

Studies on the Polythiophene(PT)/GC Electrode for the Determination of Some Metals by Differential Pulse Anodic Stripping Voltammetry (DPASV)

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Studies were carried out on the fabrication of glassy carbon electrode modified with polythiophene (PT/GC). Cu(II), Pb(II), Cd(II), and Zn(II) were determined by using the PT/GC modified electrode by DPASV. The PT/GC electrode was easily fabricated by cyclic voltammetry applying the potential from -0.5 V to $+1.8$ V (*vs.* SCE) at the scan rate of 50 mV/sec in 0.1 M thiophene -1 M tetrabutylammonium perchlorate (TBAP)-acetonitrile mixture. The thickness of the polymer film could be controlled by the number of potential cycling. PT/GC electrode showed Cu oxidation peak at 0.1 V *vs.* SCE, which is more positive potential than DME (at -0.1 V). The calibration graph for the Cu(II) was linear from 10 ppb to 450 ppb with correlation factor of 0.99. Anodic oxidation peaks of Pb, Cd, and Zn were observed at -0.5 V, -0.7 V, and -1.2 V *vs.* SCE, respectively. The PT/GC modified electrode could replace the conventional mercury electrode for the voltammetric study.

Keywords : PT/GC, DPASV, Metals, Cu, Pb, Cd.

Introduction

The polarographic techniques has very rapidly been grown since the dropping mercury electrode (DME) developed. The treatment of used mercury and the purification of the re-used mercury has come to great problems in environmental pollution. Recently, mercury has been included in endocrine disruptor group and therefore should be managed with a special case. The development of an alternative electrode for mercury has to urgently be required for the voltammetric study.¹

Electropreparation,^{7,11,12} redox chemistry,⁸ anodic over-oxidation,^{9,13} and irreversible reduction¹⁰ of polythiophene have already widely been studied by many research workers.

The polythiophene conducting polymer which has the structure of π -electrons conjugated on the polymer backbone shows superior electrical conductivity than the ordinary polymer molecule. The electrical conductivity can also be controlled by doping with certain kind of non-redox dopant. Generally, the synthetic polymer materials have got some drawback due to their insolubility in organic solvent.

Santos *et al.*² reported the determination of lead by using the electrode coated with polyaniline followed by doping polyvinyl sulfonate (Na-PVS) on it.

The polythiophene (PT) polymeric film coated on the glassy carbon (GC) electrode - PT/GC modified electrode - was tried to determine copper, lead, cadmium, and zinc ions by differential pulse anodic stripping voltammetry (DPASV) in this study.

The electrode surface contaminated by metals also was regenerated by simple oxidation process EDTA solution.

Chemicals and Apparatus

The electrolytic cell used 3-electrode system composed of PT/GC working electrode, SCE reference electrode and Pt

counter electrode ($A = 2.0$ cm²), respectively. PT/GC modified electrode was prepared by the electrolytic polymerization of thiophene using cyclic voltammetric technique in the mixture of 0.1 M thiophene (>99.9%, Aldrich Co., USA) and 0.1 M tetrabutylammonium perchlorate (TBAP, GR grade, Fluka Co., Swiss) in acetonitrile.

All of metal ions were determined in 0.1 M KCl solution (GR grade, OCI Co., Korea) by DPASV technique using PT/GC modified working electrode.

CV and DPASV were carried out by 273A Potentiostat/Galvanostat (EG&G PAR Co. USA) coupled with electrochemistry software (model 270).

Ultra-pure water obtained from the Millipore plus II UHQ (Millipore Co. USA) was used through out the work.

Results and Discussions

Fabrication of PT/GC electrode. Polythiophene prepared by batch process cannot be applicable to the GC electrode surface because of the insolubility³ of the polythiophene in any organic solvent. Direct electrolytic polymerization process either by cyclic voltammetry (CV) or by controlled potential coulometry (CPC) can only be useful for the modification of GC electrode.

Polymerization of thiophene was carried out by the cyclic voltammetry applying the potential range of -0.5 V to $+1.8$ V (*vs.* SCE) at the scan rate of 50 mV/sec. The oxidation of thiophene in Figure 1 could be observed at two peaks, Pa₁ and Pa₂. The oxidation peak (Pa₂) of polythiophene was similar to reported by Tourillon, G. *et al.*^{4,5}

The peak current of Pa₂ tends to decrease by increasing the number of polymerization cycle. This phenomena will be attributed to loss of electroactivity of PT by increasing the membrane thickness. The voltammogram has been reached a steady state at 20 times of potential scanning by CV.

The conductivity of PT polymer has been reported to be

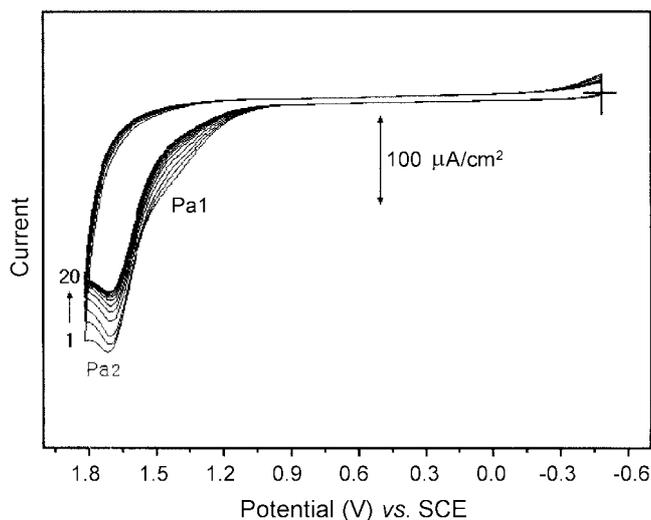


Figure 1. Fabrication of PT/GC modified electrode by CV in 0.1 M thiophene - 0.1 M TBAP - acetonitrile mixture.

worse than PANI or polypyrrole by 10^{-3} times.⁶ The most appropriate thickness of the PT film could be obtained at the 20 times polymerization by CV and used for DPASV study. The PT film formed by controlled potential coulometry (CPC) was rapidly completed in shorter period of time than CV, but difficult to control the thickness of the film with more coarse surface than the one by CV.

The modified PT/GC electrode with more dense surface could be completed by CV process than CPC in the thiophene solution

Effect of deposition time. Polythiophene which has sulfur atom in the repeating unit of the polymer would have negative charge¹⁴ by reduction reaction, and could join to certain metal cations. Both of Cu(II) and Pb(II) were electrolytically deposited at the polymer modified electrode at -0.7 V vs. SCE.

The voltammogram for Cu(II) and Pb(II) on Figure 2 were obtained by differential pulse anodic stripping voltammetry (DPASV) using PT modified electrode at -0.7 V for the different deposition times. The single oxidation peak of Pb(Pa₁, 0.1 ppm) and double peaks for Cu(I) (Pa₂, 0.1 ppm) and Cu(II) (Pa₃) were observed at -0.5 V, -0.2 V and $+0.1$ V, respectively.

In general, the currents at three peaks were linearly enhanced by the deposition time increase. The optimum deposition time for the study would be 240 sec for all components. Negative deviation of the linearity could be resulted for the longer time such as 360 sec.

Effect of supporting electrolyte. Supporting electrolytes such as 0.1 M KCl, 0.1 M NH₄Cl, 0.1 M Na₂SO₄, 0.1 M KClO₄, and 0.1 M CH₃COONa were investigated for the DPASV study of Cu(II), Pb(II), Cd(II), and Zn(II).

These supporting electrolytes were generally used for the determination of metal ions by electrical technique.¹⁵

0.1 M NH₄Cl solution, however, shows the similar voltammograms for the metals like in 0.1 M KCl, but less sensitive than the one obtained from 0.1 M KCl in Figure 3. The

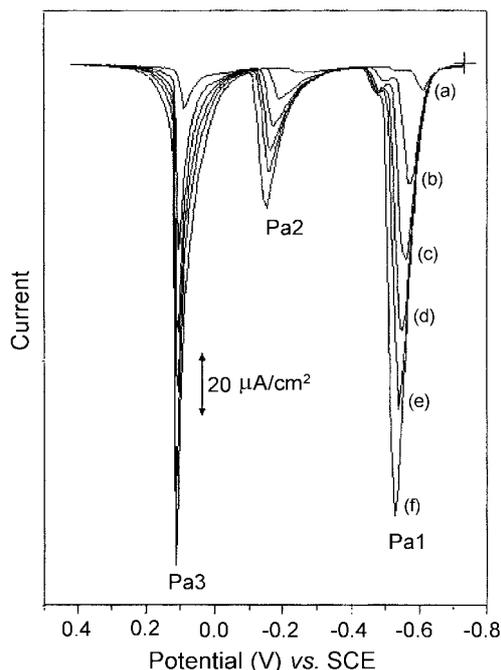


Figure 2. Voltammograms of 0.1 ppm Cu(II) and Pb(II) by DPASV in 0.1 M KCl. [(a) 0 sec, (b) 60 sec, (c) 120 sec, (d) 180 sec, (e) 240 sec, and (f) 360 sec.]

other ones have produced poor baseline for DPASV of the metal ions. The most suitable supporting electrolyte would probably be the 0.1 M KCl for the voltammetric study of those metal ions

Regeneration of PT/GC electrode. The modified electrode used for DPASV study of metal ions was contaminated by the elements. Three methods were applied to remove the

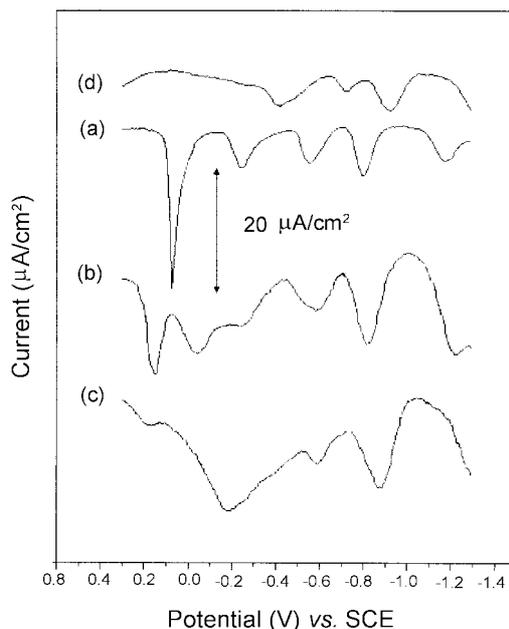


Figure 3. DPASV of Cu(II), Pb(II), Cd(II), and Zn(II) in several supporting electrolytes. (a) NH₄Cl, (b) NaClO₄, (c) NaOAc, and (d) Na₂SO₄.

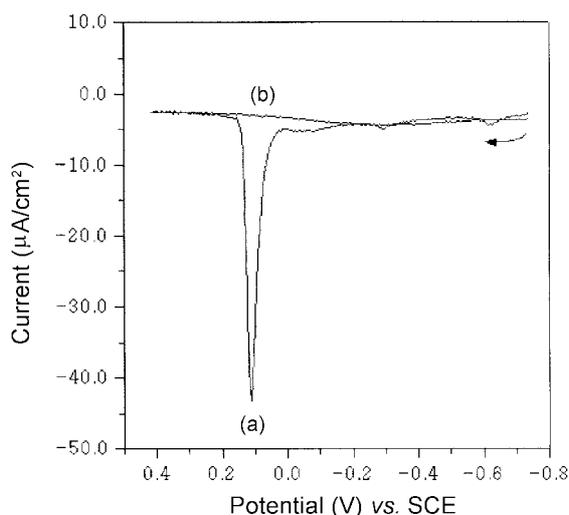


Figure 4. Regeneration of PT/GC electrode by oxidation at +0.5 V in 0.01 M EDTA and 0.1 M KCl mixture. (a) contaminated electrode (b) electrode regenerated

metal contaminants: (1) Oxidation of the electrode at +0.5 V, (2) Soaking the modified electrode in 0.01 M EDTA, and (3) Oxidation of the modified electrode in 0.01 M EDTA/0.1 M KCl solution at +0.5 V.

The regeneration effect of the modified electrode was not satisfied by the methods (1) and (2) Treatment of the electrode by the method (3) could remove all of the metal ions within 30 sec as can be seen on Figure 4(b).

The PT/GC modified electrode can be used at least 80 times or more by occasional regeneration.

Calibration for metal ions. DPASV study for Cu(II), Pb(II), Cd(II), and Zn(II) has been carried out to get a linear calibration curves. The voltammetric condition for the metal

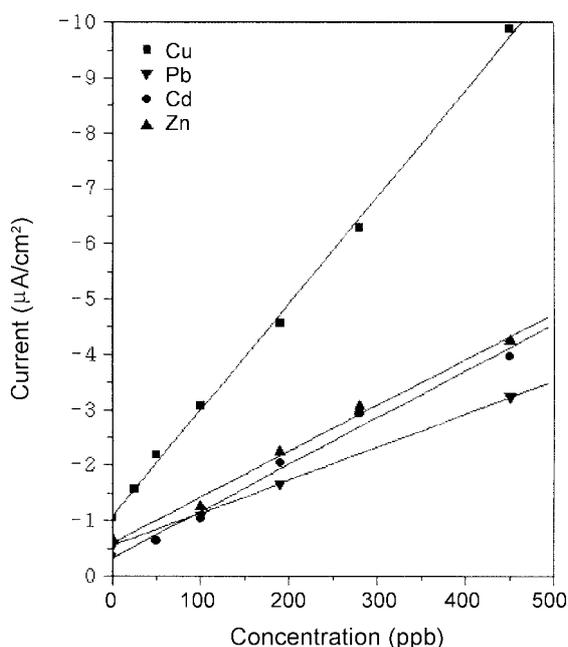


Figure 5. Calibration graphs of metal ions by DPASV.

Table 1. Reproducibility of the currents for the components (100 ppb) by OPASV

Components Measurements	Cu(II) ($\mu\text{A}/\text{cm}^2$)	Pb(II) ($\mu\text{A}/\text{cm}^2$)	Cd(II) ($\mu\text{A}/\text{cm}^2$)	Zn(II) ($\mu\text{A}/\text{cm}^2$)
1	191.7	98.7	108.3	81.0
2	191.7	98.6	108.5	81.2
3	191.8	99.0	108.5	80.9
4	191.6	98.7	108.4	81.0
5	192.3	98.8	108.1	81.1
6	191.9	99.1	108.3	81.2
7	192.1	98.4	108.7	81.1
8	191.8	98.8	108.2	80.9
9	191.6	98.5	108.3	81.1
10	192.0	98.6	108.5	80.0
Average	191.9	98.7	108.4	81.0
Standard deviation	0.17	0.07	0.01	0.17

ions from 10 to 450 ppb were as follows: applied potential; $-1.3 \sim +0.6$ V, deposition potential; -1.3 V for 240 sec, scan rate; 50 mV/sec.

The oxidation peak potentials of the metals tend to appear at more negative potentials than the one obtained by mercury electrode, such as -1.2 V for Zn(II), -0.7 V for Cd(II) and -0.5 V for Pb(II), but slightly positive for Cu(II) at $+0.1$ V.

The relationships between concentration (10 ppb-450 ppb) and current of Cu(II), Pb(II), Cd(II), and Zn(II) in Figure 5 were shown good linearity with the slope factor of 19-8 $\mu\text{A}/\text{ppb}$ and correlation factor of 0.99.

Anodic stripping current of the components (100 ppb) in the mixture has shown good reproducibility for 10 measurements by DPASV. The average current densities and standard deviations of each component were 191.9 $\mu\text{A}/\text{cm}^2$, 0.17 for Cu, 98.7 $\mu\text{A}/\text{cm}^2$, 0.07 for Pb, 108.4 $\mu\text{A}/\text{cm}^2$, 0.01 for Cd, and 81.0 $\mu\text{A}/\text{cm}^2$, 0.17 for Zn, respectively.

Conclusions

PT/GC modified electrode can easily be prepared by electro-polymerization of thiophene on GC electrode for 20 times potential cycling from -0.5 V to $+1.8$ V vs. SCE. Thicker PT film would cause to loss the sensitivity of the voltammetric study.

The DPASV study for Cu(II), Pb(II), Cd(II), and Zn(II) made them possible to determine down to 10 ppb level of the components in 0.1 M KCl supporting electrolyte.

The contaminated electrode by metal could be easily regenerated in 0.01 M EDTA-0.1M KCl solution by the oxidation of the electrode at $+0.5$ V for 30 sec.

The oxidation potential of the components for DPASV tends to shift up to about -0.3 V than the one obtained by mercury electrode.

The method developed in this study, which is free from environmental pollution, could replace the use of conventional mercury electrode for most of voltammetric study.

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References

1. Cheek, G. T.; Nelson, R. F. *Anal. Lett.* **1978**, *5*, 393.
 2. Santos, J. H.; Smyth, M. R.; Blanc, R. *Anal. Commum.* **1998**, *35*, 345.
 3. Nalwa, H. S. *Handbook of Organic Conductive Molecules and Polymers*: John Wiley & Son: New York, U. S. A., 1997; Vol 3, pp 87-120.
 4. Tourilion, G.; Garnier, F. J. *J. Electrochem. Soc.* **1983**, *130*, 2024.
 5. Bard, A. J. *Electroanalytical Chemistry*; Merceel Dekker Inc.: New York, U. S. A., 1986; Vol. 13.
 6. Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymer*: Merceel Dekker Inc.: New York, U. S. A., 1986; Vol 2, pp 531-821.
 7. Can, M.; Pekmez, K.; Pekmez, N.; Yildiz, A. *J. of App. Polymer Sci.* **2000**, *77*(2), 312.
 8. Hapiota, P.; Audeberth, P.; Guyardh, L.; Catelc, J.-M.; Duchenete, V.; Coustumere, G. Le. *Synthetic Metals* **1999**, *101*(1-3), 642.
 9. Barscha, U.; Becka, F. *Electrochim. Acta* **1998**, *41*(11-12), 1761.
 10. Zotti, G.; Schiavon, G.; Zecchin, S. *Synthetic Metals* **1995**, *72*(3), 275.
 11. Mua, B. S.; Parka, S. M. *Synthetic Metals* **1995**, *69*(1-3), 311.
 12. Visy, Cs.; Lukkari, J.; Kankare, J. *Synthetic Metals* **1995**, *69*(1-3), 319.
 13. Harada, H.; Fuchigami, T.; Nonaka, T. *J. Electroanal. Chem.* **1991**, *303*, 139.
 14. Lachkar, A.; Selmani, A.; Sacher, E.; Leclerc, M.; Mokhliss, R. *Synthetic Metals* **1994**, *66*(3), 209.
 15. Sawyer, D. T.; Sobkowiak, A.; Roberts, Jr., J. L. *Electrochemistry for Chemists*, 2nd; John Wiley & Sons, Inc.: New York, U.S.A., 1995; pp 100-130.
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