Development of an Amperometric Acetic Acid Sensor in Organic System

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Abstract

An amperometric method was developed by using a lead working electrode in acetonitrile organic solution for detecting acetic acid. The mechanisms of electrochemical reaction were corresponding to the reduction of acetic ions in acetonitrile organic solution. The steady state amperometric current resulted from the reduction of acetic ions to produce the aldehyde in a two-electron process. In the organic sensing system, the organic salt, [CH3(CH2)3]4NBF4, was added into the solution to increase the conductivity of the acetonitrile organic solution. The potential window of limiting current of acetic ion reduction at the lead interface was determined in acetonitrile electrolyte in the range from $-1.5$ to $-2.3$ V (vs. Ag/Ag⁺ in acetonitrile). The effect of supporting electrolyte concentration on sensitivity was also discussed. The response time of acetic acid in the sensing system was 30 s. Meanwhile the stability of the sensing system was also tested.

Key Words: Acetic Acid, Sensor, Lead, Amperometry, Acetonitrile

1. Introduction

The acetic acid is an important raw material commonly used in food, solvent, medical and chemical industries, etc. A sensor to determine concentration of acetic is useful. Particularly, the sensor can be used for a medical disaffection purpose to detect concentration of acetic acid dissociated from peracetic acid solution that is a low temperature disaffection agent that can oxidize and disrupt bacteria and viruses [1-3]. Thus, disaffection efficiency can be directly evaluated in the acid-peracetic acid system. Besides, the acetic acid concentration contained in the wastewater to drain away has to the satisfied the regulation of government.

In conventional, acetic acid can be analyzed by several methods such as: acid-base titration [4], UV spectroscopy [5] and gas chromatography [6,7]. But these methods are time consuming or costly for the complicated instruments. Currently some sensor techniques are engaged in looking for immediately detecting the acetic acid. For examples, an enzyme electrode immobilized trichosporon brassucae was used to indirectly analyzed acetic acid compound in solution based on a property of certain bacteria which digested the acetic acid and produced the oxygen, then the oxygen was detected by a commercial amperometric oxygen sensor [8] and estimated the acetic acid concentration indirectly. An AT-cut piezoelectric crystal coated with diethylenetriamine film was employed for selectively adsorbed the acetic acid gas to change the crystal’s vibration frequency [9]. These sensor also exist some problems such as the enzyme electrode has short lifetime and the electric quartz crystal sensor has a high interference with humidity. The semiconductor sensor is based on the ISFET to change the voltage between the sensing interfaces adsorbed by hydrogen ions [10].

In order to monitor acetic acid concentration,
an acetic acid amperometric sensor was developed by preparing in the organic system including the lead working electrode in order to prevent the reduction of water containing few amounts in the organic solution. The chosen organic solvent, acetonitrile, is one of the most used aprotic solvents, which is suitable for anodic and cathodic reactions. It is an excellent solvent for many substrates and salt solutions showing an appropriate conductivity due to its high dielectric constant ($\varepsilon = 37$) [11].

2. Experimental

2.1 Chemical Reagents

Acetonitrile, acetic acid, silver nitrate, and tetrabutylammonium tetrafluoborate (TBAT) were purchased from Riedel-deHaen. All chemical reagents used were guaranteed assay and the 99.9% purity. The lead foil was specified as 1 cm$^2$, 99.9% purity. The acetonitrile was pretreatment by molecular sieve to remove the residual water and impurities before using.

2.2 Electrode Material and Sensing Conditions

Some of the cathodic materials are suitable for electrosynthesis reaction such as mercury, lead, tin, platinum and carbon [11,12]. But only the lead electrode has response current for the reduction of acetic ions in the sensing system. The Ag/Ag$^+$ reference electrode is homemade by dissolving the silver nitrate in acetonitrile contacting with silver wire and the silver ions are equilibrium with the silver wire at the interface [13]. The sensing performance including sensitivity and response time was examined by changing the acetic acid concentration and measuring the steady state limiting current. The potential window of acetic acid reduction was obtained by sweeping the linear potential from $-1.0$ to $-3.5$ V (vs. Ag/Ag$^+$ in acetonitrile) with a rate of 100 mV/s.

2.3 Sensing System

The sensing system was composed of an undivided cell with working, counter, and reference electrodes. The cell was made by Pyrex glass containing the volume of solution about 50mL and dissolved the supporting electrolyte. The prepared working electrode, lead foil, was polished and washing with hydrogen chloride aqueous solution to remove the oxides before using. The response current and applied potential was controlled by the potentiostat, EG&G 273A. The cathodic reduction of acetic acid was carried out by applied a negative potential and the response current was recorded with time when acetic acid concentrations were changed. The sensitivity was obtained by step change of acetic acid concentration. After response current approaching to a steady state in etch step concentration, the slope of current change with concentration per unit area can be estimated as:

$$S = \frac{\Delta I}{(\Delta C \times A)}$$

where S is sensitivity which the current based on the concentration and geometric area, $\Delta I$ (mA) is reducing current and is defined as positive value, and $\Delta C$ is difference of acetic acid concentration (ppm), and A is the geometric area of working electrode (cm$^2$).

3. Results and Discussion

3.1 Determination of Potential Window

Figure 1 shows the cyclic voltammograms of the lead electrode in the acetonitrile solution. The results reveal that the lead electrode behaves no redox manner between the potential ranges from $-1.0$ to $-3.5$ V (vs. Ag/Ag$^+$ in acetonitrile) with acetic acid free. After adding the acetic acid, the reduction current was enhanced because of acetic acid reduction. The reduction peaks of acetic acid are located at $-1.65$ and $-2.3$ V (vs. Ag/Ag$^+$ in acetonitrile), respectively. It is corresponding to the two electron-process of acetic acid reduction to produce the aldehyde as following [11,14,15]:

$$RCOOH + 2e^- \rightarrow RCHO + H_2O$$

The potential window of the lead electrode to reduce the acetic acid is shown in Figure 2. The steady-state I-E curves were used to obtain the limiting current. In the reduction reaction, it is convenient to define the reduction potential and reduction current as positive value. On the other hand, the electrochemical reaction was kinetically controlled and the current increased with applied potential before 2.0 V (vs. Ag/Ag$^+$ in acetonitrile). When the reaction reached the mass-transfer control, the boundary layer approached steady state and the oxidation current was kept constant in the potential range from 1.5 to 2.3 V (vs. Ag/Ag$^+$ in acetonitrile). In this range, the limiting current does not changed with applied potential but is proportional to the concentration of analyte and can be described as following [13]:

$$\text{S} = \frac{\Delta I}{(\Delta C \times A)}$$

where $\text{S}$ is sensitivity which the current based on the concentration and geometric area, $\Delta I$ (mA) is reducing current and is defined as positive value, and $\Delta C$ is difference of acetic acid concentration (ppm), and $A$ is the geometric area of working electrode (cm$^2$).
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Figure 1. Cyclic voltammograms of lead electrode in acetonitrile salt solution, dot line: acetic acid free; solid line: acetic acid 1000 ppm; scanning conditions: W (Pb, 1 cm²), C (Pt, 1 cm²), RE (Ag/Ag+ in acetonitrile); supporting electrolyte: 0.01 M TBAT; scan rate: 100 mV/s; Temp: 25 °C; stirred rate: no agitation

Figure 2. The I-E curve at different acetic acid concentrations, measuring conditions: W (Pb, 1 cm²), C (Pt, 1 cm²), RE (Ag/Ag⁺ in acetonitrile); supporting electrolyte: 0.01 M TBAT; Temp: 25 °C; stirred rate: no agitation

\[ \text{i}_{\text{lim}} = \frac{nFDC_b}{\delta} \quad (3) \]

where \( \text{i}_{\text{lim}} \) is the current approaching steady state, \( n \) is electron transfer number, \( F \) is Faradic constant, \( D \) is the diffusivity, \( C_b \) is the bulk concentration of analyte, and \( \delta \) is the boundary layer thickness.

3.2 Effect of Supporting Electrolyte Concentration

Figure 3 shows the effect of electrolyte concentration. The results indicated that at low TBAT concentration, the sensitivity was proportional to the supporting electrolyte concentration and the conductivity was controlled by ion concentration. The sensitivity decreased obviously when TBAT concentration was larger than the 0.01 M, it is suggest that ions shielding the lead electrode between the acetic ions at high TBAT concentration. Meanwhile, the viscosity of acetonitrile increases with the TBAT concentration. The optimum concentration of TBAT is 0.01 M for measuring the acetic acid in acetonitrile.

3.3 Amperometric Measurement

The typical current response depended on the acetic acid concentration as shown in Figure 4. The results indicated that the base line of lead electrode approached the steady state at the beginning of a run and the background current was 0.11 mA in the batch sensing system. After adding 100 ppm acetic acid in the test chamber, the current rose from 0.11 to 0.13 mA and then the reduction reaction of acetic acid reached equilibrium at the lead surface. The response time of the current was 90% that of the steady state current was 30 s. The response time was faster than that of other types of acetic acid sensors [8,9,16].

Figure 5 showed the calibration curve of the acetic acid concentrations corresponding to the response currents, which based on the background. The calibration curve passed through the zero point and resulted a straight line. The curve behaved the good linear relationship in the acetic acid concentration from 0 to 1000 ppm and had \( R^2 = 0.990 \). The results of linear fit was \( Y = 0.135X + 0.000221 \). The sensitivity in the lead
sensing system was 0.135 μA/(ppm × cm²).

3.4 Stability Test

The stability test including sensitivity and response time was also performance as shown in Figure 6. The lead was not pretreated after each running test. During the testing period of 60 days the sensitivity showed a little vibration and the change was smaller than 20%. The sensitivity dropped to 28% after the 90 days but the response time increased to 100 s. It is possible that the aldehyde producing from the reduction of acetic ions adsorbs onto the lead surface and difficultly diffused away. Thus the surface of lead electrode must be renewed in several sensing processes to increase the reproducibility.

4. Conclusions

The amperometric acetic sensor made by using lead as the working electrode was developed and its sensing characteristics were tested. The optimum sensing condition was: applied potential −2.2 V (vs. Ag/Ag⁺ in acetonitrile), 0.01 M TBAT concentration in acetonitrile solution. In the optimum sensing condition, the acetic acid concentration and response current had good linearity with R² = 0.9900 and the sensitivity was 0.135 μA/(ppm × cm²). The stability test of lead electrode in acetonitrile salt solution was 90 days and the sensitivity drifted in 20% within 60 days.

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