Cu and CuPb Electrodes Electrodeposited from Metal Oxides in Hydrophobic Protic Amide-Type Ionic Liquid/Water Mixture for Nonenzymatic Glucose Oxidation

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Cu and CuPb were electrodeposited from the mixture of water and a protic amide-type ionic liquid (IL), the protonated betaine bis(trifluoromethyl)sulfonyl)amide ([Hbet][TFSA]), in which CuO and PbO were dissolved. The electrodeposited Cu electrode showed electrocatalytic activity toward glucose oxidation in alkaline conditions, and the activity was significantly enhanced when Cu was doped. Activity enhancement might result from the changes of the surface morphologies and the electronic states of Cu, which were concluded according to the SEM observations and XPS analyses.

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Experimental

Voltammetric study and electrodeposition of Cu and CuPb was conducted in the mixture of 9 wt% water in the ionic liquid (IL) protonated-betaine bis([trifluoromethyl]sulfonyl)amide ([Hbet][TFSA]) (denoted as [Hbet][TFSA]/H2O) under ambient atmosphere at 40°C. The same electrolyte has been used previously for zinc electrodeposition,16 and the same procedures previously reported were used to prepare [Hbet][TFSA].17 A three-electrode electrochemical cell controlled with a CHI 660E electrochemical analyzer (CH Instruments, Inc.) was used. The working electrode was a detachable glassy carbon or stainless steel (304 steel) disc electrode (GCE or SSE. 3 mmø. Cusco, LTD). Before using the electrodes, they were carefully polished using 0.3 μm alumina slurry on a polish pad, and then cleaned using an ultrasonic cleaner. For the voltammetric study and electrodeposition of Cu, Pb, and CuPb alloys in [Hbet][TFSA]/H2O, a Ag/AgCl, and a Pt spiral (made of 0.5 mm Pt wire purchased from Alfa Aesar. Purity is 99.95%) was used as the reference and counter electrodes, respectively. Tuning the activity of Cu can be feasible.

Voltammetric study and electrodeposition of Cu and CuPb was conducted in the mixture of 9 wt% water in the ionic liquid (IL) protonated-betaine bis((trifluoromethyl)sulfonyl)amide ([Hbet][TFSA]), in which CuO and PbO were dissolved. The electrodeposited Cu electrode showed electrocatalytic activity toward glucose oxidation in alkaline conditions, and the activity was significantly enhanced when Cu was doped. Activity enhancement might result from the changes of the surface morphologies and the electronic states of Cu, which were concluded according to the SEM observations and XPS analyses.

Nonenzymatic glucose oxidation is a very important issue not only to glucose determination but also to glucose fuel cells1,2 because the natural protein-based enzymes are usually poor of robustness and not suitable of being used in critical conditions such as high or low pH values and temperatures although they are usually extremely selective to their target molecules. Inorganic electrocatalysts usually show higher stability and tolerance to environmental changes in contrast to the natural protein-based enzymes. The poorer selectivity of the common inorganic electrocatalysts, however, make them deficient in the use for glucose sensing but qualified or even better than enzymes for energy devices; the reason for the latter is focused on their tolerance toward some critical reaction conditions. Selectivity, however, can be significantly improved via using a low detection potential (∼0 V) but only the precious metal-based (ex. Pt-based) nanomaterials are sufficiently active.3–6 Some of which can even be used in neutral media, and vitamin C (one major interferent in glucose sensing) shows no interference because of the very low detection potential.4–6 Interference can also be suppressed by modifying the electrodes with a film, such as over-oxidized polypyrrole (OPPy).3 Non-precious metal-based electrocatalysts, the non-precious metal-based electrocatalysts, the non-precious metal-based electrocatalysts are usually prepared in their metal-oxide forms such as Co3O4 or converted to the oxide forms before using them because their oxides rather than metals showed the activity, and graphene,8,10 carbon nanotubes (CNTs),7 and nano-configurations (i.e. porous and hollow structures, and nanofibers9,11) were employed to improve the activity. The activity could be improved because the electrocatalysts were able to be dispersed much well on nanomaterial-based substrates (ex. CNTs) to expose more active sites. To make the electrocatalysts nano-structured (dendritic, porous, and etc.) showed the similar manner. In addition to the abovementioned materials, copper and copper oxides, which are relatively abundant in the crust, are also frequently used as the electrocatalysts of glucose.3–15 Similarly, nanostructured substrates such as CNTs are used to enhance the activities.

In this study, the facile electrodeposition of Cu on stainless steel was used to prepare the Cu-modified electrodes for the nonenzymatic glucose oxidation without using nanomaterials such as CNTs in order to make the preparation convenient. A protic amide-type IL was used as the electrolyte because water-insoluble CuO, which was usually a waste from metal processes or devices, is soluble in this IL to be used as the Cu source for the electrodeposition. Here, it was found that the activity of the copper-electrodeposited electrode was greatly improved by Pb doping during the electrodeposition. As the same reason as to CuO, PbO was used as the Pb source in this study. It is, therefore, possible to use metal wastes such as metal oxides to prepare metal catalysts for various applications by using ILs as the electrolytes. It has been reported that the activity of Pt can be significantly increased by introducing Pb but no interpretation was provided.5,6 In this study, the activity enhancement of the electrodeposited-copper electrodes was concluded by the significant changes of surface morphologies (extremely dendritic) and the electronic states of copper, respectively. Tuning the activity of Cu can be feasible.

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the coulombic density of 4.25 C cm\(^{-2}\). After the electrodeposition, the electrodes were washed using ethanol to remove the residual IL. Before the electrodeposited Cu and CuPb electrodes, respectively, were used to study the electrochemical oxidation of glucose in 0.1 M NaOH, the electrodes were anodized in neat 0.1 M NaOH by cycling the potential between 0.1 and 0.8 V for 30 cycles under a scan rate of 50 mV s\(^{-1}\) in order to form a stable layer of metal oxides that catalyzed the oxidation of glucose. The electrodeposits were analyzed with field emission scanning electron microscope (FE-SEM; JEOL 6330) coupled with an energy dispersive X-ray spectrometer (EDX) (the detachable electrodes can be directly used for the observation), powder X-ray diffractometer (XRD; Siemens D5000), and X-ray photoelectron spectrometer (XPS; PHI 5000 VersaProbe) to obtain the information of surface morphologies, elemental compositions, crystallinity, and surface states.

Results and Discussion

Voltammetric study of Cu(II) and Cu(II)/Pb(II) mixture prepared from CuO and PbO—CuO and PbO are soluble in [Hbet][TFSA]/H₂O to provide Cu(II) and Pb(II) complex ions for the electrodeposition. The probable coordinating structure and the voltammetric behavior of the Pb(II) species have been previously reported.\(^{19}\) A similar coordinating sphere might be applicable to the Cu(II) species. However, the experiment is still being undertaken. In short, water molecules and the deprotonated zwitterion [bet] produced from the reaction of [Hbet] cations and metal oxides (ex. PbO + 2[Hbet] → [Pb(bet)₂(H₂O)]\(^{2+}\)) were coordinated to Pb\(^{2+}\) or Cu\(^{2+}\) to form positively-charged Pb(II) and Cu(II) species, respectively. For other frequently used [TFSA]-based ILs, the positively charged metal species are unusual because negatively charged [TFSA]-coordinated metal species were formed. The different species may show some key effects on the obtained electrodeposits.

Before SSE\(_{\text{Cu}}\) and SSE\(_{\text{CuPb}}\) electrodes were prepared by electrodeposition, the voltammetric behavior of Cu(II) and the mixture of Cu(II)/Pb(II) in 1:1 molar ratio was generally studied at GCE and SSE, respectively. Figures 1a and 1b show the cyclic voltammograms (CVs) of Cu(II) recorded at GCE and SSE, respectively. The potential was reversed at various switching potentials as indicated in Fig. 1a. The oxidative wave \(a_1\) initially raised and then diminished when the switching potential became more negative in front of wave \(c_2\). Once wave \(a_1\) decreased, the oxidative wave \(a\) appeared and continuously increased, and then wave \(a\) disappeared while the switching potential was moved more negative across wave \(c_2\) but wave \(a\) continuously increased. These behavior indicated that the \(c_1/a_1\) redox couple corresponded to the reaction Cu(II) + \(e^-\) \(\Rightarrow\) Cu(I), waves \(c_2\) was associated with the reduction Cu(I) + \(e^-\) \(\Rightarrow\) Cu and/or Cu(II) + 2\(e^-\) \(\Rightarrow\) Cu, and wave \(a\) was due to the oxidation Cu \(\Rightarrow\) Cu(II) + 2\(e^-\). At SSE, only one redox couple \(c/a\) was observed. Wave \(c\) is due to a two-electron reduction because the electrogravimetric experiment (data not shown) indicated that the electron transfer number of wave \(c\) was two, and Cu metal (verified by XRD and would be discussed latter) was obtained at this wave. Both evidences indicated that the redox couple \(c/a\) corresponds to the reaction Cu(II) + 2\(e^-\) \(\Rightarrow\) Cu (Fig. 1b). Once Pb(II) was introduced into the Cu(II) solution, the redox couple of Pb(II)/Pb appeared (\(c_3/a_3\) in Fig. 1c). However, this couple shifted in anodic direction (dotted), compared with that in Pb(II)-only solution (dashed), indicating the overpotential needed for Pb reduction decreased in the Cu(II)/Pb(II) mixture. The reaction at wave \(c_2^*\), which is the under potential deposition (UPD) of Pb on Cu surface,\(^{20}\) might cause the decrease of overpotential. On the other side, the oxidation wave of deposited Cu shifted anodically in the Cu(II)/Pb(II) solution (compared...
Electrodeposition and characterization of Cu and CuPb.— Constant-potential electrodeposition of Cu and CuPb was conducted at SSE using various applied potentials. The detailed compositions of the electroplating baths can be found in the experimental section. Figures 2a–2h show the SEM images of SSE/Cu (Figs. 2a–2d) and SSE/CuPb (Figs. 2f–2h) obtained by electrodeposition at the indicated potentials, and the atomic contents determined by EDX are also shown. It can be found that a higher overpotential was applied the more dendritic Cu electrodeposits were obtained (Fig. 2a–2d). This behavior makes sense because more nuclei can be formed and the growth rate is faster when a higher overpotential is applied for the electrodeposition. More importantly, when Pb(II) was contained in the solution, the reduction waves of Cu(II) (waves $c_1$ and $c_2$ in Fig. 1c) became smaller when Pb(II) existed. This phenomenon was more evident when using SSE electrode (dotted curve in Figs. 1d). This behavior was not seen at higher temperatures such as 80°C (the reductive current of Cu(II) was observed and the size was same as that in a Cu(II)-only solution; data not shown). This behavior implied that Pb(II) might be adsorbed on the electrode surface to suppress the reduction of Cu(II). At a high temperature, the adsorption behavior may be hindered because of the more violent thermal motions.
Figure 3. CVs recorded at the indicated electrodes in 0.1 M NaOH with 0, 1, and 5 mM of glucose at 25°C under scan rate of 50 mVs⁻¹.

extremely dendritic Cu electrodeposits were obtained (Figs. 2e; EDX shows no Pb) if a potential merely sufficient for Cu reduction is applied. What caused the dendritic electrodeposits of Cu might be due to the Pb(II) adsorption as mentioned for Figs. 1c and 1d where the reductive waves of Cu(II) were suppressed, especially in a relatively low temperature such as 40°C, in Cu(II)/Pb(II) mixture because of Pb(II) adsorption on electrode or electrodeposits surface. However, it is also possible that Pb was co-deposited with Cu but EDX was not sufficiently sensitive to detect it because −0.05 V is very close to the UPD wave of Pb on Cu. Whether or not Pb was co-deposited with Cu (for the sample shown in Fig. 2e), the existence of Pb or Pb(II) indeed show a significant effect on the surface morphologies of Cu electrodeposits. On the other hand, the CuPb electrodeposits became more and more dendritic and porous along with the increment of Pb content in the electrodeposits when a higher overpotential was applied (Figs. 2f–2h). The effect of Pb-doping on surface morphologies evidently demonstrated on the samples electrodeposited at −0.12V (Figs. 2d and 2f). Compare with the Cu electrodeposits (Fig. 2d), CuPb (Fig. 2f) showed obvious wire-like/porous structures, which might show a particular effect on electrochemical glucose oxidation and would be discussed later.

Crystalline Cu was obtained even the deposits were dendritic (SSE/Cu(−0.05V) in Fig. 2r; the same sample for Fig. 2e). The crystallinity of Cu deposits was weakened once more Pb was co-deposited (especially for SSE/CuPb(−0.19 and −0.26V) in Fig. 2i). Small and broad Pb diffraction signals were observed when a sufficiently high overpotential (−0.19 or −0.26 V) was applied for the electrodeposition. The abovementioned observations indicated that the crystal size of Cu became smaller once more Pb was co-deposited with Cu. This result is consistent with the SEM observations in which a more dendritic surface was obtained if the content of Pb is higher; a more dendritic surface of the electrodeposits usually contains smaller grains composed of tiny crystals, which makes the Cu diffraction signals weakened.

XPS can only be used to study the crystal phase of the electrodeposits. However, the surface electronic states and compositions of the electrodeposits may have a crucial effect on the electrocatalytic activity. XPS was conducted to analyze the surface states of Cu because XPS is more surface sensitive in contrast to XRD. It has to be emphasized here that a SPCE (please see experimental section) was used as the substrate for XPS analysis. SPCE showed a very similar electrochemical behavior in [Hbet][Tf2N]/H2O as the SSE did, and the electrodeposits obtained at the same potential showed similar morphology and atomic contents no matter which electrode was used. Figure 2j shows the XPS spectra of Cu2p electrons (inset shows the entire spectra), which indicated that BE of the Cu2p electrons became smaller when Pb was introduced (black curves) but became larger after the electrodes were anodized in 0.1 M NaOH (red curves). Anodization of electrodes prior to the study of glucose oxidation was essential because a stable layer of metal oxides could be formed on electrode surface as mentioned in the experimental section. The electronegativity of Cu atom (1.90) is slightly higher than that of Pb (1.87), which might be able to explain the decrease of BE of the Cu2p electron when Cu and Pb were co-deposited. Electrons might flow from Pb to Cu when Pb was doped into Cu, leading to a higher electron density on Cu atoms. After the anodization, BE of the Cu2p electron in CuPb deposits became larger than that in Cu deposits (red curves), indicating that Cu in oxidized CuPb was probably existing in a higher oxidation state in contrast to Cu in the oxidized Cu deposits. This higher oxidation state might make CuPb more active (compared to Cu deposits) toward the glucose oxidation because glucose should be catalytically oxidized by a high oxidative state of Cu such as Cu(III). The details would be discussed in the next section.
dodynamic chronoamperograms (HCAs) individually recorded at SSE/Cu (0.1V) and SSE/CuPb (0.12V) at 0.5 V in stirred 0.1 M NaOH with successive injections of standard glucose stock solutions. The steady-state reaction currents were used to establish the calibration curves as shown in Fig. 4a in which the data from other electrodes were also included. SSE/CuPb (−0.12V) showed the superior sensitivity over other electrodes, and the current was linearly dependent on the concentration from 5 μM to 6000 μM; the linear equation and regression coefficient are \( j(\text{mA cm}^{-2}) = 0.0024 \times [\text{glucose}] (\mu\text{M}) + 0.139 \) and \( R^2 = 0.996 \), respectively. The concentration range of linearity was significantly widened if chronoamperometry is used. The inset of Fig. 4b shows the chronoamperograms (CAs) of glucose with various concentrations. The currents at 100th second were used to establish the calibration curves as shown in Fig. 4b. Again, SSE/CuPb (−0.12V) showed the best performance with a linear concentration range from 5 μM to 10000 μM; the linear equation and regression coefficient are \( j(\text{mA cm}^{-2}) = 0.00033 \times [\text{glucose}] (\mu\text{M}) + 0.0163 \) and \( R^2 = 0.999 \), respectively. Figure 4c shows the changes of current on time for the indicated electrodes during the constant-potential electrolysis of 0.1 M glucose in 30 minutes. This time, SSE/CuPb (−0.19V) showed the best performance but SSE/CuPb (−0.12V) still showed a much better activity than SSE/Cu (−0.10 and −0.12V), indicating that the activity of the copper electrode could be significantly improved as long as lead was doped. Without glucose, the reaction currents recorded at all electrodes were negligible as the gray curves showed. The SSEPb showed no activity toward glucose oxidation. Its reaction current toward 0.1 M glucose fell in the region of the gray curves.

In short, doping Pb into Cu electrodeposits could greatly increase the activity of the electrode toward glucose oxidation. The extremely dendritic/porous structures of CuPb (compared to Cu; please see Figs. 2a–2h) might explain the significant enhancement of activity because higher surface areas were obtained, and Cu atoms with lower coordination numbers were exposed; atoms with lower coordination numbers have been reported showing higher activity, compared with the atoms on a flat surface. 22 Except for the change of surface morphologies, crystalline facets may also show a certain effect on the electrode activity. However, the XRD patterns (Fig. 2i) are only able to show that the crystal size of Cu decreased with the increase of Pb content in the electrodeposits. No phase transformation could be observed. Therefore, the enhancement of electrode activity toward glucose oxidation might not result from the phase transformation after the Pb doping. The XPS analysis indicated that the Cu atoms in the anodized CuPb probably existed in a higher oxidation state in contrast to Cu in the anodized Cu deposits (Fig. 2j). This higher oxidation state explained the higher activity of CuPb electrodes because glucose oxidation can be more efficiently catalyzed by the higher oxidative state of Cu (ex. Cu(III)). Pb might behave as a glucose adsorbent as mentioned for Fig. 3b. Cu and Pb, therefore, showed a synergistic effect on glucose oxidation. This synergistic effect was especially apparent in the electrolysis of a relatively high concentration of glucose (Fig. 4c) in which all CuPb electrodes showed a superiority over the Cu electrodes. However, a high Pb content did not guarantee a high activity (Pb content in SSE/CuPb (−0.26V) was the highest but its activity is not) because Cu instead of Pb is the active site. Too much Pb co-deposited with Cu naturally decrease the reaction current of the electrode. An optimized ratio between Cu and Pb is needed to obtain the maximum activity. This synergistic effect, on the other hand, was not so obvious for relatively low concentrations of glucose (Figs. 4a and 4b).

Conclusions

CuO and PbO are soluble in [Hbet][TFSA]/H₂O mixture to supply Cu(II) and Pb(II) for electrodeposition. Metal oxides, which might come from metal wastes and energy devices, thus can be used for metal electrodeposition. The Cu electrodeposits show stable activity toward glucose oxidation, and the activity can be significantly increased by doping small amounts of Pb. Activity enhancement might result from...
the very dendritic and porous structures of the electrodeposits and the higher oxidation state of Cu (compared with pure Cu deposits after anodization in NaOH solutions) once Pb was doped. These features made the electrode showing the sensitivity of 2400 μA mM⁻¹ cm⁻² and linearity up to 6–10 mM. A further investigation will be important and essential in order to elucidate the dendrite formation and high oxidation state of Cu in the near future.

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