Journal of Electroanalytical Chemistry 651 (2011) 160–165

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Comparison of Pt and Ni foil electrodes for amperometric sensing of ascorbic acid

Yu-Ching Weng *, Yu-Lun Hsiao

Department of Chemical Engineering, Feng Chia University, Taichung 407, Taiwan

ARTICLE INFO

Article history:
Received 17 August 2010
Received in revised form 23 November 2010
Accepted 26 November 2010
Available online 1 December 2010

Keywords:
Pt
Ni
Ascorbic acid
Amperometric sensor
Electrocatalysis

ABSTRACT

Metal foils made of Pt and Ni show amperometric responses to ascorbic acid (H_2A). This study compares the sensitivity of a Pt foil electrode to that of a Ni foil electrode. Both electrodes were highly sensitive to H_2A; the Pt foil electrode was more sensitive at an applied potential of 0.2 V vs. Ag/AgCl in KOH than it was in H_2SO_4 and Na_2SO_4. These electrodes showed excellent selectivity for H_2A over glucose, fructose, sucrose, tartaric acid, citric acid, oxalic acid, and sodium benzoate. Both electrodes displayed rapid responses and good linearity levels in the range from 0.57 to 5.68 mM. Compared to the Ni foil electrode, the Pt foil electrode possessed better long-term stability, because it maintained 99% of its initial sensitivity for more than 67 days.

1. Introduction

Ascorbic acid (H_2A), commonly known as vitamin C, is an essential nutrient in human diets; it is found in many foods, such as citrus fruits and leafy vegetables. It plays an important role in preventing diseases like scurvy; it scavenges free radicals. H_2A is widely used as an anti-oxidant in food processing, pharmaceutical formulations, and clinical applications. Rapid, sensitive real time detection of H_2A concentration is of great interest. Many analytical methods have been developed for determination of H_2A, including titrimetry [1], enzymatic methods [2,3], spectrophotometry [4,5], chemiluminescence [6], electroanalysis [7–12] and chromatography [14,15]. Among these methods, electroanalysis is noteworthy because it offers simplicity, convenience, and sensitivity.

Amperometric determination of H_2A in aqueous solutions has been extensively explored. High overpotential in H_2A oxidation can interfere with practical applications; several chemically modified electrodes (CME) have been designed to reduce overpotential. Table 1 summarizes the operating conditions, sensitivity levels, and H_2A concentration ranges for various CMEs [11–13,16–28]. Glassy carbon (GC) and carbon paste electrodes (CPEs) are often used as CME substrates. Conducting polymers, such as polyaniline, polypyrrole, and polythiophene, have been used to immobilize mediators, complexes, and desired chemical species on substrate surfaces. Killard et al. [11] fabricated an H_2A sensor by drop-casting dodecylbenaebe sulphonic acid-doped polyaniline nanoparticles onto a screen-printed carbon paste electrode. At a very low applied potential, namely 0 V vs. Ag/AgCl, the sensor was operable but its sensitivity was only 10.75 $\mu A\ cm^{-2}\ mM^{-1}$. Pillai et al. [12] developed an octacyanomolybdate-doped-poly (4-vinylpyridine) modified electrode for electrocatalytic oxidation of H_2A that showed a very high sensitivity, 687 $\mu A\ cm^{-2}\ mM^{-1}$. However, this sensor operated at a high applied potential, 0.57 V vs. saturated calomel electrode (SCE). Even though extensive research has been done on CMEs, most CME preparation procedures are complicated and costly.

It has been reported that the direct electrochemical oxidation of H_2A at a bare Pt electrode requires potentials a potential of 0.6 V vs. SCE [11], but this has only been established for acidic solutions with low pH values. Relatively little work has been presented on electrochemical oxidation of H_2A in alkaline solutions; any substantial negative movement of the potential window might reduce the applied potential. For biological applications, if electrochemical oxidation of ascorbic acid were performed in acid or alkali solutions, real samples should be acidified or alkalized before sensing. One aim of this study is to discover whether Pt foil electrode at low operating potential can detect H_2A amperometrically.

Manufacturers prefer to use low-cost materials, such as non-noble metals, for mass-produced H_2A sensors. Pournaghi-Azar et al. [29] deposited Ni on Al and modified the surface with nickel pentacyanonitrosylferrate (NiPCNF) film. The NiPCNF/Ni/Al electrode showed excellent electrocatalytic activity toward H_2A oxidation. Kalakodimi and Nookala [27] reported electrooxidation of H_2A on a polyaniline-deposited nickel electrode in 0.1 H_2SO_4 solutions; the best sensitivity of their electrode was about 190 $\mu A\ cm^{-2}\ mM^{-1}$ at an applied potential of 0.3 V vs. SCE. These studies fabricated H_2A sensors with nickel-based electrodes, but, to the best of our

---

* Corresponding author. Tel.: +886 4 24517250x3689; fax: +886 4 24510890.
E-mail address: ycweng@fcu.edu.tw (Y.-C. Weng).

1572-6657/$ - see front matter Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2010.11.031

Table 1
Comparison of various amperometric H_2A sensors.

Sensing electrodes	Applied potential (V)	Electrolyte	Sensitivity ($\mu A\ cm^{-2}\ mM^{-1}$)	H_2A conc. range (mM)	Ref.
Dodecylbenzene sulphonic acid – doped polyaniline nanoparticles modified carbon paste electrode (CPE)	0 (vs. Ag/AgCl)	Phosphate buffer (pH = 6.8)	10.75	0.5–8	[11]
Screen-printing ruthenium dioxide electrode	0.1 (vs. Ag/AgCl)	Phosphate buffer (pH = 7.4)	2.67	0–4	[16]
Congo red immobilized on a silica/aniline xerogel modified CPE	0.18 (vs. SCE)	0.5 M KCl			
(pH = 7)	4.53	0.79–6.7	17		
Polypyrrole/$Fe(CN)_6^{3-}$/Fe	0.2 (vs. Ag/AgCl)	Phosphate buffer (pH = 7)	240[a]	0.5–9	[18]
Copolymerization of 3,4-dihydroxybenzoic acid and aniline at microdisk gold electrode	0.2 (vs. SCE)	Phosphate buffer (pH = 7)	210	0.1–10	[19]
β-Cyclodextrin-ferrocene inclusion complex modified CPE	0.2 (vs. SCE)	NH_3-NH_4Cl buffer (pH 10.0)	65.46	$5 \times 10^{-3} \sim 0.01$	[20]
			46.92	0.01–0.1	
			50.14	0.1–1	
$Ni(Me_2(CH_3CO)_2$ tetraeno$N_4)$ complex modified glassy carbon electrode (GCE)	0.22 (vs. Ag/AgCl)	Phosphate buffer (pH = 6.6)	23.3	0.03–6.2	[21]
Polypyrrole nanowire modified graphite electrode	0.25 (vs. SCE)	0.1 M phosphates	46.51	0.5–20	[22]
Dihydroxybenzaldehyde (DHB) isomers modified GCE	0.25 (vs. SCE)	Phosphate buffer (pH = 7)	6.2 (2,5-DHB)	0.16–3	[23]
			8.45 (3,4 DHB)	0.05–3	
Terbium hexacyanoferrate modified carbon ceramic electrodes	0.28 (vs. SCE)	0.5 M KCl			
(pH = 7)	139[a]	$5 \times 10^{-4} \sim 0.1$	13		
Ferricyanide-doped tosflex modified GCE	0.3 (vs. Ag/AgCl)	Phosphate buffer (pH = 5)	120[a]	0–0.05	[24]
Poly(glutamic acid) modified GCE	0.3 (vs. SCE)	Phosphate buffer (pH = 5)	460[a]	$1.2 \times 10^{-4} \sim 0.25$	[25]
Poly-D-lysine/hexacyanoferrate/cysteamine modified gold electrode	0.3 (vs. SCE)	TRIS buffer (pH = 7)	62.9	$1 \times 10^{-3} \sim 0.91$	[26]
Polyaniline modified nickel electrode	0.3 (vs. SCE)	0.1 M H_2SO_4 (pH = 1)	190	5–35	[27]
Vanadium oxide polypropylene carbonate modified GCE	0.5 (vs. SCE)	Britton–Robinson (pH = 8.06)	418.31	$4 \times 10^{-5} \sim 10$	[28]
Octacyanomolybdate-doped-poly(4-vinylpyridine) modified GCE	0.57 (vs. SCE)	0.1 M H_2SO_4 (pH = 1)	687	0.01–10	[12]

[a] Geometric area is unknown (unit = $\mu A\ mM^{-1}$).

knowledge, the electrooxidation of H_2A on a Ni foil electrode has not been reported in the literature. Since nickel is a common and inexpensive material, nickel-based H_2A sensors might be very affordable.

The present research reports on the characteristics of H_2A electrooxidation on Pt and Ni foil electrodes at a low applied potential. Cyclic voltammetry and chronoamperometry were employed to analyze the electrochemical behaviors of these two electrodes in the presence and absence of H_2A. The Pt and Ni foil electrodes were compared with regard to factors such as sensitivity, response time, selectivity, and long-term stability.

2. Experiment

2.1. Preparation of the sensing electrodes

Doubly distilled water and analytical-reagent grade chemicals were used for all experiments. The Pt foil and Ni foil were evaluated in separate experimental runs. Both the Pt and Ni foil electrodes were carefully polished with sand-paper (from 800 grit up to 2000 grit) to remove oxide layers from the surfaces. After polishing, the electrodes were degreased with acetone, rinsed with water, and sonicated in DI water for 30 min. Following the surface treatments, 1 cm^2 of each electrode was left uncovered and all other electrode surfaces were sealed with Teflon tape.

2.2. Electrochemical characteristics

All electrochemical measurements were carried out in a cell with a three-electrode configuration. All experiments used a Pt foil counter electrode and an Ag/AgCl reference electrode (in saturated KCl) electrode; the working electrode was made of Pt or Ni foil. Three different supporting electrolytes were used, namely 0.1 M H_2SO_4, $NaSO_4$, and KOH solutions. The electrochemical properties of the electrodes were measured by electroanalytical methods that involved a CHI 824B potentiostat. All potentials were specified with respect to the reference electrode.

2.3. Sensing procedure

The applied potential was determined by polarization curves measured in the presence and absence of H_2A. Any applied potential within an appropriated range enabled the mass transfer of H_2A to the electrode surface. First, the appropriate range was determined; then, when the background current was stable, a measured amount of H_2A was injected into the flask and the amperometric response current of the working electrode was recorded.

3. Results and discussion

3.1. H_2A oxidation on the Pt foil electrode in the acid and alkaline solutions

Fig. 1a shows cyclic voltammograms of a Pt foil electrode in 0.1 M H_2SO_4 with and without 5.68 mM H_2A; Fig. 1b shows corresponding voltammograms for a Pt foil electrode in 0.1 M KOH. The dotted curve in Fig. 1a shows that in the absence of H_2A, the Pt foil electrode in H_2SO_4 exhibited behavior typical of polycrystalline Pt [30]. The peaks H_s', H_w', correspond to hydrogen adsorption; the peaks H_w, and H_s correspond to hydrogen desorption; these peaks appear at potentials between −0.25 and 0.05 V. The H_w'/H_w peaks at −0.16 V can be attributed to weakly adsorbed and desorbed hydrogen on Pt(1 1 0) surfaces whereas H_s'/H_s peaks at approximately −0.03 V can be explained by strongly adsorbed and desorbed