



Trade Science Inc.

ISSN : 0974-7419

Volume 12 Issue 11

# Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 12(11) 2013 [403-407]

## Electroanalysis of ethanol at a Pt-Pb<sub>(ad)</sub> and Pt-Pb<sub>(ad)</sub>-I<sub>(ad)</sub> adatom electrodes

Wojdan W.Qaddumi, Mohammed Khair Hourani\*  
Department of Chemistry, University of Jordan, Amman, (JORDAN)  
E-mail : mhourani@ju.edu.jo

### ABSTRACT

The hyperrecativity of platinum electrodes renders these electrodes useless for routine electrochemical analysis. The present work utilizes modification of polycrystalline platinum with Pb for enhancing the reactivity of Pt electrode towards oxidation of ethanol and I atoms for suppression of its liability towards molecular adsorption. The notion of enhancement of oxidation of ethanol was fully tested by cyclic voltammetry. For better sensitivity, ethanol was analyzed at the Pt-Pb<sub>(ad)</sub>-I<sub>(ad)</sub> electrode by differential pulse voltammetry. The electrode showed a linear response for ethanol within a concentration range of  $5 \times 10^{-6}$  M to  $4 \times 10^{-5}$  M with a minimum detectability of  $1.1 \times 10^{-7}$  mol l<sup>-1</sup> (0.11 ppm ethanol). The accuracy of analysis of ethanol at the Pt-Pb<sub>(ad)</sub>-I<sub>(ad)</sub> electrode was tested by comparing it with a spectrometric analysis of ethanol. © 2013 Trade Science Inc. - INDIA

### KEYWORDS

Adatom electrodes;  
Modified platinum electrodes;  
Electroanalysis of ethanol;  
Differential pulse voltammetric  
analysis of ethanol.

### INTRODUCTION

Surfaces with adatoms, which in a sense imitate “surface alloys” are known to impart a new chemistry to metallic solid surfaces<sup>[1]</sup>. A vast number of publications in the last two decades indicated that adatoms may enhance catalytic properties<sup>[2]</sup>, induce surface passivation for corrosion inhibition<sup>[3]</sup> or might be used for tuning selectivity and reactivity of the solid surfaces for electrocatalytic<sup>[4]</sup> and electroanalytical applications<sup>[5]</sup>.

In this context, electrooxidation of ethanol was found to be enhanced by lead adatoms on platinum electrodes<sup>[6]</sup>. On the other hand, we have used iodine adatoms on platinum for imparting passivation to the platinum electrode towards molecular adsorption within a fair potential range rendering it useful for electroanalysis<sup>[7]</sup>.

On the premise that we can add adatoms to passivate the surface or enhance its catalytic properties, the

present work was undertaken with the aims of modifying platinum electrodes with adatoms for selective analysis of ethanol. The atom of choice for passivation was the iodine atom while the atom for imparting the desired catalytic properties was the lead atom.

### EXPERIMENTAL DETAILS

A home-made potentiostat based on operational-amplifier circuitry and an x-y recorder (EG&G model RE0074) were used for collection of cyclic voltammetric data. A conventional, three-electrode cell equipped with a multiple-inlet system for admission of supporting electrolyte and the other solutions and for purging and blanketing the solution with oxygen-free nitrogen was used. The working electrode used for voltammetric measurements was a 1.0 mm diameter polycrystalline platinum electrode (99.95%, Johnson Matthey, USA) rounded at the end to provide a repro-

## Full Paper

ducible surface area upon immersion underneath the surface of the solution in the working electrode compartment. The reference electrode was a Ag/AgCl/[Cl<sup>-</sup>] = 1.0 mol l<sup>-1</sup>. The auxiliary electrode was a spiral shaped platinum wire (99.95%, Johnson Matthey, USA). The solutions were positioned on a shelf to facilitate the flow of solutions to the cell by gravity action.

A 173 polarographic analyzer (Princeton Applied Research) coupled to an SMDE model 303 was modified by disabling the mechanical functions associated with the mercury electrode. The mercury capillary was replaced by a 2-mm diameter polycrystalline platinum wire embedded snugly in a 1.95 mm bore-size PTFE sleeve by dipping in liquid nitrogen before insertion into the sleeve. The SMDE electronics were bypassed by connecting the electrodes directly to the analyzer. Thus, all the potential waveforms that could be supplied to the SMDE were made available to the modified platinum electrode. This setup was used for differential voltammetric and stripping analysis experiments.

All the reported potentials were measured and reported against Ag/AgCl/[Cl<sup>-</sup>] = 1.0 mol l<sup>-1</sup> and all measurements were carried out at ambient temperature (~25 °C).

### Materials

All the reagents used were of analytical-reagent grade and were used as received without further purification. Platinum wires were supplied by Johnson Matthey, (USA). Lead perchlorate, potassium iodide, spectroscopic grade ethanol, acetonitril (A.R.), acetone (A.R.), and formaldehyde (A.R.) were supplied from Aldrich (USA). The gases used were CP-grade products supplied by National Gas and coupled with Oxosorb (Supelco) for removal of residual traces of oxygen. All solutions were prepared from the reagents dissolved in triply distilled water; the second distillation of which was carried out from basic potassium permanganate solution.

### Procedures

Polycrystalline platinum electrode was iodinated from the gas phase by following the procedure reported by Wieckowski and his associates for preparation of platinum<sup>[8]</sup> and rhodium<sup>[9]</sup> single crystal electrodes. Briefly, the electrode was held over a plunger that con-

tained iodine crystals. The plunger was placed at the bottom of a glass tube that was purged with oxygen-free nitrogen. The electrode holder was free floating on the nitrogen stream. Gas-phase iodination lead to an iodine coat that was more stable and associated with lower background compared to that obtained by adsorption from an iodide-containing solution.

Potentiostatic adsorption of lead at a clean platinum electrode and at iodinated surface was carried out by equilibrating the Pt or the Pt-I<sub>ad</sub> electrodes with a 1.0x10<sup>-3</sup> mol l<sup>-1</sup> Pb<sup>2+</sup> solution at 0.2 V (in the double layer region) for five minutes.

## RESULTS AND DISCUSSION

### Cyclic voltammetry

Figure 1-A shows the equilibrium cyclic voltammogram for polycrystalline platinum electrode along with the the voltammogram for the platinum electrode that is dosed with lead (Figure 1-B). The cyclic voltammogram for the Pt-Pb<sub>ad</sub> electrode shows distinct features from those of the clean platinum electrode. The charge under hydrogen adsorption/desorption peaks is highly suppressed indicating that the free platinum surface is highly reduced (i.e., a large proportion of the surface is occupied by lead atoms). A prominent oxidation peak at about 0.0 V is observed along with its counter cathodic peak. The voltammetric features in the oxidation region on the voltammogram of the Pt-Pb<sub>ad</sub> electrode seemingly involve platinum surface oxidation in addition to reversible oxidation/reduction of the adsorbed lead species.

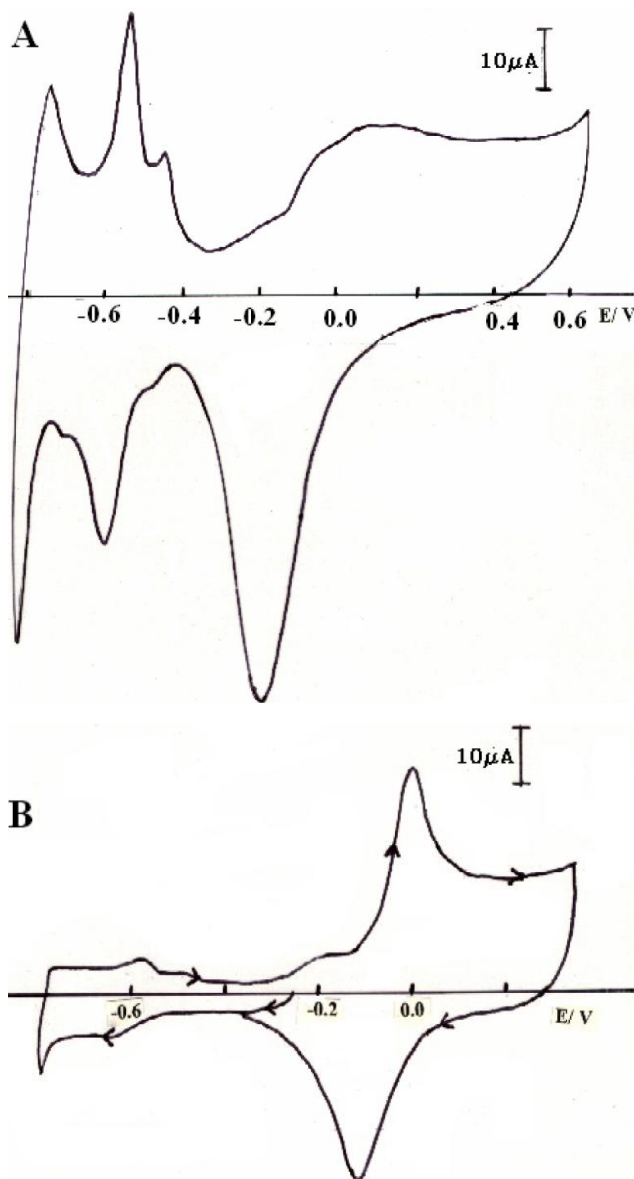
Stability of lead on the surface was investigated by cycling the electrode potential within the potential limits -0.9 V and -0.2 V. The voltammogram showed no change upon cyclization. The voltammogram was amenable to reproduction even after leaving the electrode in pure water for 72 h.

Figure 2 shows the LSV voltammograms for the Pt-Pb(ad) electrode in 0.10 M NaOH solution containing a variable concentration of ethanol. Oxidation of ethanol is manifested by a peak centered at ~ -0.24 V. The peak currents were extracted from the voltammograms and plotted against ethanol concentration to establish the calibration curve (Figure 3). The

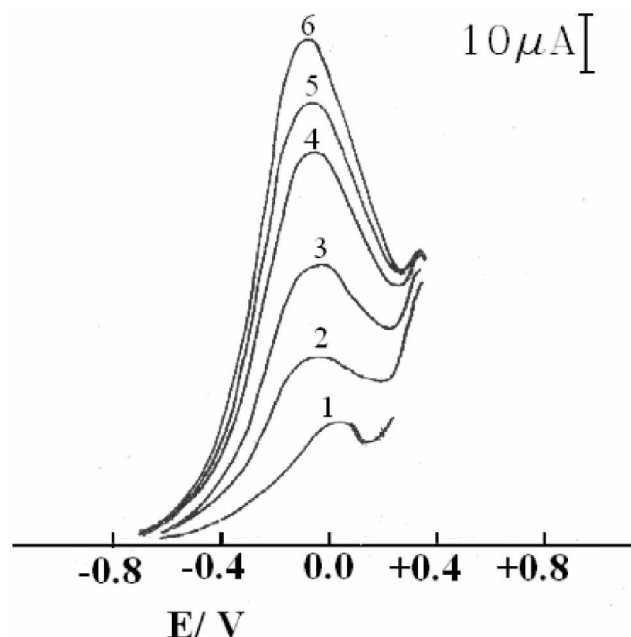
calibration curve showed excellent linearity between the peak current and the concentration of ethanol in the solution (correlation coefficient = 0.9937). The linear regression equation is

$$i(\mu\text{A}) = 7634 [\text{C}_2\text{H}_5\text{OH}] + 2.3133$$

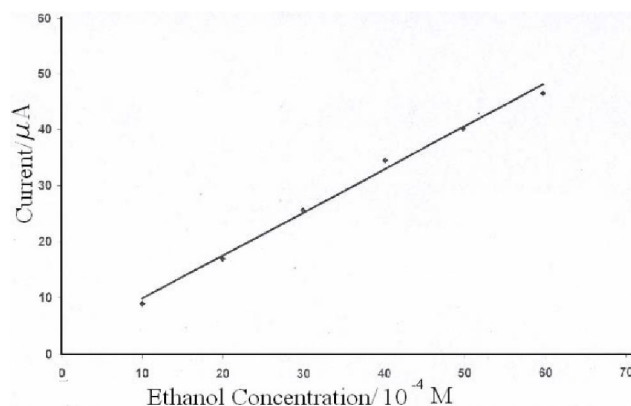
The higher sensitivity of the Pt-Pd<sub>ad</sub> electrode compared to unmodified platinum electrode is attributed in part to the catalytic effect imparted by lead adatoms and harnessing the hyperactivity of platinum surface towards molecular adsorption.



**Figure 1 :** The cyclic voltammogram of polycrystalline platinum electrode (A) in plain 1.0 M NaOH solution and,  $dE/dt = 50 \text{ mV/s}$  (B) after open circuit dosing with  $1.0 \times 10^{-3} \text{ M Pb}^{2+}$  solution. The voltammogram was recorded in 0.10 M NaOH solution,  $dE/dt = 30 \text{ mV/s}$ .



**Figure 2 :** The linear sweep voltammograms of a Pt-Pb(ad) electrode in 0.1 M NaOH solution containing (1)  $1.0 \times 10^{-3} \text{ M}$  (2)  $2.0 \times 10^{-3} \text{ M}$  (3)  $3.0 \times 10^{-3} \text{ M}$  (4)  $4 \times 10^{-3} \text{ M}$  (5)  $5.0 \times 10^{-3} \text{ M}$  and (6)  $6.0 \times 10^{-3} \text{ M}$ .  $dE/dt = 20 \text{ mV/s}$ .



**Figure 3 :** Plot of the ethanol oxidation peak at Pt-Pb(ad) electrode versus concentration of ethanol in 0.1 M NaOH solution. The voltammetric data were extracted from the voltammograms shown in Figure 2.

Selectivity of Pt-Pb(ad) electrode toward oxidation of ethanol was investigated by running the voltammogram in presence of some potential organic interferences such as acetone, acetonitrile and formaldehydes. The cyclic voltammogram for a Pt-Pb(ad) electrode in a solution containing acetone is identical with the voltammogram of Pt-Pb(ad) electrode in acetone-free electrolyte. This indicates that the electrode is insensitive towards acetone up to  $2.5 \times 10^{-5} \text{ mol L}^{-1}$ . Moreover, the calibration curve for ethanol in solutions containing acetone indicated that the linear relationship

## Full Paper

between the peak current and the concentration of ethanol is not affected by the presence of ethanol ( $R^2 = 0.9966$ ).

Similarly, another potential interference, acetonitrile was investigated by adding acetonitrile to the ethanol-containing supporting electrolyte to make a solution from  $4.2 \times 10^{-7}$  M to  $2.5 \times 10^{-5}$  M in acetonitrile. The results were similar to those results obtained in the case of acetone. Neither the voltammogram nor the ethanol calibration curve were affected by the presence of acetonitrile ( $R^2 = 0.9965$  in presence of acetonitrile).

Addition of formaldehyde to the electrolyte containing ethanol showed an enhancement of the oxidation peak current. This enhancement is dependent on the concentration of formaldehyde in the solution. Cyclic voltammetric investigation of formaldehyde interference indicated that formaldehyde raises the background level in the potential range from nearly 0 V to 0.5 V. Thus, the effect of formaldehyde resides in the increase in the level of the background and its effect can be eliminated by addition of a constant concentration of formaldehyde to all standard solutions and analyzed samples.

Linear sweep voltammetry is known to be a technique of relatively poor sensitivity, it, however, demonstrated that platinum electrodes coated with lead are applicable to selective analysis of ethanol. Enhancement of the sensitivity can be brought about by using differential pulse voltammetry.

### Strategic modification of platinum electrode with Pb and I adatoms

Iodine adatoms impart a remarkable inertness to platinum electrodes towards molecular adsorption. The surface electrochemistry is entirely suppressed in presence of iodine adatoms.

On the premise that Pb adatoms enhance electrooxidation of ethanol at one hand and iodine adatoms suppress molecular adsorption on the other hand, iodine was added to form a binary adatom system for increasing the immunity of the electrode towards molecular adsorption as proved in previous investigations<sup>[10]</sup>. Differential pulse voltammetry was used for enhancing the sensitivity of the Pt-Pd<sub>ad</sub>-I<sub>ad</sub> electrode towards ethanol. Platinum electrode was potentiostatically pretreated with Pb<sup>2+</sup> at -0.17 V and then pretreated with  $1.0 \times 10^{-4}$  M I<sup>-</sup> solution at the same

potential.

Figure 4 shows the differential pulse voltammetric curves obtained at the Pt-I<sub>ad</sub>-Pb<sub>ad</sub> electrode in ethanolic solutions. The peak currents were extracted from the voltammograms and plotted against the concentration of ethanol. The calibration curve equation is

$$\text{Peak current } (\mu\text{A}) = 50.196 C_{\text{ethanol}} + 304.51$$

with  $R^2 = 0.9941$  which attests to the remarkable linearity of the calibration curve. This indicates that the Pt-Pb<sub>ad</sub>-I<sub>ad</sub> electrode is applicable to analysis of ethanol in aqueous solutions.

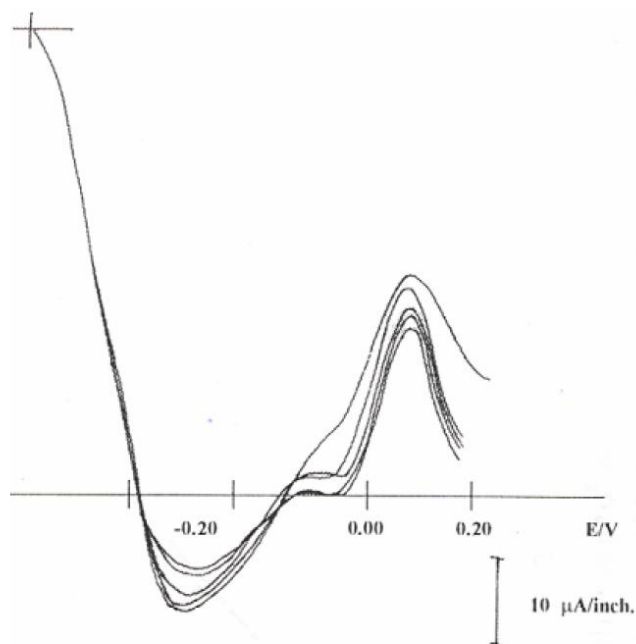


Figure 4 : Differential pulse voltammograms for Pt-Pb(ad)-I(ad) electrode in 0.10 M NaOH solution + (a)  $1.82 \times 10^{-5}$  M ethanol (b)  $2.27 \times 10^{-5}$  M ethanol (c)  $2.73 \times 10^{-5}$  M ethanol (d)  $3.18 \times 10^{-5}$  M ethanol (e)  $3.64 \times 10^{-5}$  M. Instrument parameters: scan rate = 5 mV/s, clock time = 0.5 s, and modulation amplitude = 50 mV/s.

The working range is rather limited to the range  $5 \times 10^{-6}$  M to  $1.4 \times 10^{-5}$  M. The lowest detection limit on basis of S/N ratio of 3 gave a value of  $1.1 \times 10^{-7}$  mol l<sup>-1</sup> (0.11 ppm ethanol). Compared to spectrophotometric methods, the developed method is very convenient and less liable to interferences<sup>[11]</sup>.

The developed method was applied to analysis of a real sample of commercial local wine Jordan River Shiraz (Yousif M. Haddad). The nominal concentration of the original wine sample was 12% (w/v). An aliquot from the original sample was diluted to provide a con-

centration of  $1.0 \times 10^{-3} \text{ mol l}^{-1}$ . Analysis of ethanol in the sample gave a value of  $9.5 \times 10^{-4} \text{ mol.l}^{-1}$ . Based on the nominal value of the concentration of the original sample (12 (w/v)%,  $2.60 \text{ mol.l}^{-1}$ ) the deviation from the nominal value is about  $2.3 \times 10^{-4} \text{ mol l}^{-1}$ . This deviation is attributed to the volatility of ethanol which decreases the concentration of ethanol rendering it lower than the nominal value. This result attests to the applicability of modified electrode to analysis of real-life samples.

### CONCLUSIONS

The present work presented a simple voltammetric method for analysis of alcohol. On the contrary of the hyperactive unselective unmodified platinum electrode, Pt-Pb<sub>ad</sub>-I<sub>ad</sub> electrode showed higher selectivity higher selectivity towards ethanol and remarkable inertness towards interferences. Modification of platinum surfaces with lead adatoms and iodine involves a simple procedure not more than allowing the electrode to contact a solution containing Pb<sup>2+</sup> followed by equilibration of the electrode with I containing solution at open circuit. The electrode is stable as far as the potential scan is not extended to the oxidation region.

In contrast with the unmodified platinum electrode where impurities with concentrations in the order of  $10^{-9}$  or less render the electrode completely useless<sup>[12]</sup>, analysis of ethanol at Pt-Pb<sub>ad</sub>-I<sub>ad</sub> electrode showed that the Pt-Pb<sub>ad</sub>-I<sub>ad</sub> electrode is not affected by impurities. The electrode response towards ethanol was linear in a fair dynamic range and minimum detectability.

### REFERENCES

- [1] D.P.Woodruff (Ed); The chemical physics of solid surfaces, Surface alloys and alloy surfaces, Elsevier: Amsterdam, **10**, (2002).
- [2] O.Voznyy, J.Dubowski, J.T.Yates, P.Maksymovych; J.Am.Chem.Soc., **131(36)**, 12989–12993 (2009).
- [3] M.Hourani, F.Wedian; Corrosion Science., **42**, 2131-2144 (2000).
- [4] B.F.Giannetti, C.M.Almedia, S.H.Bonilla, M.O.A.Mongod, T.Z.Raboczky; Phys.Chem., **217**, 35 (2003).
- [5] M.Hourani; Analyst, **119**, 1975-1978 (1994).
- [6] A.A.El-Shafei, M.Abd El-Maksoud, M.N.H.Mousa; J.Electroanal.Chem., **336**, 73-83 (1992).
- [7] M.Hourani, E.Shamayleh, K.Ibrahim, Arab Gulf; J.Scient.Res., **13(2)**, 225-238 (1995).
- [8] D.Zurawski, L.Rice, M.Hourani, A.Wieckowski; J.Electroanal.Chem., **230**, 221 (1987).
- [9] M.Hourani, A.Wieckowski; J.Electroanal Chem., **227**, 259 (1987).
- [10] R.F.Lane, A.Hubbard; J.Phys.Chem., **79(8)**, 808 (1975).
- [11] Mei-Ling Wang, Youk-Meng Choong, Nan-Wei Su, Min-Hsiung Lee; J.Food and Drug.Analysis, **11(2)**, 133 (2003).
- [12] S.Sarangapani, E.Yeager; In comprehensive treatise of electrochemistry, E.Yeager, J.O'M.Bockris, B.Conway, S.Sarangapani (Eds.); Plenum Press: New York, Chapter 1, **9**, (1990).