodic decomposition is attributed to the enediol transformation of glucose and ribose and is not attributed to the aldehyde transformation of four saccharides. Because the EMD catalyst for glucose oxidation does not have good selectivity to glucose unlike enzyme electrode, polyanion complex (PIC) layer formed onto the surface of EMD electrode by simple drop-cast method was further applied to effectively suppress the interference by typical interferences of ascorbic acid and uric acid, which is due to PIC’s molecular sieving ability. The PIC-modified EMD electrode exhibited superior glucose response with a wide detection range of 0.7 and 7.5 mmol dm−3 glucose.

Enzymatic glucose biosensors, which are generally fabricated by combining enzymes like glucose oxidase and an electron mediator,1–5 have been widely used for monitoring/determining glucose concentration in blood of diabetes patients. Recently, the new idea comes up to expand its application fields to chemical analysis of food, and biosensors have gained attentions as simple and eminent small-gadgets. However, the cost of enzyme-based electrodes is relatively high due to expensive enzyme used and they show high performance only under limited conditions such as neutral pH and room temperature with a short-lived activity duration. Under these circumstance, research on non-enzymatic electrode has attracted much attention to realize inexpensive and high performance glucose-oxidizing-electrodes,6,7 and transition-metal based electrodes have been proposed by applying copper(II) oxide, nickel(II) hydroxide and manganese(IV) oxide as a catalyst.8,9 Among the reported transition metal oxide electrodes with Cu2-, Ni-, and Mn-based oxides, Cu- or Ni-based ones show high catalytic activity only in alkali solutions and they are unsuitable for analyzing glucose in physiological condition of human blood whose pH is approximately 7.4. Furthermore, they should be a nano-sized particle to effectively oxidize glucose, which leads to increase in cost.10 On the other hand, manganese(IV) oxide, which is broadly known to work as a catalyst for organic material decomposition, shows more applicable isomerization, decomposition, and caramelization. In particular, Mn(IV) oxide, which is broadly known to work as a catalyst for organic material decomposition, shows more applicable catalytic decomposition behaviors of four saccharides, glucose, deoxyglucose, ribose, and deoxyribose, with consideration of equilibration of their molecular transformation. We find that anodic decomposition of glucose and ribose is catalyzed at the EMD electrode, however no catalytic behaviors of deoxyglucose and deoxyribose are observed. The catalytic activity is influenced by pH and temperature conditions. Form these observations, it is believed that the anodic decomposition is attributed to the enediol transformation of glucose and ribose and is not attributed to the aldehyde transformation of four saccharides. Because the EMD catalyst for glucose oxidation does not have good selectivity to glucose unlike enzyme electrode, polyanion complex (PIC) layer formed onto the surface of EMD electrode by simple drop-cast method was further applied to effectively suppress the interference by typical interferences of ascorbic acid and uric acid, which is due to PIC’s molecular sieving ability. The PIC-modified EMD electrode exhibited superior glucose response with a wide detection range of 0.7 and 7.5 mmol dm−3 glucose.

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series of carbohydrate including glucose, fructose, and ascorbic acid to discuss how reducing abilities of those carbohydrate influence to overall oxidation process, and it has been concluded that the oxidation behavior was considerably affected by molecular structures of the carbohydrates. All kinds of monosaccharides are known to have reducing ability because their open-chain structure in aqueous solution carries a formyl group at the end of structures. Hereinafter, we use the term of “aldehyde group” instead of “formyl group” for simple descriptions. With standing on this simple idea, the driving force in the oxidation process of glucose on EMD should correlate to the reducing activity of reducing sugar, and the activity should be different among the monosaccharides due to individual structural difference. In this paper, we use several saccharides and newly investigate their electrochemical oxidizability and electrochemical behaviors on the EMD electrode. Among common monosaccharides, we select glucose and ribose as a hexose and pentose, respectively, and further compare them with their dehydrated sugars of 2-deoxy-D-glucose and 2-deoxy-D-ribose, so as to discuss the electrochemical oxidation process of glucose based on molecule structures of these saccharides with consideration of the previous investigation. In addition, to solve the drawbacks of low selectivity for EMD electrocatalysis, a polyion complex (PIC) was applied as surface modifier of the EMD electrode as molecular-sieving layer to improve its selectivity for glucose detection as non-enzymatic electrodes.

**Results and Discussion**

**Characterization of EMD and electrochemical behavior of EMD electrodes.**—The photos of Pt electrodes before/after EMD deposition are shown in Fig. 2a. The black material is clearly seen on the electrode surface after the electrolysis, implying the deposited material mainly composes of MnO2. The electrolytic deposition was regulated at 100 mC cm\(^{-2}\), which brought MnO2 deposition of no less than 45 µg cm\(^{-2}\), which can be calculated by assuming two-electron reduction of Mn(II) according to Faraday law, (57 g/mol of MnO2) ÷ 2F × 0.1 C = 45 µg. Figure 2b shows SEM images of surface morphology of the EMD deposited on the stainless-steel plate. We note that electrode substrate materials of Pt and stainless steel do not give a substantial effect on the EMD deposition process according to previous paper. From this fact, we reasonably think that we basically synthesized the identical EMD containing Mn(IV) ions on different substrates of Pt and steel. The grain size of EMD is approximately 500 nm with a wrinkled surface, and the surface morphology of the obtained EMD is similar to that in the previous report. Figure 2c presents the XRD pattern of EMD prepared on the stainless steel plate and Bragg positions of crystal polymorphs of MnO2. In the XRD pattern, broad peaks appear at approximately 2θ = 37°, 56° and 66° with low intensity, indicating that the γ-MnO2 polycrystalline forms as a main phase of the thin layer.

In order to confirm the functionality of the EMD electrode prepared by the method described above, we first conducted cyclic voltammetry. Figures 3a and 3b show the cyclic voltammograms of the bare Pt electrode and EMD electrode in PBS where pH value was adjusted to 8.0. In Fig. 3a, the bare Pt electrode brings no cathodic and anodic current either with or without D-glucose. On the other hand, the EMD electrode exhibits apparent double-layer capacity and surface redox even without D-glucose due to cationic absorption/desorption on EMD, and a significant anodic current appears over 0.6 V vs. Ag/AgCl in a D-glucose containing solution (Fig. 3b). Since pH values of the PBS solution did not change after dissolving glucose, the oxygen gas evolution should appear above 1.0 V vs. Ag/AgCl in both solutions. The anodic current over 0.6 V is therefore attributable to the anodic oxidation of D-glucose catalyzed at EMD electrode. Additionally, we examined the optimal deposition charge of EMD, 10–500 mC cm\(^{-2}\) for larger current response to glucose (see Fig. S2) and found that 100 mC cm\(^{-2}\) is optimal for the response.

We examined temperature dependency of the EMD electrode performance in the range of 15–40 °C as shown in Fig. 3c. As temperature elevates the anodic current increases and its onset of potential lowers. This result implies that no significant degradation or catalyst poisoning occurs even at the high-temperature measurement,
resulting in no serious deactivation of the EMD catalyst. Since enzymes generally consist of proteins and show denaturation at around 60 °C, enzyme-immobilized electrodes are eventually deprived of the substrate specificity to lose biocatalytic activity under high temperature. On the other hand, the EMD electrodes deliver the stable anodic current of glucose because of insignificant influence from temperature and pH condition, and this characteristic could be one of the potential advantages as electrodes for application to sensor probes.

Figure 3d shows a chronoamperogram of the EMD electrode to check anodic current dependency on D-glucose concentration under the constant potential of 0.85 V. The current proportionally increases with a stepwise manner as concentration of D-glucose increases, and the obtained stepwise signals exhibit well correspondence to increases of D-glucose concentration. The anodic current, however, was not enough stable as exhibiting a gradual decrease just after the addition of 15–50 mmol dm⁻³ D-glucose, implying instability in MnO₂ catalyst in the higher concentrations range. It is supposed that the manganese(III) on the electrode surface would be partially disproportionated into manganese(IV) and manganese(II) during the catalytic reaction of manganese(IV), followed by dissolution of the latter into solution. Aside from specificity, such instability is a serious drawback to be improved before practical use of EMD electrodes for glucose sensors, which is expected to be solved by PIC coating as described below.

Study of glucose oxidation process on EMD electrodes.—In order to further discuss oxidation process of glucose at the non-enzymatic electrodes, we selected D-glucose and D-ribose among monosaccharides as typical hexose and pentose to examine their electrochemical behaviors. Both D-glucose and D-ribose are known to exhibit reducing ability originating from aldehyde groups (CHO) in chain structures which is transformed from six-membered or five-membered pyranose as shown in Fig. 4. The existence ratios of aldehyde structures in the equilibrium are 0.05% and 0.03% for D-ribose and D-glucose, respectively. Fig. 5a shows cyclic voltammograms of the EMD electrode in PBS (pH 8.0) with D-ribose or D-glucose and without sugars. Anodic currents are observed from 0.5 V with addition of sugars, and their current peaks appear at about 0.9 V. D-ribose leads to the larger anodic current density with lower onset potential of 0.5 V and its anodic current peak appears at slightly lower potential than those of glucose. The difference observed in the CV curves in D-ribose and D-glucose solution is consistent with the results-reported in previous work, and would be simply explainable from difference of their reducing activities. Since the ratios of the aldehyde forms in the equilibrium with 0.05% and 0.03% for D-ribose and D-glucose, respectively, would be identical to their concentration ratios, D-ribose shows pronounced response due to higher concentration of the aldehyde forms in PBS. Aside from the increase in catalytic activity of EMD in Fig. 5a, one possible explanation for increase in the anodic current under the elevated temperatures shown in Fig. 3c would be due to the change in the equilibrium concentration of aldehyde forms which should increase under the higher temperature condition. Since the reactivity of sugars as reducing agent has a direct influence to resultant electrochemical signal from the EMD electrodes, we further investigated the electrochemical oxidation behavior of other sugars having different reactive character. According to the previous our investigation, the hydroxyl group at a C2 position is a structure sensitive to resultant electrochemical signal from the EMD electrodes; they are therefore selected as deoxysugar of D-glucose and D-ribose, respectively. Anodic decomposition of these two deoxysugars, 2-deoxy-D-glucose and 2-deoxy-D-ribose, are also examined by using the EMD electrodes due to the presence of an aldehyde group in their chain structures.

Figures 5b and 5c compares the cyclic voltammograms of the EMD electrode in D-glucose, 2-deoxy-D-glucose, D-ribose, and 2-deoxy-D-ribose solutions under the same electrochemical condition. It is widely recognized that aldehyde forms (chain form) is one common intermediate in rearrangement of one ring form to another, and all sugars dissolved in water including PBS are supposed to take aldehyde forms which are generally considered to be oxidizable. However, no anodic current is observed in the 2-deoxy-D-glucose and 2-deoxy-D-ribose solutions except the Mn(III)/Mn(IV) pseudocapacity and double layer capacity of EMD, while D-glucose and D-ribose exhibit a large anodic current as shown in Fig. 5. This difference is reasonably explained on the basis of the previous discussion on chemical oxidation behavior of glucose via the common 1,2-hexose enediol of glucose.
the chain structure, D-glucose and D-ribose further take equilibrium between the aldehyde form, \([-\text{CH(OH)}=\text{CHO}]-\), and enediol form, \([-\text{C(OH)}=\text{CH(OH)}]-\), as shown in Fig. 6a, while 2-deoxy-D-glucose and 2-deoxy-D-ribose remain in the aldehyde forms and they cannot transform an enediol form due to lack of hydroxyl groups at C2 position. As reported previously,\(^{42,43}\) the enediol forms are readily and easily oxidized by oxidizing agents such as copper acetates at the lower potential than that of the aldehyde forms, and it has been electrochemically confirmed that the oxidation potential of deoxysugars is much higher than those of conventional sugars such as D-glucose and D-ribose.\(^{31,32}\) One can note that ascorbic acid which is readily oxidized (see Fig. S3(a)) also possesses the enediol structure in its

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**Figure 3.** Cyclic voltammograms of (a) Pt electrodes and (b) EMD-deposited Pt electrodes in 0.04 mmol dm\(^{-3}\) PBS (pH 8.0) with or without 0.05 mmol dm\(^{-3}\) glucose. (c) Cyclic voltammograms for the EMD electrode in 0.04 mmol dm\(^{-3}\) PBS (pH 8.0) with 0.05 mmol dm\(^{-3}\) glucose at different temperatures of (i) 15°C, (ii) RT, (iii) 40°C, (iv) 50°C, and (v) 60°C. (d) Oxidation current dependency on the glucose concentration for the EMD electrode at constant potential of 0.85 V vs. Ag/AgCl.
molecule. In case of 2-deoxy-D-glucose and 2-deoxy-D-ribose solutions, therefore, any anodic decomposition did not occur in this potential range, while D-glucose and D-ribose exhibit the remarkable electrochemical response on the MnO₂ electrode as seen in Figs. 5b and 5c. From these results, we believe that the oxidation of glucose on the EMD electrode is truly attributable to the oxidation of the enediol form of glucose. We note that the enediol rearrangement of glucose has been mainly investigated under the strong alkali solution at pH > 9.5, and additional discussion would be required to confirm this process under such weak base condition of pH = 8.0. Since acidic condition is expected to retard the rearrangement of aldehyde forms to enediol as suggested by Fig. 6a, electrochemical performances of the EMD electrode in PBS of which pH values range between pH 8.0 and 5.0 were further examined to confirm involvement of the enediol rearrangement reaction.

Figures 6b and 6c show the pH dependency of electrochemical property of the EMD electrode in D-glucose and D-ribose solutions, respectively. The anodic current densities of D-glucose and D-ribose gradually decrease by changing pH values from 8.0 to 5.0, and the onset potentials at/below pH 7.0 are higher than that in pH 8.0. This result agrees with the idea that stronger basic condition leads shift to the right in the equilibrium of Fig. 6c, resulting in an increase in the enediol concentration in D-glucose and D-ribose solutions. Accordingly, electrochemical oxidation of D-glucose and D-ribose in aqueous solution is enhanced with increase in pH values higher than 7.0. More importantly, the anodic current is still observed in the
neutral condition of pH 7.0, suggesting the possibility of involvement of OH\(^-\) from self-ionization of water in the rearrangement process.

As a result of our investigation on relationship between the chemical rearrangement and electrochemical behavior of several sugars including glucose, we found that 1) deoxy-sugars do not show electrochemical anodic response, 2) anodic current increases under higher pH condition, and 3) electrochemical oxidation tendency of the tested sugars on the EMD shows correlation with its reducing activity which is governed by enediol rearrangement. Consequently, the response to glucose oxidation on the EMD electrode is attributable to...
Electrochemical test of double-layered PIC/EMD electrodes.— Human blood contains reducing chemical compounds such as ascorbic acid (AA), uric acid (UA), and fructose (Fru), and especially ascorbic acid has been known as an enediol compound and hence shows strong reducing ability. Figure 7a shows a chronoamperogram of the EMD electrode tested at 0.85 V with sequential additions of 10 mM glucose, 0.1 mM AA, 0.5 mM UA, and 0.1 mM Fru. Concentration of each substance was adjusted based on that in human blood where glucose, AA, UA, and Fru exist in 4.5–7.3 mM, 0.023–0.085 mM, 0.18–0.48 mM, and 0.02 mM, respectively. The EMD electrode shows the anodic signal at the injection points of glucose and AA, and the continuous increase in current is observed after drop of UA and Fru solutions. As can be clearly seen in Fig. 7a, these substances bring considerable interference in monitoring glucose.

In the previous reports, polyion-complex (PIC) modification on electrodes, which provides ionically bonded polymer network structures, is one of the most suitable techniques for enzyme immobilization without any additional covalent modification of enzyme.33,34 Furthermore, we demonstrated PIC layer formed on Pt electrode shows a molecular sieve behavior which originates from the ladder structure with polycation-polyanion network (Fig. S1). The PIC behaves as a size-dependent molecular sieve allowing penetration of only glucose and avoiding larger molecules of interferences.33,44 Among the series of our investigation, the PIC layer composed of poly-L-lysine (PLL) and polyacrylic acid (PAA) has been proved to serve an effective membrane for a glucose sensor with glucose oxidase and effectively...
eliminates the electrochemical interference in analytes such as ascorbic acid and uric acid. Figure 7b shows the chronoumperometric response for glucose, AA, UA, and Fru with the PLL-PA/EMD electrode. No anodic current appears when AA, UA, and Fru were added, and much higher current is observed at the drop of glucose solution compared to that of the EMD electrode observed in Fig. 7a. The same trend was confirmed in a condition where 0.10 mmol dm\(^{-3}\) ascorbic acid was first added to PBS before sequential additions of 5.0 mmol dm\(^{-3}\) glucose (Fig. S3). Coexistence of reductive agents in glucose solution strongly hinders current response from glucose for pristine EMD electrode, however, the PLL-PA layer formed on the EMD surface effectively inhibits anodic oxidation of ascorbic acid and enables to specifically respond to glucose in the mixed solution. We also examined series of PIC membranes, and only the PLL-PA/EMD electrode brought sufficient performance on glucose detection (Fig. S4 and S5). The reason of this idiosyncratic feature of the PIC layer against glucose is still unclear, and further investigations will be carried on in near future.

The PLL-PA/EMD electrode also shows linearity dependence of anodic current on glucose concentration. Figure 7c shows the oxidation current of the PLL-PA/EMD electrode when the glucose concentrations vary from 0 to 50 mM at 0.85 V. The electrode exhibits larger current compared with the EMD electrode at even high glucose concentration of 50 mM, and the current density linearly changes as increasing the glucose concentration up to 7.5 mmol dm\(^{-3}\) as seen in the inset of Figure 7c. This suggests that the PLL-PA/EMD electrode has a wide detection range of 0.7–7.5 mmol dm\(^{-3}\) which sufficiently covers the range of physiological glucose levels of 3.8–7.2 mmol dm\(^{-3}\) in human blood. The PIC layer enables to eliminate the influence from interference in aqueous solution. For the application as non-enzymatic glucose sensor, sensing performance such as precision, reproducibility, and life time are under investigation since we first proposed the mechanism of oxidation process of glucose with considering its transformation equilibrium at EMD and adapted the polyion complex layer for the EMD electrode.

Conclusions

The electrochemical property of the EMD electrode for glucose detection and the mechanism of the catalytic electrochemical oxidation were examined and discussed systematically in the light of the reducing ability of the saccharides. Their anodic oxidation catalyzed at EMD electrode is related intimately to ratio of chain structures under the equilibrium of the saccharides in aqueous solution and the presence or absence of a hydroxyl group at its C2 position. We found that the enedial rearrangement is an important reaction for understanding the mechanism for the electrochemical oxidation of saccharide. Moreover, since the molecular sieving ability of the PLL-PA/EMD electrode was proved electrochemically, the PLL-PA/EMD electrode demonstrated satisfactory selective response for glucose with a wide detection range up to 7.5 mmol dm\(^{-3}\) glucose. Further study will be needed to elucidate the more detailed mechanism of the non-enzymatic saccharide oxidation catalyst and to realize high-performance amperometric glucose sensor based upon double-layer scheme of polymeric and manganese oxide layers.

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