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Surface Poisoning During Electrocatalytic Monosaccharide Oxidation Reactions at Gold Electrodes in Alkaline Medium

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Abstract
In the present study, the surface poisoning of electrocatalytic monosaccharide oxidation reactions at gold electrodes were investigated. In the cyclic voltammetric studies, the electrocatalytic oxidation of aldohexose and aldopentose type monosaccharides, aminosugars, acetyl-glucosamine and glucuronamide were observed at gold plate electrodes in alkaline medium. However, in controlled-potential electrolytic studies ranging -0.3 to -0.2 V in reaction solutions, current flows during electrolyses decreased quickly with time, except when glucosamine was used as a substrate.

Results from surface enhanced infrared adsorption (SEIRA) spectroscopic measurements at an evaporated gold electrode for the electrocatalytic oxidation of glucose in 0.1 mol dm$^{-3}$ NaOH at -0.3 V and Gaussian simulated spectra indicated that the gluconic acid as a 2-electron oxidation product and/or its analogs adsorbed onto the gold surface. Electrochemical quartz crystal microbalance (EQCM) measurement results, along with surface adsorption results from surface poisoning at the gold electrode during electrolytic reactions, suggested that gluconic acid and/or its analogs adsorbed vertically onto electrode surfaces in a full monolayer packing-like conformation. In the case of the electro oxidation of glucosamine in 0.1 mol dm$^{-3}$ NaOH at -0.2 V, the obtained SEIRA spectra and EQCM results, clearly indicated that the glucosaminic acid as a 2-oxidation glucosamine product did not strongly bind onto the gold electrode surface.

**Keywords**

Electrochemistry, oxidation, glucose, gold, poisoning, monosaccharide
1. Introduction

The electrocatalytic oxidation of glucose has been extensively studied for applications in glucose-oxygen fuel cells and for the development of glucose sensors for medical and food industries [1-11]. The electrocatalytic oxidation of glucose in an alkaline medium was investigated using Cu, Ni, Fe, Pt and Au electrodes. Glucose oxidation reactions at Cu, Ni and Fe electrodes occurring from more positive potentials than ca. 0.6 to 0.7 V (vs. Ag/AgCl), produce formic acid (a 12-electron oxidation product) as the main electro oxidation product [12-17]. Glucose oxidation reactions at a Pt electrode occur at -0.3 V, and glycolic acid (a 6-electron oxidation product) is obtained as a main electro oxidation product [17]. When using a gold electrode, oxidation reactions occur from ca. -0.6 V, and gluconolactone (a 2-electron oxidation product) is generated by the electrolysis at electrode potential of -0.3 V [8,9]. Gold is an attractive metal for the oxidation of glucose, because its oxidation potential is more negative in comparison to other metal electrodes. Therefore, the electrocatalytic oxidation of glucose has been examined extensively. A single crystal gold electrode modified with catalytically active metals (such as Ru, Ag, Cu, Pt, Pd and Cd) by under potential deposition (UPD) gives rise to an effective electrode for the oxidation of glucose. Especially, the Ag-UPD single crystal gold electrode is the most effective in comparison to other metal-UPD gold electrodes [6,7]. However, as described above, previously developed gold-based electrodes which measure glucose oxidation, are significantly inhibited during controlled-potential electrolyses. The inhibition would be attributed to a propensity towards the poisoning of the electrode surface by adsorbed intermediates or electrolytic products.

Recently, we reported the electrocatalytic oxidation of glucose using gold and gold-silver alloy nanoparticle-modified carbon electrodes. Controlled-potential electrolyses with glucose were performed in both alkaline and neutral solutions, and electrolytic products with current efficiencies were determined [9]. Results from electrolyses at gold-silver nanoparticle-modified electrodes
suggest that the design and preparation of catalysts with bifunctional properties are important in achieving high activities and selectivities in the electrocatalytic oxidation of glucose. However, the surface poisoning problem during the electro oxidation of glucose at gold-based electrodes was not solved. Unfortunately, surface poisoning occurs even when gold-based nanoparticle-modified electrodes are used. According to our knowledge, gold surface poisoning has never been investigated in previously published reports.

In the present study, surface poisoning during electrocatalytic oxidations of monosaccharides at gold electrodes were investigated. Glucose, galactose, mannose, allose and talose used as an aldohexose type monosaccharides, and xylose and ribose used as an aldopentose type gave surface poisoning during electrolyses. Galactosamine and mannosamine used as aminosugars, and acetyl-glucosamine and glucuronamide also gave the surface poisoning. On the other hand, glucosamine, an amino sugar, did not give rise to surface poisoning during electrocatalytic reactions. During the electro oxidation of glucose at a gold electrode, it was suggested that the gluconic acid, a 2-electron oxidation product of glucose and/or its analogs adsorbed onto the gold surface based on results from surface enhanced infrared adsorption spectroscopic and electrochemical quartz crystal microbalance measurements. In the case of glucosamine, the adsorbed species was not detected at an electrolytic potential of -0.2 V (vs. Ag/AgCl) in an alkaline medium.

2. Experimental Section

2.1. Chemicals

Scheme 1 shows monosaccharides and related compounds used in this study. D-glucose, D-glucono-1,5-lactone, D-allose, D-xylose, D-talose, D-glucosamine hydrochloride and N-acetyl-D-glucosamine were obtained from Wako Pure Chemical, Japan. D-galactose, D-mannose, D-ribose and D-galactosamine hydrochloride were purchased from Nacalai Tesque, Japan. D-glucuronamide
and D-mannosamine hydrochloride were purchased from Tokyo Kasei, Japan and Aldrich, respectively. All chemical reagents used in experiments described herein were of analytical grade. Water was purified with a Millipore Milli-Q water system.

2.2. Electrochemical and electrochemical quartz crystal microbalance (EQCM) measurements

Cyclic voltammetric measurements and controlled-potential electrolyses were performed with an electrochemical analyzer (ALS/Chi, Model 600A) in a conventional three electrode cell with Ag/AgCl (saturated KCl) as the reference electrode and a Pt plate as the counter electrode. The gold disk (0.02 cm², Bioanalytical Systems) and gold pale (6 cm², 99.95%, Nilaco Co., Japan) electrode as working electrodes were used for cyclic voltammetry and electrolysis, respectively, which were polished with 0.1 and 0.05 µm alumina slurries (Baikalox), followed by successive sonication in water. For electrolytic studies, working and counter electrodes were separated by a glass filter. All potentials were reported with respect to the Ag/AgCl (saturated KCl) electrode.

Electrochemical quartz crystal microbalance (EQCM) measurements were carried out using a UEQ-200 (USI System Co., Japan). Gold film was deposited onto an AT-cut of quartz crystal with a 9 MHz fundamental resonance frequency, and its surface was polished to a mirror like finish. The QCM gold electrode surface (0.152 cm²) was cleaned by the use of a piranha solution (1:3 H₂O₂ (30%) + H₂SO₄ (conc.)) for 3 min, and rinsed with Milli-Q water.

2.3. Surface enhanced infrared adsorption spectroscopic measurements

Surface enhanced infrared adsorption (SEIRA) spectroscopy [18] was carried out using a Bio-Rad FTS-6000 spectrometer, which was purged with dry nitrogen gas. The spectrometer was equipped with a liquid nitrogen-cooled HgCdTe detector. The working electrode was coated with a ca. 20 nm thick gold film (99.99%) evaporated on the flat plane of a Si hemicylindrical prism.
3. Results and Discussion

3.1. Voltammetric oxidation reactions of monosaccharides and controlled-potential electrolyses

Fig. 1 shows typical voltammetric curves at a gold electrode in 0.1 mol dm\(^{-3}\) NaOH aqueous solutions in the presence of 5 mmol dm\(^{-3}\) monosaccharides. Aldohexose type monosaccharides such as glucose, galactose, mannose, allose and talose, and aldopentose type monosaccharides such as xylose and ribose showed well-defined catalytic oxidation peaks from -0.6 to -0.8 V, as shown in Fig. 1a-g. Oxidation reactions of aldehyde groups in both aldohexose and aldopentose type monosaccharides occurred at the aforementioned potentials. For example, the controlled-potential electrolysis of glucose at -0.3 V gave rise to gluconolactone as a 2-electron oxidation product [8]. Catalytic oxidation currents of aminosugars such as glucosamine, galactosamine and mannnosamine were also observed from around -0.6 V in alkaline medium as shown in Fig. 1h-j, which were very similar to voltammetric behaviors of aldohexose and aldopentose type monosaccharides. Electrocatalytic behaviors of acetyl-glucosamine and glucronamide were also similar to those of aldohexose and aldopentose type monosaccharides (Fig. 1k,l). Aldehyde group oxidations of aminosugars, acetyl-glucosamine and glucronamide would occur at the aforementioned potential in alkaline medium.

Controlled-potential electrolyses of monosaccharides, aminosugars and acetyl-glucosamine and glucronamide were performed at gold electrodes in 0.1 mol dm\(^{-3}\) NaOH solutions at potentials ranging from -0.3 to -0.2 V. Fig. 2 shows the change in current ratios (I/Ii) on initial currents (Ii) and currents (I) obtained during electrolyses. Except for the controlled-potential electrolysis of glucosamine, oxidation currents of monosaccharides, aminosugars, acetyl-glucosamine and glucronamide during electrolysis decreased quickly with time, and no current flow was observed.
after 10 to 20 min. The decrease of the catalytic oxidation current would be due to the electrode surface poisoning.

In the case of glucosamine, the electrolytic current flow was not inhibited, and was monitored until the total charge flow reached the equivalent of the theoretically calculated value for the 2-oxidation of glucosamine. After the electrolysis, glucosaminic acid was obtained as a 2-oxidation product of glucosamine with a current efficiency of 100 % [19].

3.2. SEIRA spectroscopic measurements

To investigate gold surface poisoning during electrolyses at -0.3 V in alkaline medium, SEIRA spectroscopic measurements were performed using glucose and gluconosamine as a typical substrates. Fig. 3a shows the SEIRA spectra at an evaporated gold electrode at -0.8 and -0.3 V in 0.1 mol dm\(^{-3}\) NaOH in the presence of 10 mmol dm\(^{-3}\) glucose. Adsorption peaks around 1450 and 1350 cm\(^{-1}\) were observed when the potential was held at -0.3 V. When the electrode potential was held at -0.8 V, which precludes the electrocatalytic oxidation of glucose, no peaks were observed between 1300 to 1550 cm\(^{-1}\). These results led us to hypothesize that surface poisoning could be caused by adsorbed species observed around 1450 and 1350 cm\(^{-1}\), and the species were 2-electron oxidized intermediates or gluconic acid as 2-electron oxidized products. To identify adsorption species, SEIRA spectroscopic measurements were carried out at -0.8 and -0.3 V in gluconic acid, as shown in Fig. 3b. Two broad peaks were observed at both potentials around 1450 and 1350 cm\(^{-1}\), which were almost the same as peaks from the electrolysis of glucose at -0.3 V. At a potential of -0.8 V, the oxidation reaction does not take place on the electrode surface, which provides strong evidence that the adsorption species is gluconic acid molecules and/or its analogs. Frequency analyses were performed using the Gaussian 03 program package [20]. Fig. 3c shows spectra of gluconic acid and its dissociated species in the region of 1250 to 1550 cm\(^{-1}\) as simulated by
Gaussian 03 programs. Obtained and simulated peaks located around 1450 cm\(^{-1}\) for gluconic acid and its dissociated type spectra are attributed to C-H bending, wagging and C-C stretching modes [21-28]. The obtained peak located around 1350 cm\(^{-1}\) in Fig. 3b, though it appears at 1380 cm\(^{-1}\) by Gaussian 03 programs as shown in Fig. 3c, was only observed in the case of the dissociated gluconic acid, which is attributed to the symmetric stretching of -COO\(^-\) [21-28]. The obtained results as described above clearly indicate that adsorption species causing gold surface poisoning during electrolyses around -0.3 V are dissociated gluconic acid molecules and/or its analogs.

Fig. 4a shows the SEIRA spectra at an evaporated gold electrode at -0.8 and -0.2 V in 0.1 mol dm\(^{-3}\) NaOH in the presence of 10 mmol dm\(^{-3}\) glucosamine. No specific peak was observed at both potentials in the region of 1300 to 1550 cm\(^{-1}\) in comparison to that of glucose. Also, no peak was observed, when glucosaminic acid as a 2-electron oxidation product of glucosamine at -0.2 V, was measured at potentials of -0.2 and -0.8 V by SEIRA spectroscopy, as shown in Fig. 4b. Simulated IR spectra of the dissociated glucosaminic acid were obtained by the Gaussian 03 program (Fig. 4c), which indicate that IR peaks corresponding to C-H bending, wagging and C-C stretching modes (located around 1450 cm\(^{-1}\)) and the symmetric stretching of -COO\(^-\) (located around 1350 cm\(^{-1}\)) should be observed, when gluconic acid is adsorbed onto the electrode surface. The electrolysis of glucosamine at a gold electrode at -0.2 V in an alkaline solution was not inhibited by surface poisoning as described in the above section. The obtained SEIRA spectra and simulated spectra together with the electrolysis results for glucosamine, clearly indicate that glucosaminic acid as a 2-oxidation product of glucosamine does not strongly bind onto the gold surface.

3.3. EQCM measurements

In the previous section, from the results of SEIRA spectra, it was indicated that the adsorption of dissociated gluconic acid or its analogs onto a gold electrode surface would induce the surface
poisoning during electrolyses at -0.3 V. To investigate the surface excess of the adsorption species, the EQCM measurements were carried out.

Fig. 5a shows frequency changes in EQCM measurements for glucosamine in 0.1 mol dm$^{-3}$ NaOH, when the potential was held at -0.3 V for 60 min. Significant frequency changes were not observed in comparison to control experiments, indicating that the adsorption species does not exist during the electrolysis of glucosamine at -0.3 V. This obtained result is in agreement with results from SEIRA spectroscopic measurements.

In comparison to results from glucosamine, large frequency changes in EQCM measurements were observed during the electrolysis of glucose at -0.3 V in a 0.1 mol dm$^{-3}$ NaOH solution (Fig. 5b). The frequency quickly decreased about 10 min after the beginning of the electrolysis, and became almost constant. This frequency change behavior is in good agreement with a decrease in current flow during the electrolysis of glucose at -0.3 V in an alkaline solution as shown in Fig. 2a. It is expected that the adsorption species on the gold electrode surface of the EQCM electrode would be gluconic acid or its analogs by SEIRA spectroscopic results. The frequency change was ca. 50 Hz, corresponding to a mass change of ca. 41 ng cm$^{-2}$. Assuming the adsorption species is gluconic acid, the obtained mass change value corresponds to the surface adsorption of ca. 2.1 x 10$^{-10}$ mol cm$^{-2}$. The roughness factor of the EQCM electrode surface was evaluated to be ca. 1.3. Taking into account the roughness factor for the electrode surface, the surface coverage of gluconic acid was expected to be ca. 11 x 10$^{-10}$ mol cm$^{-2}$. This obtained mass change value is in relatively good agreement with the expected value, when gluconic acid molecules vertically adsorb onto the surface with a full monolayer packing-like configuration (ca. 9.0 x 10$^{-10}$ mol cm$^{-2}$) as shown in Fig. 6a. The value of the surface coverage of gluconic acid horizontally adsorbed onto the surface is 5.0 x 10$^{-10}$ mol cm$^{-2}$, with a full monolayer packing-like configuration as shown in Fig. 6b. These results enable us to conclude that gluconic acid and/or its analogs vertically adsorb onto the surface in a full
monolayer-like packing configuration, and give rise to adsorption results observed in the surface poisoning of gold electrodes during electrolyses.

4. Conclusions

In conclusion, surface poisoning during the electrocatalytic oxidation of monosaccharides at gold electrodes were investigated. In cyclic voltammetric studies, the electrocatalytic oxidation of aldohexose and aldopentose type monosaccharides, aminosugars, acetyl-glucosamine and glucuronamide were observed at a gold plate electrode in alkaline medium. However, in controlled-potential electrolysis studies with electrode potential of -0.3 to -0.2 V, current flows for monosaccharides, aminosugars, acetyl-glucosamine and glucuronamide during electrolyses decreased quickly with time, and no current flow was observed after 10 to 20 min, except when glucosamine was used as a substrate.

Results from surface enhanced infrared adsorption spectroscopic measurements and Gaussian simulated spectra suggested that the gluconic acid as a 2-electron oxidation product and/or its analogs adsorbed onto the gold surface during the electro oxidation of glucose at gold electrodes. Furthermore, the EQCM and adsorption results from the surface poisoning of gold electrodes during electrolytic reactions suggested that gluconic acid and/or its analogs adsorb vertically onto the electrode surface with a full monolayer packing-like conformation. In the case of the electro oxidation of glucosamine, the obtained SEIRA spectra and simulated spectra together with EQCM results, clearly indicate that the glucosaminic acid as a 2-oxidation product of glucosamine did not strongly bind onto the gold surface.

Further investigations concerning surface poisoning at gold electrodes are underway to develop catalysts for glucose sensors and glucose-oxygen fuel cell applications.
Acknowledgement

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References


**Figure Captions**

Scheme 1. Structures of aldohexose and aldopentose type monosaccharides, aminosugars, acetyl-glucosamine and glucuronamide.

Fig. 1. Typical voltammetric curves for 5 mmol dm\(^{-3}\) aldohexose (a-e) and aldopentose (f, g) type monosaccharides, aminosugars (h-j), acetyl-glucosamine (k) and glucuronamide (l) at a gold plate electrode in N\(_2\) saturated 0.1 mol dm\(^{-3}\) NaOH solution, and its control curves (broken line). Potential sweep rate: 50 mV s\(^{-1}\). Electrode area: 0.02 cm\(^2\).

Fig. 2. Changes in current ratios (I \(I_i\)) of initial currents (I\(_i\)) and currents (I) obtained during the electrolysis of 10 mmol dm\(^{-3}\) solutions of aldohexose and aldopentose type monosaccharides (a), aminosugars, acetyl-glucosamine and glucuronamide (b) at a gold plate electrode in 0.1 mol dm\(^{-3}\)
NaOH solution (20 ml) at an electrolysis potential of -0.3 ~ -0.2 V. The electrode area of the gold plate electrode was 6 cm².

Fig. 3. SEIRA spectra at an evaporated gold electrode at -0.8 and -0.3 V in 0.1 mol dm⁻³ NaOH in the presence of 10 mmol dm⁻³ glucose (a) and gluconic acid (b), and Gaussian simulated spectra (c).

Fig. 4. SEIRA spectra at an evaporated gold electrode at -0.8 and -0.3 V in 0.1 mol dm⁻³ NaOH in the presence of 10 mmol dm⁻³ glucosamine (a) and glucosaminic acid (b), and Gaussian simulated spectra (c).

Fig. 5. Frequency changes in EQCM measurements for 10 mmol dm⁻³ glucosamine (a) and glucose (b) in a 0.1 mol dm⁻³ NaOH, when the potential was held at -0.3 V.

Fig. 6. Schematic illustration for the gluconic acid molecular adsorption onto a gold surface with a vertically full monolayer packing-like configuration (a) and with a horizontal full monolayer packing-like configuration (b).
The figure shows voltammograms for various sugars compared to Ag/AgCl (sat. KCl) reference electrode.

- **D-Glucose** (a): 4 µA
- **D-Galactose** (b): 4 µA
- **D-Mannose** (c): 4 µA
- **D-Allose** (d): 4 µA
- **D-Talose** (e): 10 µA
- **D-Xylose** (f): 10 µA
- **D-Ribose** (g): 10 µA
- **D-Glucosamine** (h): 10 µA
- **D-Galactosamine** (i): 10 µA
- **D-Mannosamine** (j): 2 µA
- **D-Acetyl-glucosamine** (k): 5 µA
- **D-Glucronamide** (l): 5 µA

**Figure 1**
Figure 2

- **Figure 2a**: Graph showing the decrease in concentration over time for different sugars. The x-axis represents time in minutes, and the y-axis represents the ratio of concentration (I/li). The sugars include D-Glucose, D-Galactose, D-Mannose, D-Altrose, D-Talose, D-Xylose, and D-Ribose.

- **Figure 2b**: Graph showing the decrease in concentration over time for different sugars. The x-axis represents time in minutes, and the y-axis represents the ratio of concentration (I/li). The sugars include D-Glucosamine, D-Galactosamine, D-Mannosamine, D-Acetyl-glucosamine, and D-Glucuronamide.

**Fig. 2**

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Figure 3

(a) Glucose
(b) Gluconic acid
(c) Simulated spectra

1550 1500 1450 1400 1350 1300 1250
Wavenumber / cm\(^{-1}\)

Absorbance
-0.3 V
-0.8 V
0.01
100

Glucose
Gluconic acid
Dissociated gluconic acid

Fig. 3
Fig. 4

a) Glucosamine

b) Glucosaminic acid

c) Simulated spectra

-0.2 V
-0.8 V

Glucosamine

Glucosaminic acid

Dissociated glucosaminic acid

Fig. 4
Figure 5

- **Graph Details**
  - **Y-axis**: \( \Delta f / \text{Hz} \)
  - **X-axis**: Time / min

- **Curves**
  - **Curve a)**
  - **Curve b)**

- **Text**
  - Fig. 5
Fig. 6
Bottom view
Side view

ca. 0.46 nm
ca. 0.73 nm

a) Gold surface

b) Gold surface

Fig. 6
Scheme 1