

## Utilization of Polyaniline (Emeraldine Salt) as Modifier of Graphite Paste Electrodes for Heavy Metal Detection

*Elmer-Rico E. Mojica, Jelynn P. Tamayo and Jose Rene L. Micor*

Institute of Chemistry, University of the Philippines Los Baños, College, Laguna, 4031, Philippines

**Abstract:** Polyaniline (emeraldine salt) samples prepared with different acid dopants namely hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>), perchloric acid (HClO<sub>4</sub>) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were used as modifier by mixing it with graphite powder and Nujol oil to form a paste. The fabricated Graphite Paste Electrodes (GPE) were characterized by Cyclic Voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV). Voltammetric analysis using different heavy metal ions (mercury, lead, cadmium, copper, zinc, nickel and cobalt) in aqueous solution was performed using the prepared electrodes. All polymer graphite paste electrodes detected the presence of mercury (II) ions. In addition to mercury ions, the modified electrodes containing polyaniline prepared with dopants (HNO<sub>3</sub> and HCl) also detected the presence of cadmium (II) ions.

**Keywords:** Polyaniline . dopant . mercury . graphite paste electrodes

### INTRODUCTION

Conducting polymers like polyaniline (PANI) has been popular lately due to its high electrical conductivity [1], unusual and unique redox properties [2] and favorable environmental stability. It had been the object of numerous studies because of its excellent processability and the presence of a number of intrinsic redox states. It had found potential applications ranging from light-emitting diodes [3], sensors, electronic noses [4, 5], electromagnetic shielding and military camouflage [6] to intelligent materials and anti-corrosion protection.

PANI has a variety of oxidation states that are dependent on both the pH and potential and these result to a number of forms that have different chemical and physical properties. Literature have shown that PANI has three common forms namely leucoemeraldine (LEB, fully reduced), emeraldine (EB, half-oxidized) and pernigraniline (PNB, fully oxidized) [7]. The emeraldine base (EB-PANI) can be doped by protonic acids (Brønsted acids) allowing the coordination of the protons with the imine nitrogen of Emeraldine Base (EB) to produce emeraldine salt (ES-PANI), the conducting form of PANI [8, 9]. Protonic acid doping is the most useful way to achieve high conductivity since this lead to the charge delocalization on the polymer backbone that gave increased dc conductivity [10, 11] and increased spin density [12].

Since polyaniline (emeraldine salt) possess functional groups with high affinity towards heavy metals ions, this study try to look at its application as modifiers of graphite paste electrode. Graphite paste electrode is one form of Chemically Modified Electrodes (CME) wherein a material is added (modifier) to increase the selectivity of the electrode. The fabricated polyaniline-modified graphite paste electrode (PMGPE) was then used in the voltammetric analysis of heavy metals in aqueous samples.

### MATERIALS AND METHODS

**Preparation of polymer:** Polyaniline was prepared adopting the method of Stejskal and Gilbert [13]. One hundred mL (100) of 0.25 M of aqueous solution of ammonium persulfate (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 0.20 M solution of aniline was dissolved in 100 mL of 1 M aqueous hydrochloric acid (HCl) at 5°C.

Polymerization was allowed to proceed overnight in a refrigerator. The green precipitate that formed was removed by filtration, washed with 1 M HCl followed by acetone until clear filtrate was obtained. The obtained polymer was dried in a vacuum oven at room temperature (30°C) for 6 hours. The green material obtained was identified as the emeraldine hydrochloride.

The emeraldine hydrochloride was converted into the emeraldine base by mixing 1 gram with 10 mL of 3% solution of ammonium hydroxide (NH<sub>4</sub>OH). The mixture was allowed to settle for several hours. The

resulting blue material was filtered and washed with distilled water and vacuum dried at room temperature for 6 h.

Aside from hydrochloric acid, other acids like sulfuric acid ( $\text{H}_2\text{SO}_4$ ), nitric acid ( $\text{HNO}_3$ ) and perchloric acid ( $\text{HClO}_4$ ) were used in order to obtain doped polyaniline with the corresponding counter-ion.

**Fabrication of electrode:** The polymer obtained was used as modifier by mixing with graphite powder and mineral oil to form a paste. The prepared polymer (200 mg) was mixed with graphite powder (800 mg) and enough oil to form a paste. Electrode assembly was done by filling the open tip of the copper wire inserted with plastic straw with the polymer-graphite paste until thoroughly packed. The paste was compacted around copper wire and smoothened with a glass spatula.

**Electrochemical analysis:** Voltammetric analysis was done on the Metrohm 694 VA processor connected to a three-electrode cell system: the auxiliary electrode (platinum wire), the reference electrode (Ag/AgCl electrode) and the working electrode (polymer modified electrode). Electrochemical characterization of the polymer modified graphite electrode was done using Cyclic Voltammetry (CV). Heavy metal analysis using the modified electrode was performed by differential pulse anodic stripping voltammetry (DPASV). The voltammetric readings before and after accumulation of the polymer modified electrodes in different analytes (cobalt, cadmium, lead, mercury and nickel at  $100 \mu\text{g L}^{-1}$ ) were compared. These analyte solutions were prepared by diluting each metal standard solution ( $1000 \mu\text{g L}^{-1}$ ) obtained from J.T. Baker with deionized distilled water. Accumulation was done on an open circuit wherein the polymer modified electrode is dipped in an analyte solution in a cell with constant stirring for three minutes.

The parameters used for the DPASV on the different heavy metals as follows:

U. Amplitude: 50 mV	Rot Speed: 0/min
t. Step: 0.20 s	t. meas: 16.7 ms
U. Meas: -1000 mV	t. pulse: 33.3 ms
U. Start: -1000 mV	U step: 10 mV
U. End: 1000 mV	

## RESULTS AND DISCUSSION

The electrochemistry of the prepared polyaniline modified graphite paste electrode (PMGPE) was first investigated using cyclic voltammetry (CV). CV is the most widely used technique for acquiring qualitative

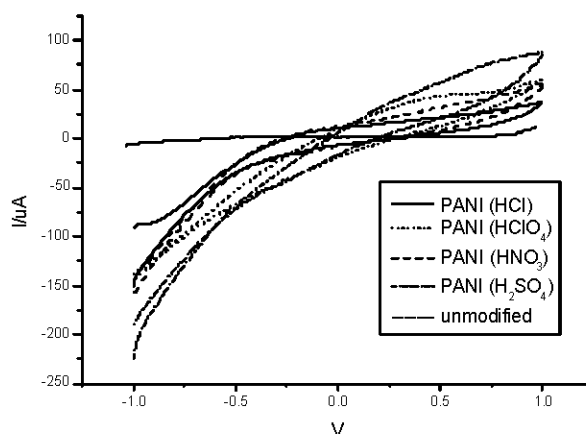


Fig. 1: Comparison of cyclic voltammogram of different polyaniline graphite modified electrodes

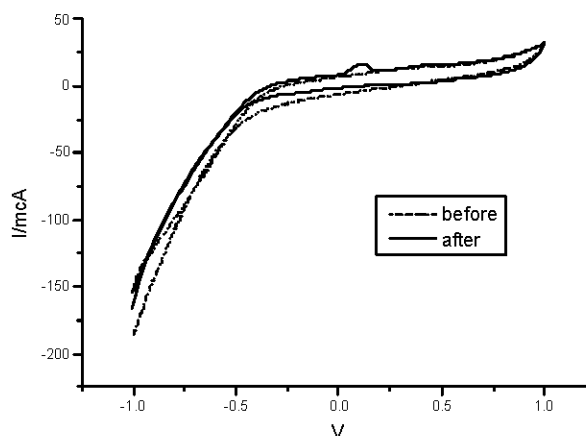


Fig. 2: Cyclic voltammograms of polyaniline (dopant: HCl)-modified graphite modified electrode before and after accumulation with mercury solution

information about electrochemical reactions due to its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions and on coupled chemical reactions or adsorption processes. CV was performed on all the prepared PMGPE to determine their potential window or potential range.

Results of the cyclic voltammograms (CVs) (Fig. 1), by comparing the CV scan of the unmodified and modified GPE in 0.1M HCl as supporting electrolyte showed that incorporation of the modifier significantly increase the charging current of the working electrode. This deviate from one of the desirable characteristics of the graphite paste electrode which is of low residual current [13], that is usually preserve even with the addition of the modifier. This

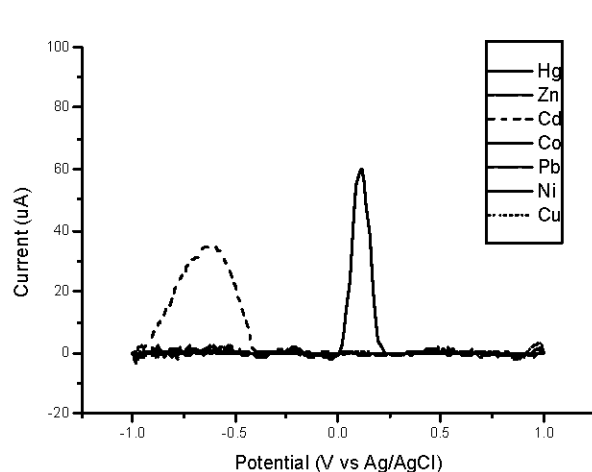


Fig. 3: DPASV of polyaniline (dopant: HCl)-modified graphite paste electrode on different heavy metals

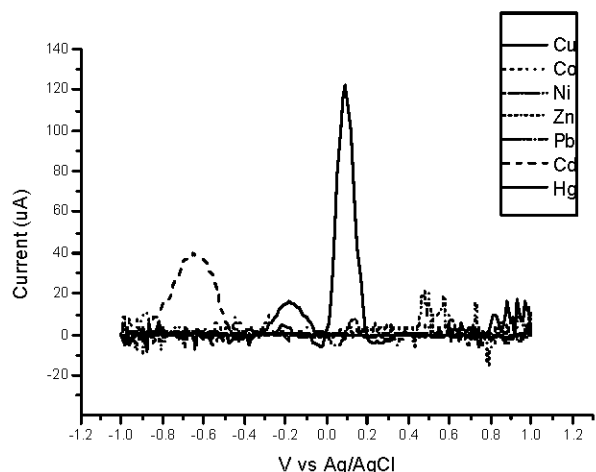


Fig. 5: DPASV of polyaniline (dopant: HNO<sub>3</sub>)-modified graphite paste electrode on different heavy metals

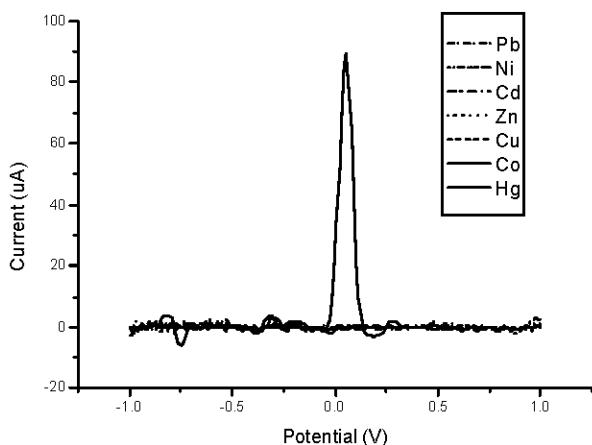


Fig. 4: DPASV of polyaniline (dopant: HClO<sub>4</sub>)-modified graphite paste electrode on different heavy metals

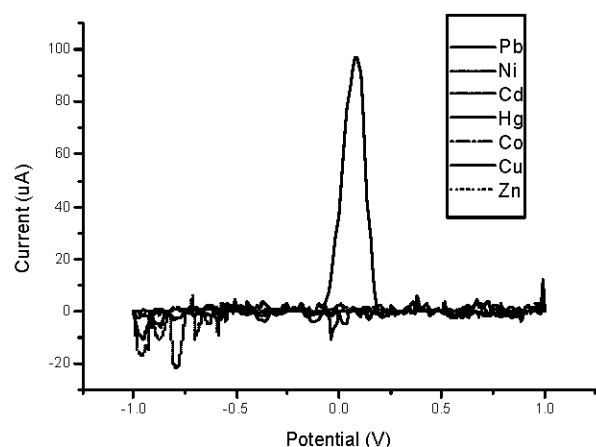


Fig. 6: DPASV of polyaniline (dopant: H<sub>2</sub>SO<sub>4</sub>)-modified graphite paste electrode on different heavy metals

only showed that the modifier (polyaniline emeraldine salt) used exhibits its conductivity property as the broadening of CV is due to the redox reactions caused by the modifier. However, not all potential range was affected by the modifier. It is still possible that an analyte of interest can undergo a redox reaction within a potential range not affected by the modifier.

Figure 2 shows a CV before and after a GPE modified with polyaniline was preconcentrated in a 1000 mg L<sup>-1</sup> mercury (II) solution. The CV produced a distinct peak at voltage range near 0 mV, which is the voltage range for the reduction of mercury ions (II) ions. This is the only metal that the PMGPEs were able to detect or gave positive result or a distinct peak on CV after dipping the different electrodes in different heavy metal solution. The nature of the modifier used in the

PMGPEs may have prevented the other metals to be detected by using CV.

Differential pulse anodic stripping voltammetry (DPASV) was done to determine clearly if heavy metals can bind with the different modifiers on the GPEs. DPASV is a common method used for detection of metals. Just like in CV, all the prepared PMGPEs detected the presence of mercury ions. A peak around 0 V was observed in solution containing mercury ions using the prepared electrodes modified with polyaniline with different dopants (Fig. 3-6). In addition, in graphite paste electrode modified with polyaniline doped with nitric acid and hydrochloric acid (Fig. 3 and 5), a peak was observed when the electrode was dipped in cadmium solution. A peak was also observed for nitric acid doped polyaniline-modified GPE soaked in

copper solution. The peaks observed were due to the metal ions present in the solution used.

This only means that mercury ions in general bind with the polyaniline prepared using different dopants. Studies have shown that polyaniline preconcentrated mercury ions and methyl mercury [15, 16]. A composite of polyaniline with polystyrene successfully removed mercury ions from aqueous solutions. Desorption experiments showed that the process of Hg (II) ion adsorption by polyaniline was almost irreversible and chemisorptive in nature [17]. On the other hand, cadmium ions can bind in some acid-doped polyaniline. It was successfully detected by bismuth/polyaniline film electrode [18] and by sulfonated polyaniline modified electrode [19]. However, both electrodes can also detect lead ions. No peak was observed when lead solution was used.

### CONCLUSION

Polyaniline (emeraldine salt) samples prepared with different acid dopants were successfully used as modifier of graphite paste electrodes. The fabricated polyaniline graphite paste electrodes (PGPE) detected the presence of mercury ions by voltammetric analysis (CV and DPASV). Graphite paste electrodes modified with polyaniline using  $\text{HNO}_3$  and  $\text{HCl}$  as dopants also detected the presence of cadmium (II) ions.

### REFERENCES

- MacDiarmid, A.G., S.L. Mu, M.L.D. Samasiri, W. Wu, 1985. Electrochemical characteristics of polyaniline cathodes and anodes in aqueous electrolytes. *Mol. Cryst. Liq. Cryst.*, 121: 187-190.
- Moon, D.K., M. Ezuka, T. Maruyama, K. Osakada and T. Yamamoto, 1993. Kinetic study on chemical oxidation of leucoemeraldine base polyaniline to emeraldine base. *Macromolecules*, 26: 364-369.
- Bloom, P.W.M., C.J.M. Vissenberg, J.N. Hulberts, H.C.F. Martens and H.F.M. Schoo, 2000. Optimum charge-carrier mobility for a polymer light-emitting diode. *Appl. Phys. Lett.*, 17: 2057-2059.
- Chidsey, C.E.D. and R.W. Murray, 1986. Electroactive polymers and macromolecular electronics. *Science*, 231: 25-31.
- Hale, P.D., L.I. Boguelavsky, T. Inagaki, H.I. Karan, H.S. Lee, T.A. Skotheim and Y. Okamoto, 1991. Amperometric glucose biosensors based on redox polymer-mediated electron transfer. *Anal. Chem.*, 63: 677-682.
- Shacklette, L.W., N.F. Colaneri, V.G. Kulkarni, B. Wessling, 1992. EMI shielding of intrinsically conductive polymers. 1992. *J. Vinyl. Technol.*, 14:118-122.
- Huang, W.S., B.D. Humphrey and A.G. MacDiarmid, 1986. Polyaniline, a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes. *J. Chem. Soc. Faraday Trans.*, 82: 2385-2400.
- Stafstrom, S., J.L. Bredas, A.J. Epstein, H.S. Woo, D.B. Tanner, W.S. Huang, A.G. MacDiarmid, 1987. Polaron lattice in highly conducting polyaniline: Theoretical and optical studies. *Phys. Rev. Lett.*, 59: 1464-1467.
- MacDiarmid, A.G. and A.J. Epstein, 1989. Polyanilines: a novel class of conducting polymers. *Faraday Disc. Chem. Soc.*, 88: 317-333.
- Joo, J., Z. Oblakowski, G. Du, J.P. Pouget, E.J. Oh, J.M. Weisinger, Y. Min, A.G. MacDiarmid and A.J. Epstein, 1994. Microwave dielectric response of mesoscopic metallic regions and the intrinsic metallic state of polyaniline. *Phys. Rev. B*, 49: 2977-2980.
- Epstein, A.J., J. Joo, R.S. Kohlman, G. Du, A.G. MacDiarmid, E.J. Oh, Y. Min, J. Tsukamoto, H. Kaneko and J.P. Pouget, 1994. Inhomogeneous disorder and the modified Drude metallic state of conducting polymers. *Synth. Met.*, 65: 149-157.
- Javadi, H.H.S., R. Laversanne, A.J. Epstein, R.K. Kohli, E.M. Scherr and A.G. MacDiarmid, 1989. ESR of protonated "emeraldine": insulator to metal transition. *Synth. Met.*, 29: E439-E444.
- Stejskal, J. and R.G. Gilbert, 2002. Polyaniline. Preparation of a conducting polymer (IUPAC Technical Report). *Pure Appl. Chem.*, 74: 857-867.
- Khoo, S.B. and S.X. Guo, 1999. Rapidly renewable and reproducible electropolymerized surface at a monomer modified carbon paste electrode. *J. Electroanal. Chem.*, 465: 102-113.
- Krishna, M., V. Balarama, D. Karunasagar, S.V. Rao and J. Arunachalam, 2005. Preconcentration and speciation of inorganic and methylmercury in waters using polyaniline and gold trap-CVAAS. *Talanta*, 68: 329-335.
- Devi, P., S. Remya, S. Kumar, R. Verma and M. Sudersanan, 2006. Sorption of mercury on chemically synthesized polyaniline. *J. Radioanalytical Nuclear Chem.*, 269: 217-222.
- Gupta, R.K. and S. Shankar, 2004. Toxic waste removal from aqueous solutions by polyaniline: A radiotracer study. *Adsorption Sci. Tech.*, 22: 485-496.
- Zhu, W.W., N. B. Li and H.Q. Luo, 2006. Anodic stripping voltammetry determination of Pb(II) and Cd(II) at a bismuth/poly(aniline) film electrode. *Anal. Lett.*, 39: 2273-2284.
- Fungaro, D.A., 2004. Voltammetric determination of Cd and Pb using sulfonated polyaniline modified electrode. *Ecletica Quimica*, 29: 63-68.