UNIVERSITI TEKNOLOGI MARA

STUDIES ON ELECTROPOLYMERIZATION OF *ORTHO*-PHENYLENEDIAMINE ON PLATINUM MICROELECTRODE AND ITS DETECTION OF HYDROGEN PEROXIDE AND ASCORBIC ACID USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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ABSTRACT

Poly-*ortho*-phenylenediamine (P*o*PD) has been successfully electropolymerized and characterized on Platinum disk (125 μm internal diameters) using Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV). *o*PD was first prepared using CV by dissolving *o*PD monomer into Phosphate Buffer Saline (PBS) using various monomer concentration, pH of PBS and scan rate to determine the optimum condition. The optimum condition (300 mM *o*PD in pH 7.2 PBS with scan rate 100 mVs^{-1}) recorded oxidation potential E = 500 mV at the highest anodic peak current, 9.16 x 10^5 mA cm^{-2}. Electropolymerization of *o*PD was carried out by EIS with applying the optimum condition and oxidation potential to determine the redox-kinetic parameters and electrical behavior of the system. Up to our knowledge, *o*PD electropolymerization on Pt disk microelectrode is firstly reported in this work. The redox-kinetic parameters of P*o*PD obtained from impedance data are charge transfer resistance, R_{ct}, (1.80x 10^2 kΩ), diffusion coefficient, *D*, (1.23 x 10^5 cms^{-1}) and double-layer capacitance, C_{dl}, (0.14 μF). These parameters were obtained as the impedance spectra were fitted to three proposed equivalent circuit models beginning with simple Randles Model, (R(Q[RW]) to a more complex models such as ([R(RQ)([RW]Q)] and [R([RW]C)(RC)]. They showed chi square values, χ^2, less than zero indicating the models fits to the impedance spectra. The P*o*PD coated electrode was used as analytical probes towards the detection of Hydrogen Peroxide (H_2O_2) and Ascorbic Acid (AA). EIS used to investigate the blocking ability of P*o*PD to the ascorbic acid and hydrogen peroxide is also firstly reported in this work. In various analytes concentrations, the impedance value of AA higher (4.4 kΩ to 6.6 kΩ) than H_2O_2 (2.8 kΩ to 3.7 kΩ) indicated the larger size of AA species impeded by P*o*PD layer to the electrode surface compared with smaller size of H_2O_2 species allowed to permeate. Meanwhile, dielectric constant values were also determined from the impedance data and exhibited higher values for ascorbic acid compared hydrogen peroxide as well. PoPD formation onto the electrode surface was confirmed by FESEM by exhibited a rough and crater-like surface formed.

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CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND

Electropolymerization is the most convenient method in constructing a conductive polymer or non conductive polymer modified electrode compared by a variety of method such as chemical polymerization. The electrochemical reaction occurred at the electrode surface caused by the immobilization of polymer species. The advantages of electropolymerization method are convenient and versatility process, it provide a direct reaction of the monomer at the electrode surface then follow by doping (charge injection) onto the surface with under optimized and controlled conditions. Other advantages include facile, reproducible control over film thickness and the ability to use diverse electrode geometries and form thick films (up to 1 micrometer).

Oyama and Ohsaka, (1987) discovered the electrochemical properties of aromatic compound with amino group by using electrochemical polymerization technique. This technique could generate conductive polymer or non-conductive polymer depend on the materials and preparations used. The example of conductive polymer that commonly electropolymerized and characterized are polythiophene (Kabasakaloglu, Kiyak, Toprak, and Aksu, 1999; Shi, Sun, Yang, Gao, and Li, 2002), polyfuran (Demiborga and Onal, 2000), polypyrrole (Sahrifidad, Omrani, Rostami, and Khushroo, 2010), phenylenediamine (Losito, Giglio, Cioffi, and Malitesta, 2001; Li, Duan, Huang, and Rodriguez, 2005). The electropolymerization of non-conducting polymers onto the electrode surface are not involved in electron transfer reactions, and therefore they are behave partially or totally passivating. Even though it behave as passsivating layer, these polymers are very useful in constructing permselective films as it is enhance the analysis of many different molecular entities especially for biosensor applications.