



UNIVERSITI PUTRA MALAYSIA

**ELECTROCHEMICAL STUDIES ON ACRYLONITRILE GRAFTED
POLYSTYRENE AND CARBON NANOMATERIALS AS MODIFIED
ELECTRODES**

MUHAMMED MIZHER RADHI

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By

MUHAMMED MIZHER RADHI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
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Chairman: Associate Professor Tan Wee Tee, PhD

Faculty : Science

Acrylonitrile was successfully grafted on polystyrene using gamma-irradiation technique. The new grafted polymer (GP) was characterized and its properties were investigated. In this study, it is found that 2 gm of polystyrene, 90% (w/w) acrylonitrile monomer, 2% (w/w) ferrous ammonium sulfate (FAS) catalyst and 1.25 Mrad gamma dose are the optimized conditions required for the polymerization of GP. The grafted polymer was proved by Fourier transform infrared (FTIR), thermogravimetry analysis (TGA) and viscosity techniques. A mechanism is presented to explain the formation of GP.

A grafted polymer electrode (GPE) and a grafted polymer reference electrode (GPRE) were fabricated as a working and reference electrode respectively and used in electroanalysis. These new GPE and GPRE were evaluated using $K_3[Fe(CN)_6]$ in 0.1 M KCl as standard solution during cyclic voltammetry. The redox waves of Fe(III)/Fe(II) couple match well with those reported. Both the new GPE and GPRE

show good hardness, insolubility, reliability and stability at high temperature and at different pH.

A glassy carbon electrode (GCE) was modified to mediate a GP by using a solution evaporation method to produce a new modified electrode, GP/GCE. The redox process of $\text{K}_3[\text{Fe}(\text{CN})_6]$ during cyclic voltammetry was studied using the GP/GCE. It was found that the peak separation ($\Delta E_{pa,c}$) between the redox peaks of ferricyanide ion in aqueous solution is 82 mV and the current ratio of redox peaks, (I_{pa}/I_{pc}) is 1 for the GP/GCE, indicating that good reversibility with good conductivity of the modified electrode. Hence, it can be used for voltammetric analysis.

The modified electrode GP/GCE shows good hardness, high adhesion to metal surfaces of electrode collectors, insolubility and stability at high temperatures and at different pH levels. In addition, the sensitivity of the electrode under the cyclic voltammetry is significantly dependent on pH, the electrolyte used, temperature and the scan rate. Based on the surface charge determined by chronocoulometry (CC), GP/GCE appears more conductive than GCE. The diffusion coefficient of $7.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for the ferricyanide ion in the redox process was determined using a chronoamperometry (CA).

The modified glassy carbon electrodes (GCE) by microcrystals of fullerene C_{60} (C_{60}/GCE), activated carbon (AC/GCE) and carbon nanotubes (CNT/GCE) have been studied extensively mediating some selected heavy metal compounds such as Mn^{2+} , Hg^{2+} and Cd^{2+} in aqueous electrolyte.

GCE was modified with carbon nanotubes CNT, AC, and C₆₀ with and without Li⁺ dopant by mechanical attachment and solution evaporation methods. These new modified working electrodes abbreviated as CNT/Li⁺/GCE, AC/Li⁺/GCE and C₆₀/Li⁺/GCE were used in the presence of aqueous KCl electrolytes. Under conditions of cyclic voltammetry, the potential for oxidation and reduction peaks of the heavy metal ions such as Mn²⁺, Hg²⁺ and Cd²⁺ were shifted to lower potential (toward the origin) and the current was enhanced significantly relative to the modified electrodes. The sensitivity of the electrodes under the cyclic voltammetry was significantly dependent on different pH, temperature, scan rate and concentration. Positive interference with other heavy metal ions, such as Ca²⁺, Cu²⁺, Ni²⁺ were observed as the presence of these interfering metal ions causes further increase in the redox peaks of the heavy metal ions of interest.

Based on the surface charge determined by chronocoulometry (CC), the modified electrodes appear to be more conductive when the heavy metal ions were used in comparison with the bare GCE. Diffusion Coefficient (D) for the heavy metal ions was determined using chronoamperometry (CA). Excellent analytical recovery results of the heavy metal ions in blood sample and seawater were observed at the above mentioned modified GCE.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**KAJIAN ELEKTROKIMIA TERHADAP POLISTIRENA TERCANGKUK
DENGAN AKRILONITRIL DAN BAHAN KARBON NANO SEBAGAI
ELEKTROD TERUBAHSUAI**

Oleh

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September 2010

Pengerusi: Profesor Madya Tan Wee Tee, PhD

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Polistirena tercangkuk dengan acrylonitril menggunakan kaedah sinaran gamma telah berjaya disintesis. Polistirena tercangkuk ini dicirikan dan dikaji sifat-sifatnya. Dalam kajian ini, keputusan menunjukkan nisbah peratus terbaik bagi pengcangkukan diperolehi bagi kepekatan mangkin ferras ammonium sulfat (FAS) adalah 2 gm dan kepekatan monomer 90% berat pada dos 1.25 Mrad. Polistirena tercangkuk ini telah dianalisis dan dibuktikan dengan teknik-teknik FTIR, TGA dan kelikatan. Satu mekanisme bagi menjelaskan penghasilan polistirena tercangkuk di cadangkan.

Elektrod polistirena tercangkuk (GPE) dan elektrod rujukan polistirena tercangkuk (GPRE) telah dibentuk sebagai elektrod berfungsi dan elektrod rujukan dan digunakan dalam analisis kimia. GPE dan GPRE yang baru disintesis ini dinilai menggunakan $K_3[Fe(CN)_6]$ dalam 0.1 M KCl sebagai larutan piawai menggunakan voltametri kitaran. Pasangan gelombang redoks bagi Fe(III)/Fe(II) sangat sepadan

dengan yang telah dilaporkan. Sifat fizikal bagi kedua-dua elektrod GPE dan GPRE baru adalah baik dari segi kekerasan, ketidaklarutan, ketahanan dan kestabilan pada suhu dan pH yang berbeza.

Elektrod karbon berkaca (GCE) diubahsuai dengan perantaraan polistirena terangkuk (GP) menggunakan kaedah penjejatan larutan untuk menghasilkan elektrod terubasuai GP/GCE baru. Proses redoks bagi $K_3[Fe(CN)_6]$ semasa proses voltametri kitaran telah dikaji menggunakan GP/GCE ini. Didapati jarak pemisahan puncak ($\Delta E_{pa,c}$) antara puncak redoks untuk ion ferriksianida dalam larutan akues ialah 82 mV dan nisbah arus bagi puncak redoks (I_{pa}/I_{pc}) ialah 1 untuk GP/GCE yang menunjukkan elektrod ini sesuai dan dengan kekonduksian yang baik. Oleh itu, elektrod ini sesuai untuk analisis voltammetrik.

Sifat fizikal untuk elektrod terubasuai, GP/GCE ialah kekerasan yang baik, kelekitan yang baik kepada permukaan logam pemungut elektrod, ketidaklarutan, dan kestabilan yang tinggi pada GP/GCE pada suhu tinggi dan pH yang berbeza. Selain itu, sensitiviti bagi voltametri kitaran adalah sangat bergantung pada pH, elektrolit yang digunakan, suhu dan kadar imbasan. Berdasarkan muatan permukaan yang ditentukan oleh kaedah kronokoulometri (CC), GP/GCE kelihatan lebih konduktif daripada GCE; pekali penyebaran ialah $7.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ untuk redoks bagi ion ferriksianida yang ditentukan menggunakan kronoamperometri (CA).

Elektrod karbon berkaca terubasuai (GCE), oleh mikrohablur Fullerena C_{60} (C_{60}/GCE), karbon teraktif (AC/GCE) dan nanotiub karbon (CNT/GCE) telah dikaji secara mendalam dalam pencirian dan penggunaan elektrod-elektrod terubasuai

dengan perantara beberapa sebatian logam berat terpilih seperti Mn^{2+} , Hg^{2+} and Cd^{2+} di dalam elektrolit akues.

GCE diubahsuai dengan nanotub karbon CNT, AC dan C_{60} dengan dan tanpa bahan dop Li^+ dilakukan secara kaedah lekatan mekanik dan kaedah larutan meruap. Elektrod kerja terubahsuai dengan singkatannya seperti, CNT/ Li^+ /GCE, AC/ Li^+ /GCE dan C_{60}/Li^+ /CGE telah digunakan dalam kehadiran elektrolit KCl. Di bawah keadaan voltammetrik kitar, puncak keupayaan pengoksidaan dan penurunan bagi ion logam berat seperti Mn^{2+} , Hg^{2+} dan Cd^{2+} telah teranjak kepada keupayaan lebih rendah (mengarah ke asalan) dan arus dipertingkatkan dengan banyak berbanding dengan elektrod-elektrod terubahsuai. Kepekaan di bawah keadaan voltammetri kitaran banyak bergantung pada pH berbeza, suhu, kadar imbasan dan kepekatan. Gangguan positif terhadap lain-lain logam berat seperti Ca^{2+} , Cu^{2+} , Ni^{2+} dan sebagainya diperhatikan dimana kehadiran gangguan ion-ion logam menyebabkan peningkatan puncak-puncak redoks bagi logam berat terpilih iaitu Mn^{2+} , Hg^{2+} dan Cd^{2+} .

Berdasarkan kepada muatan permukaan yang ditentukan menggunakan kronokoulometri (CC), elektrod-elektrod terubahsuai di dapati lebih konduktif bila ion logam berat digunakan berbanding dengan GCE sahaja. Pekali resapan (D) bagi ion logam berat telah ditentukan menggunakan kronoamperogram (CA). Keputusan berulang secara analisis yang sangat baik bagi ion-ion logam berat dalam sampel darah dan air laut telah direkodkan menggunakan GCE yang tersebut di atas.

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I certify that a Thesis Examination Committee has met on **1st October 2010** to conduct the final examination of Muhammed Mizher Radhi on his thesis entitled "**Electrochemical Studies on Acrylonitrile Grafted Polystyrene and Carbon Nanomaterials as Modified Electrodes**" in accordance with Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U. (A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

Muhammed Mizher Radhi

Date: 3 September 2010

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