

An Amperometric Acetone Sensor by Using an Electro-Deposited Pb-Modified Electrode

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An amperometric acetone sensor was developed by using an electrodeposited Pb electrode in a sodium tartrate electrolyte. The major factors determining the electrode and sensing characteristics such as the applied potential, electrodeposition current density, electrodeposition temperature, agitation rate, and sensing temperature were explored. The best conditions for preparation of the electrodeposited Pb electrode were obtained at a 30 mA cm^{-2} electrodeposition current density and a 30°C electrodeposition temperature. Additionally, the optimal sensing conditions are a 155 rpm agitation rate and 50°C sensing temperature with the applied potential in the range from $-2.25 \sim -2.35 \text{ V}$ (vs. Ag/AgCl). The results also revealed that the electrodeposited Pb electrode has a good linearity between the response current and the acetone concentration. This type of acetone sensor has excellent selectivity and shows the highest sensitivity at $8 \mu\text{A ppm}^{-1} \text{ cm}^{-2}$.

Key words: Acetone, Sensor, Lead, Electrodeposited Pb, Amperometry

Introduction

Acetone is one of the important metabolite components in the circulated blood of the human body. According to medical reports, diabetic patients have a higher acetone concentration in their expiration gas, blood and spittle [1–2]. Thus, to determine the concentration of acetone is necessary for our health concerns. Currently, many analytical techniques have been developed to measure the concentration of acetone, such as gas chromatography, liquid chromatography, electrochemical methods, mass spectroscopy and sensors [2–8]. Among these, sensors may offer the most practical methods owing to their convenience, low price, and accuracy.

Although some acetone sensors have been developed such as an adsorption semiconductor sensor with a sensing layer containing tin oxide doped with antimony [2], image detection of acetone using light addressable potentiometric sensors [6], quartz crystal microbalance sensors modified with an Ag^+ -ZSM-5 film [7] and a chemiluminescence (CL) based gas sensor made of $\gamma\text{-Al}_2\text{O}_3$ [8], these sensors had shortcomings such as poor selectivity, higher operating temperature and long response time. In order to address these drawbacks, the aim of this study was to design a novel amperometric acetone sensor. An electrochemical method with an electrodeposited Pb electrode in a sodium tar-

trate electrolyte is used to detect the acetone concentration. Different electrode conditions were investigated to optimize the sensing characteristics. The characteristics of this acetone sensor such as its sensing range, sensitivity and response time were also explored.

Experimental Section

Sensing electrodes preparation

Deionized (DI) water and analytical-reagent grade chemicals were used for all experiments. The Pb strip (Alfa Aesar, USA) was ultrasonically cleaned in 0.1 M HNO_3 solutions and then washing thoroughly with DI water. The electrodeposited Pb films were prepared by cathodic deposition of Pb^{2+} from the solutions at a Pb substrate. The solutions contained $0.63 \text{ M Pb(BF}_4)_2$, 0.68 M HBF_4 , $0.43 \text{ M H}_3\text{BO}_3$, and 0.003 M PEG . The entire electrochemical deposition process was controlled galvanostatically. A carbon strip and Ag/AgCl (in saturated KCl) were used as the counter and reference electrodes, respectively, in the Pb deposition cell. The prepared films were partially sealed with Teflon tape to leave a working electrode area of 1 cm^2 .

Electrodes characterization and sensing procedure

The structure of the electrodeposited Pb electrode was characterized using an X-ray diffractometer (Rigaku/max3.V) with Cu-K_α radiation. The scanning diffraction angle range was from 160 to 30° in 2θ scale at a speed of

4° min^{-1} and the obtained patterns were identified according to the PCPDFWIN-power diffraction file.

A three-electrode electrochemical cell was used as sensing system. An aqueous solution containing 0.1 M sodium tartrate was added into the Pyrex flask. The electrodeposited Pb electrode and platinum foil were used as working and counter electrode, respectively. An EG&G 273A potentiostat was used to control the potential and record the corresponding current. All potentials were specified to the reference electrode, Ag/AgCl (in saturated aqueous KCl solution). After choosing the properly applied potential such that mass transfer of acetone to the electrode surface was the rate-determining step, the sensing process could be carried out. When the background current was stable, a desired amount of acetone solution was added into the test chamber and the amperometric response current was recorded. The response current as related to the acetone concentration, divided by the electrode area, was defined as the sensitivity.

Results and Discussion

Determination of the potential window

The I-E curve of the electrodeposited Pb-modified electrode for reduction of acetone in 50 ppm acetone aqueous solution is shown in Fig. 1. The working electrode for this run was prepared at the constant current density of 30 mA cm^{-2} for 2 h. The applied potential range was from -1.6 to -2.6 V and the scan rate 0.1 mVs^{-1} . The response current was kept constant at 11 mA in the potential range from -2.25 to -2.35 V . The potential region is called the limiting current region, and 11 mA is the mass controlled current of 50 ppm acetone. Since -2.3 V was the middle value

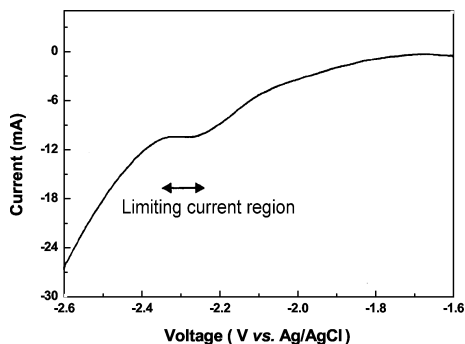


Fig. 1. The IE curve of an electrodeposited Pb electrode for reduction of acetone in 50 ppm acetone aqueous solution. Preparation conditions of the electrode: current density, 30 mA cm^{-2} ; temperature, 25°C ; agitation rate, 155 rpm; electrodeposition time, 2 h. Scanning conditions: scan rate, 0.1 mVs^{-1} ; sodium tartrate electrolyte, 0.1 M; temperature, 25°C .

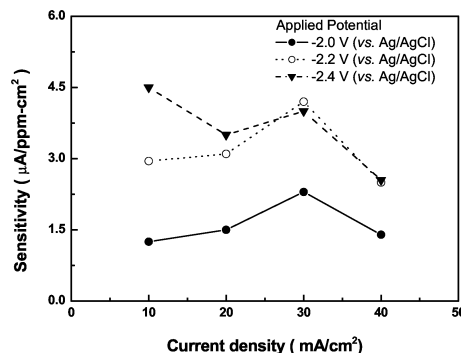


Fig. 2. The correlation between sensitivity and electrodeposition current density at different applied potentials. Preparation conditions of the electrode: temperature, 25°C ; agitation rate, 155 rpm; electrodeposition time, 2 h. Scanning conditions: agitation rate, 155 rpm; sodium tartrate electrolyte, 0.1 M; temperature, 25°C .

of this potential window, it was chosen as the sensing potential for detecting acetone concentrations.

Effect of electrodeposition current density and sensing applied potential

The effect of electrodeposition current density on sensitivity of the acetone sensor at various applied potentials was studied as shown in Fig. 2. The results show that the increase of sensitivity is obviously accompanied by an increase of the applied potential at the lowest electrodeposition current density of 10 mA cm^{-2} . As the electrodeposition current density was larger than 30 mA cm^{-2} , the sensitivity of the acetone sensor was not influenced by the applied potential in the range from -2.2 to -2.4 V . The electrodeposited Pb electrode prepared at the current density of 30 mA cm^{-2} has a higher sensitivity ($4 \mu\text{A ppm}^{-1} \text{ cm}^{-2}$) than that prepared at the current density of 40 mA cm^{-2} . Thus, the current density of 30 mA cm^{-2} was selected for further studies.

Effect of electrodeposition temperature

The effect of the electrodeposition temperature on the sensitivity of the electrodeposited Pb electrode was followed as shown in Fig. 3. The results show that increasing the electrodeposition temperature slightly increases the sensitivity. The XRD measurements of electrodeposited Pb electrodes prepared at various temperatures are shown in Fig. 4. The XRD patterns indicate that Pb crystals were well formed. As the electrodeposition temperature was above 30°C , the inten-

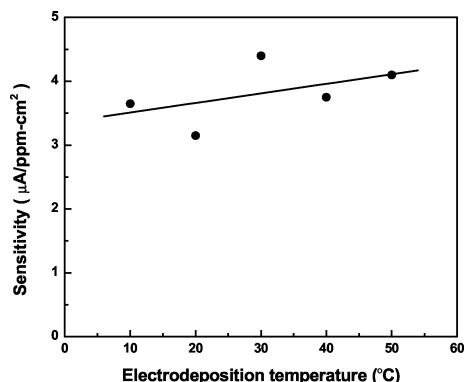


Fig. 3. Effect of electrodeposition temperature on sensitivity of acetone sensing. Preparation conditions of the electrode: current density, 30 mA cm^{-2} ; agitation rate, 155 rpm; electrodeposition time, 2 h. Sensing conditions: applied potential, -2.3 V ; agitation rate, 155 rpm; sodium tartrate electrolyte, 0.1 M; temperature, 25°C .

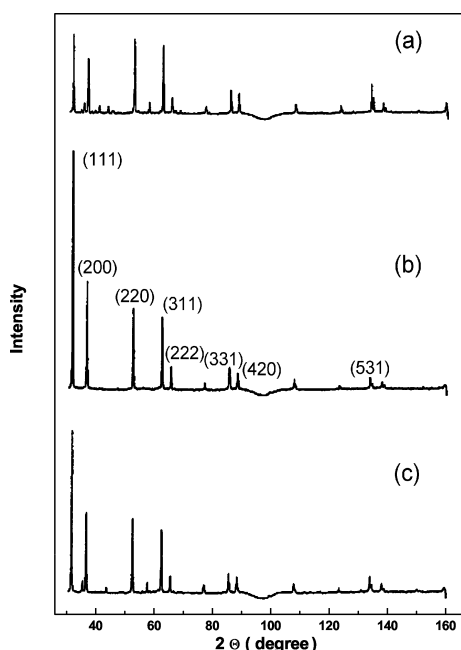


Fig. 4. X-ray diffraction patterns ($\text{Cu-K}\alpha$ radiation) of the electrodeposited Pb electrode prepared at various temperatures (a) 25°C ; (b) 30°C ; (c) 40°C .

sity of the preferred orientation of (111) was enhanced. It implied that the preferred orientation of (111) of Pb is of a benefit for the acetone sensing.

Amperometric measurement

The typical current response curve of the electrodeposited Pb electrode was obtained at the applied po-

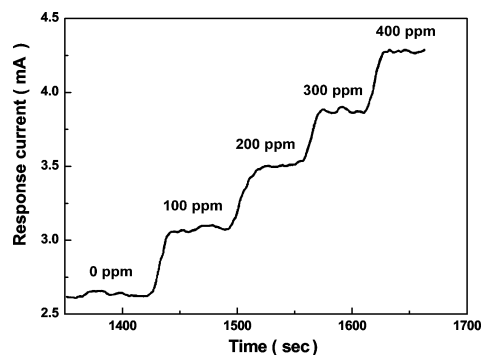


Fig. 5. Amperometric response of the electrodeposited Pb electrode. Preparation conditions of the electrode: current density, 30 mA cm^{-2} ; temperature, 30°C ; agitation rate, 155 rpm; electrodeposition time, 2 h. Sensing conditions: applied potential, -2.25 V ; agitation rate, 155 rpm; sodium tartrate electrolyte, 0.1 M; temperature, 25°C .

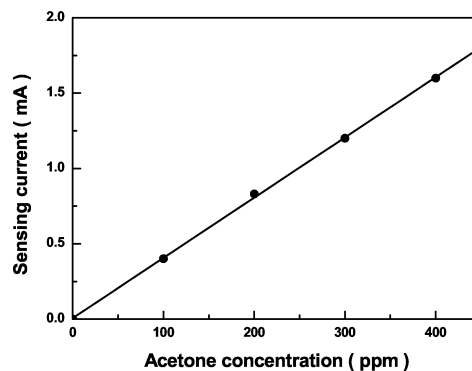


Fig. 6. Typical calibration plot of the electrodeposited Pb electrode for acetone sensing. Preparation and sensing conditions were the same as for Fig. 5.

tential -2.25 V as shown in Fig. 5. The working electrode in this test was prepared at 30 mA cm^{-2} , 30°C for 2 h. After the background current was stable, acetone solution was injected into 0.1 M sodium tartrate to increase the acetone concentration in the chamber from 0 to 100 ppm. Once the system had reached its steady state value, successive portions of acetone solution were added into the electrolyte. The results also showed that the response time and increment of response current were almost the same after each step of acetone addition.

The steady state values of the response current in Fig. 5 were plotted against the concentration of acetone as shown in Fig. 6. The linear range of acetone concentration spanned from 100 to 400 ppm with $R^2 = 0.99$. The sensitivity of this sensor was $4.16 \mu\text{A ppm}^{-1} \text{cm}^{-2}$.

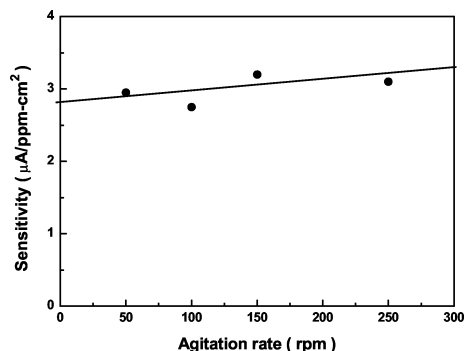


Fig. 7. Effect of agitation rate on sensitivity of acetone sensing. Preparation conditions of the electrode: current density, 30 mA cm^{-2} ; temperature, 28°C . agitation rate, 155 rpm; electrodeposition time, 2 h. Sensing conditions: applied potential, -2.3 V ; sodium tartrate electrolyte, 0.1 M; temperature, 25°C .

Effect of agitation rate

The effect of the agitation rate on the sensitivity of the electrodeposited Pb electrode was studied as shown in Fig. 7. When the agitation rate increased from 60, 100, 155 to 250 rpm, the sensitivity was 2.7, 2.9, 3.2 and $3.1 \mu\text{A ppm}^{-1}\text{cm}^{-2}$, respectively. The best sensitivity was obtained at the agitation rate of 155 rpm. An increase of the agitation rate can decrease the thickness of the boundary-layer and further increase the sensitivity. However, the sensitivity of the acetone sensor is not strongly dependent on the agitation rate in the range from 60 to 250 rpm.

Effect of sensing temperature

The effect of the sensing temperature on the response current for 400 ppm acetone was studied as shown in Fig. 8. When the sensing temperature increased from 20 to 40°C , the sensitivity of the acetone sensor increased from 4 to $8 \mu\text{A ppm}^{-1}\text{cm}^{-2}$. As we know that the diffusion rate increases as the temperature increases, the number of acetone molecules that diffuse to the surface of the electrode increases with the increasing of the temperature and results in a higher sensitivity of the acetone sensor.

Test of selectivity

Since glucose and isopropyl alcohol are present in diabetic patients' blood, they were tested as potential interfering species. The comparison of the steady state amperometric response of acetone, glucose, isopropyl alcohol is shown in Fig. 9. Clearly, there was almost

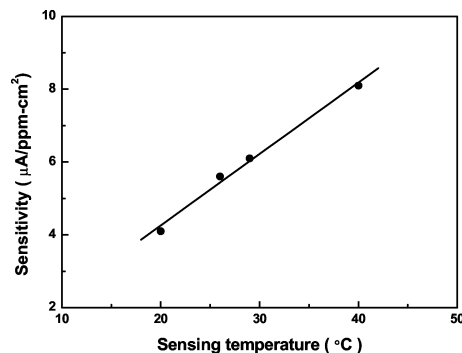


Fig. 8. Effect of sensing temperature on sensitivity of acetone sensing. Preparation conditions of the electrode: current density, 30 mA cm^{-2} ; temperature, 25°C . agitation rate, 155 rpm; electrodeposition time, 2 h. Sensing conditions: applied potential, -2.3 V ; agitation rate, 155 rpm; sodium tartrate electrolyte, 0.1 M; temperature, 25°C .

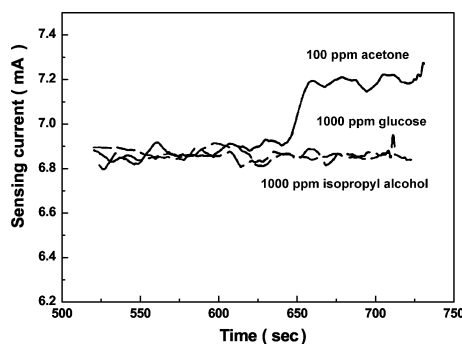


Fig. 9. The selectivity of the acetone sensor by using electrodeposited Pb electrode.

no response current for glucose and isopropyl alcohol. This observation indicates that using electrodeposited Pb as working electrode for acetone detection has excellent selectivity.

Conclusions

An electrochemical acetone sensor using electrodeposited Pb as the working electrode was developed and the characteristics of the sensor were tested resulting in a successful acetone sensor. The relationship between the response current and the acetone concentration is linear in the range of acetone concentrations from 100 to 400 ppm. The response of this sensor is fast within few seconds with the best sensitivity at about $8 \mu\text{A ppm}^{-1}\text{cm}^{-2}$. As optimum electrodeposition conditions an electrodeposition current density of 30 mA cm^{-2} at 30°C is recommended. Additionally, the best sensing conditions were 155 rpm agitation rate and 50°C sensing temperature with the applied

potential in the range from $-2.25 \sim -2.35$ V (vs. Ag/AgCl). The sensor shows good selectivity toward acetone.

Acknowledgements

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