Electrocatalytic Oxidation of Sugars on Single Crystal Gold Electrodes Modified with Ad-metals in Alkaline Solutions

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Electrocatalytic oxidation of sugars has been examined extensively from various points of view such as wastewater treatment in food industry, blood sugar sensing for medical use, and in fuel cell business. On Cu electrochemical oxidation of glucose and other sugars at potentials more positive than +0.5 V (vs. Ag/AgCl) takes place with the C-C bind cleavage to give formic acid (HCOOH) at a high current efficiency in an alkaline solution (1). The current efficiencies for oxidation of glucose depended on metal electrodes used: for example, 70% on Ni and 50% on Fe (2).

On a Pt electrode, on the other hand. glucose was oxidized at -0.3 V (vs. Ag/AgCl) to give glycolic acid (ca. 65%) as a main product (2, 3). Gold is also an attractive metal (3) and glucose was oxidized to give gluconolactone as a main product (ca. >50%) at –0.35 V (vs. Ag/AgCl) in a 0.1 M NaOH solution, but no more than 2-electron oxidation took place at such negative potentials (4).

In the present study, effects of ad-metals on gold single crystal electrodes on electrochemical oxidation of sugars to develop new better catalytic electrodes for sugar oxidation.

Oxidation of glucose on a single crystal (exa. Au(111)) gold electrode in a 0.1 M NaOH solution took place at ca. –0.4 V (vs. Ag/AgCl) as a typical oxidation peak potential for aldose type monosaccharides such as glucose, maltose, galactose and xylose to give corresponding lactones (2-electron oxidation products). Larger oxidation currents were seen at more positive potentials (around -0.15 V vs. Ag/AgCl). On the other hand, no significant oxidation current was observed at potentials more negative than –0.2 V for ketose such as fructose and sorbose. These results suggest that hydrogen atom bound to C-1 carbon was oxidized at first at negative potentials on gold electrodes.

Similar results were also obtained on both single crystal Au(111) electrodes prepared by both vacuum-evaporation and flame-annealing methods. Catalytic activity was observed in alkaline solutions and became less when the solution pH shifted toward neutral direction.

To understand the effect of ad-metals on a gold electrode, Au(111) surfaces were modified with various ad-metals (deposited ad-adoms were formed from less than monolayers to several monolayers) by using the under-potential deposition (UPD) and other techniques.

On both one-third and one-monolayer Cu ad-metal modified gold electrodes, oxidation potential of sugars shifted toward positive direction (catalytic activity became less than on bare gold surface). Similarly, Co and Cd ad-metal deposited surfaces also gave a positive shift in oxidation potential of glucose. Deposition of Rh and Pd did not give any significant shift in oxidation potential for glucose oxidation, but small oxidation current for gluconolactone was seen. On a Pt deposited surface, although the poisoning occurred on Pt electrode during glucose oxidation was suppressed, catalytic oxidation currents decreased. For Ru and Ir, UPD was not able to complete on Au surfaces in the present experiments.

On the other hand, when Ag was modified partially on the Au(111) surfaces by UPD (at one-third monolayer for Au(111) surface prepared by the flame-annealing method and around monolayer for vacuum evaporated Au(111) surfaces), a better performance for catalytic oxidation of sugars (oxidation potential shifted toward negative direction by ca. 0.1 V and small increase in oxidation current) than at a bare Au(111) electrode was obtained in an alkaline solution .

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