

Electrochemical Dissolved Hydrogen Sensor Using Securely Adsorbed Platinum Particles on Nitrogen-containing Carbon Electrodes Prepared by Stepwise Electrolysis

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Abstract:

This paper describes an electrochemically activated platinum/carbon electrode incorporating nitrogen atom containing functional groups that was fabricated by stepwise electrolysis. This electrode exhibited specific electrocatalytic activity in relation to hydrogen oxidation reaction as determined by hydrodynamic voltammetry. In spite of relatively large size platinum particles, they are securely adsorbed on the activated carbon electrode compared with electrodeposited platinum on non-treated glassy carbon electrode. Moreover, we successfully developed an electrochemical sensor for dissolved hydrogen using the electrochemically activated carbon electrode modified with platinum particles as the working electrode. Although platinum particles modified N-terminated carbon electrodes using carbon powder materials have been reported, our nitrogen-containing functional groups introduced glassy carbon electrode is first report to use solid electrode for electrodeposition of platinum particles and apply for oxidizing hydrogen molecules. The solid electrodes are more advantageous for developing hydrogen sensors because it is free standing and does not require other processes for electrode fabrication such as high temperature treatment and modification of Nafion.

Key words: Electrochemical Sensor, Dissolved Hydrogen, Stepwise Electrolysis, Electrodeposited Platinum Particles, Electrocatalytic Activity

1. Introduction

Carbon materials have been identified as an electrocatalytic material for the electrochemical determination of various species, and their wide variety of structurally dependent electronic and electrochemical properties [1]. In addition, the chemical modification of carbon surfaces has been used for their fields include electroanalytical chemistry and electrocatalysis [2]. Recently, it has been clarified that nitrogen atoms (N) containing functional groups can be easily introduced onto the glassy carbon (GC) and carbon felt (CF) electrode surface by the electrode oxidation of ammonium carbamate in an aqueous medium at a highly positive electrode potential [3]. More recently, we obtained very interesting results of a novel redox waves between hydrogen ion and hydrogen molecule (H_2) appearing at highly positive potential range after the long-term electrode reduction of the N-containing

functional groups introduced carbon electrode in a strong acid electrolyte. During the electrode reduction of the electro-oxidized carbon electrode in sulfuric acid electrolyte, platinum ion dissolved from platinum wire counter electrode is electrodeposited on the surface of N-containing functional groups introduced carbon electrode. In this paper, we describe that the electrocatalytic oxidation wave of H_2 can be observed by using platinum particles modified N-terminated carbon (Pt-NtC) electrodes. The properties of the electrocatalytic activity for H_2 oxidation have been investigated by employing hydrodynamic voltammetry. Moreover, we developed an electrochemical sensor of dissolved H_2 using Pt-NtC electrode as the working electrode.

2. Experimental

A bare GC electrode was electro-oxidized in ammonium carbamate aqueous solution at +1.1 V (vs. Ag/AgCl) for 60 minutes. Next, the

electro-oxidized GC electrode was electro-reduced in 1.0 M sulfuric acid at -1.0 V (vs. Ag/AgCl) for 20 hours at room temperature. While the electro-reduction of the electro-oxidized GC electrode in sulfuric acid electrolyte, platinum ion dissolved from platinum wire counter electrode is electrodeposited on the electro-oxidized GC electrode surface. Amperometric measurements of H_2 were performed using an electrochemical measurement apparatus based on flow injection analysis (FIA). A working Pt-NtC electrode (6 mm diameter), an aqueous Ag/AgCl (3 M NaCl electrolyte) reference and a platinum counter electrodes were integrated on a radial flow cell. Phosphate buffer (0.10 M, pH 7.0) was used as the carrier solution.

3. Results and discussion

Fig.1 shows the hydrodynamic voltammogram (HDV) of bubbling H_2 gas in 0.10 M phosphate buffer electrolyte (pH 7.0) obtained by using Pt-NtC electrode. The electro-oxidation wave of H_2 appears in the potential range from +0.4 V to -0.6 V. We examined that no oxidation wave of hydrogen molecule was observed when the bare GC electrode was used in place of Pt-NtC electrode. Then, this result means that the electrocatalytic site for H_2 is produced by multielectrolyses of GC electrode surface. Therefore, it can be recognized that the electrocatalytic site acquires its activity by the electrode oxidation at -0.6 V and lose one by further electrode oxidation at +0.4 V. Moreover, we confirmed that the electrocatalytic activity of Pt-NtC electrode for H_2 oxidation did not decrease after ultrasonication for 5 min. This fact indicates that Pt particles on N-containing functional groups are securely adsorbed.

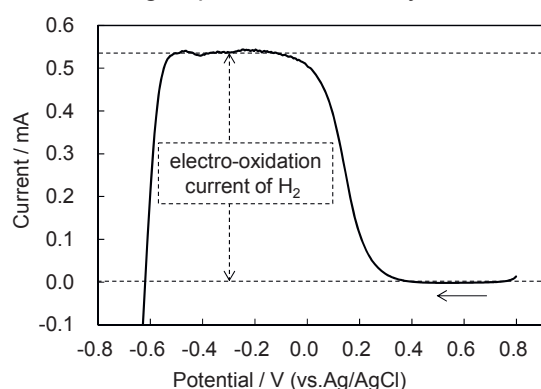


Fig. 1. HDV of bubbling H_2 gas in 0.10 M phosphate buffer solution (pH 7.0). Bubbling rate of H_2 : 50 ml/min. Sweep rate: 50 mV/sec.

We performed an electrochemical sensor based on FIA system of dissolved H_2 using Pt-NtC electrode as the working electrode. The optimal applied potential to measure the peak current was measured to be +0.05 V (vs. Ag/AgCl). When the flow rate was 5 ml/min, the current

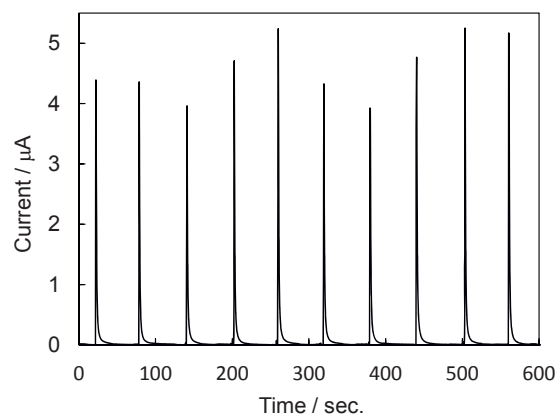


Fig. 2. Current vs. time curve obtained for the repetitive measurement of dissolved H_2 .

response was the maximum. In case of the optimal conditions for FIA system, typical current vs. time curve obtained by the repetitive measurement of the H_2 dissolved in medium are shown in Fig. 2. This curve indicates that the measurement of dissolved H_2 is finished completely in a very short time (ca. 15 sec.), and no detectable residual current fluctuation appears after the electrolysis is completed. The relative standard deviation (RSD) for tenth successive measurements was 11.8 %. The concentration of H_2 is so unstable because the H_2 dissolved in medium is gradually escaped from the solution to air, and the improvement of the stability of the concentration of dissolved H_2 water is now in progress.

4. Conclusion

The Pt-NtC electrode was prepared by the electrode reduction in 1.0 M sulfuric acid followed by the electrode oxidation in ammonium carbamate aqueous solution. The Pt-NtC electrode exhibited an electrocatalytic activity of H_2 oxidation reaction at highly positive potential range in the hydrodynamic voltammogram. The typical current vs. time curve was obtained by the repetitive measurement of H_2 dissolved in neutral medium. This result shows that the dissolved H_2 concentration can be easily monitored by using Pt-NtC electrode, and it can be expected that the electrochemical modification of carbon electrode can open the way for convenient measurement method of H_2 dissolved in water.

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