

Electrocatalytic Oxidation of Ethanol on Electrodeposited Palladium Electrode

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Abstract: The oxidation of ethanol in 1.0 mol/L NaOH was studied on Pd/GC electrode prepared by electrodeposition. The results show that (1) Pd/GC electrode can also demonstrate electrocatalytic activity towards the oxidation of ethanol; (2) two backward anodic peaks on the cathodic branch appear when the ethanol concentration is raised up to 0.5 mol/L.

Keywords: Electrodeposition; electrocatalytic oxidation; ethanol.

There are many investigations about the electrocatalytic oxidation of ethanol on the electrode of platinum electrode¹⁻⁵, which are mainly in acid medium. However, to the best knowledge of the author, there are no investigations about the oxidation of ethanol on palladium electrode, let alone on Pd/GC electrode prepared by electrodeposition. According to the experimental results in this paper, Pd/GC electrode is more electroactive to the oxidation of ethanol than to that of methanol in alkaline medium (e.g. in 1.0 mol/L NaOH), based on their oxidation peak potentials which are -0.126V (for ethanol) and -0.098V (for methanol) when the concentrations of the alcohols are 0.1 mol/L. In addition, it is worth pointing out that Pd/GC electrode is even more electroactive for the oxidation of methanol than palladium plate electrode⁶, which has been observed and will be reported in a separate paper.

Preparation of Electrode

Before deposition, glassy carbon electrodes were all polished on a fine abrasion emery paper (6[#]), degreased with acetone, and rinsed with triply distilled water. Pd/GC electrode was obtained with potentiostatic method at -0.3V (*vs* SCE) for 60 s in 0.01 mol/L Pd(NH₃)₂SO₄ + 0.1 mol/L (NH₄)₂SO₄ (pH≈2.0, adjusted with dilute H₂SO₄), the counter electrode was a platinum foil, and the reference electrode was a saturated calomel electrode (SCE). After deposition, all of the electrodes were rinsed with triply distilled water, and disposed in the potential range of -0.6V~0.6V (*vs* Hg/HgO, 1.0 mol/L KOH) by 15 potential cyclings in 1.0 mol/L NaOH to get a relatively stabilized surface state of the electrode. The surface area of the Pd/GC electrode is evaluated by assuming that the

charge in the reduction region of the voltammogram recorded in the base alkaline electrolyte is $424 \mu\text{C}/\text{cm}^2$ for the completion of an adsorbed oxide monolayer (at about 1.5V vs. SHE)⁷.

Electrochemical measurements

The working electrode was Pd/GC. Platinum foil was used as counter electrode, and a mercury/mercury oxide reference electrode (Hg/HgO, 1.0 mol/L KOH) as reference electrode. Highly purified N₂ was bubbled before (for 15 minutes) and during the measurements. The reagents used in this paper were all of analytical grade, and the solutions were prepared from triply distilled water. All of the experiments were carried out on Model 660 Electrochemical Workstation (CH Instrument Inc., USA). The experimental temperature was around 25°C.

Results and Discussion

Cyclic voltammetric behavior of Pd/GC electrode in 1.0 mol/L NaOH

Figure 1 Cyclic Voltammogram of Pd/GC electrode in 1.0 mol/L NaOH.
Potential sweep rate: 50 mV/s.

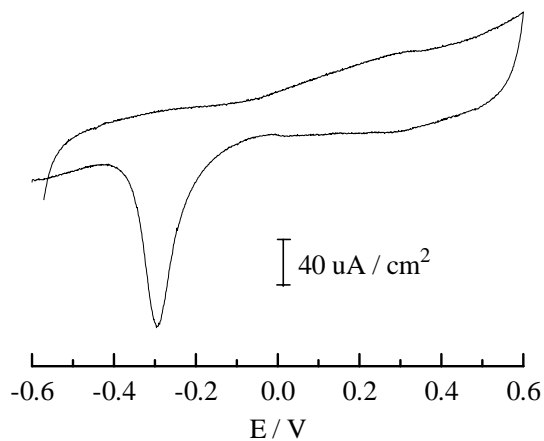


Figure 1 shows the cyclic voltammogram (third scan) of Pd/GC electrode in 1.0 mol/L NaOH. From **Figure 1**, it can be seen that palladium begins to be oxidized at around 0V, and may be further oxidized with the sweep of potential towards positive. On the cathodic scan, the palladium oxide layer is reduced, forming a reduction peak at -0.299V. The cyclic voltammetric behavior of the Pd/GC electrode was a little different from that of palladium wire electrode reported by other authors⁸⁻⁹ under the same experimental conditions—the reduction peak potential of Pd-oxide layer is shifted towards negative by about 10 mV. This is maybe because it is easier for Pd/GC electrode to be oxidized than Pd-wire electrode, and the Pd-oxide layer formed was thicker and more compact, then more difficult to be reduced.

Cyclic voltammetric behavior of Pd/GC electrode in ethanol solution

Figure 2 Cyclic Voltammogram of ethanol with various concentrations on Pd/GC electrode. [ethanol]: (1) 0.1; (2) 0.25; (3) 0.5; (4) 1.0 mol/L. Potential sweep rate: 50 mV/s.

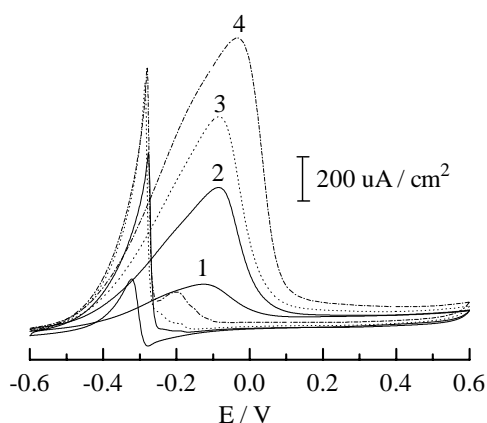


Figure 2 shows the cyclic voltammograms (third scan) of ethanol with various concentrations on Pd/GC electrode in 1.0 mol/L NaOH solution. From **Figure 2**, one can see that (1) the forward and backward anodic peak currents increase, and the corresponding peak potentials are gradually shifted towards positive with the increasing of ethanol concentration which is greater than 0.1 mol/L. Contrarily, the forward anodic peak potential is gradually shifted towards positive and backward anodic peak potential is shifted towards negative with the decreasing of ethanol concentration which is less than 0.1 mol/L (not shown here), *i.e.*, Pd/GC electrode is most electro-catalytically active for the oxidation of 0.1 mol/L ethanol. (2) when the concentration of ethanol is raised up to 0.5 mol/L, two backward anodic peaks appear on the cathodic branch, which should probably be attributed to the oxidation of some intermediates produced on the forward scan. (Further studies about these two peaks show that the appearance of them is influenced not only by ethanol concentration but also by potential sweep rate, times of potential cycling and the lower and upper potential limits under the same ethanol concentration.) (3) the reduction peak current of the Pd-oxide layer decreases and the relative peak potential is shifted towards positive with the increasing of ethanol concentration. For this phenomenon, the former is maybe due to (i) the decrease of the amount of the Pd-oxide formation because of the retardation of ethanol adsorption and oxidation; (ii) the chemical reduction of the Pd-oxide layer by ethanol; (iii) the compensation effect of ethanol oxidation for the second time. The latter, *viz.*, the positive shift of the reduction peak potential, is maybe resulted from the electrocatalytic effect of more amount of the adsorbed intermediates (such as CO_{ads} or $\text{CH}_3\text{CHO}_{\text{ads}}$) with the increasing of ethanol concentration. When the reduction peak potential is shifted towards positive, the corresponding backward anodic peak potential will certainly be shifted towards positive.

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Received 23 December 1998