



Electrochemical Behaviours of 4,4'-Methylenedianiline in Non-Aqueous Media on a Platinum Electrode Surface

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Electrochemical behaviours of 4,4'-methylenedianiline were investigated by cyclic voltammetry, differential pulse voltammetry and electrochemical impedance spectroscopy on a platinum electrode surface. The platinum working electrode surface was modified with 4,4'-methylenedianiline in acetonitrile containing 100 mM tetrabutylammonium tetrafluoroborate using 100 mV s⁻¹ scan rate from 0.0 mV to +1600 mV potential range with 30 cycles. In differential pulse voltammetry experiments, the potential range was from 0.0 mV to +1000 mV. The presence of 4,4'-methylenedianiline at the platinum electrode surface was characterized by cyclic voltammetry and electrochemical impedance spectroscopy.

Key Words: 4,4'-Methylenedianiline, Modified electrode, Surface characterization, Cyclic voltammetry.

INTRODUCTION

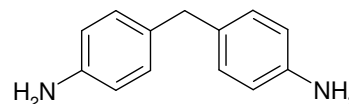
Electrode modification is an important part of the electrochemical studies and has been frequently used for last two decades. After the optimum conditions are set the modification can be performed by the electrochemical oxidation (amine and alcohol oxidation, *etc.*) or electrochemical reduction (diazonium reduction, *etc.*)¹⁻⁴.

Electrochemical modified electrodes have a broad range of applications in modern electrochemistry. They have been widely applied in electro-catalytic reactions⁵ and as electrochemical sensors^{6,7}.

In this study, 4,4'-methylenedianiline was covalently modified on the Pt electrode surface by electrochemical oxidation in non-aqueous media. Electrochemical behaviours of 4,4'-methylenedianiline were investigated by cyclic voltammetry and differential pulse voltammetry. The modification of 4,4'-methylenedianiline on the Pt electrode surface was performed between 0.0 mV and +1600 mV potential range at 100 mV s⁻¹ scan rate with 30 cycles. The presence of 4,4'-methylenedianiline at the Pt electrode surface was characterized by cyclic voltammetry and electrochemical impedance spectroscopy. The potential range was from 0.0 mV to +1000 mV in differential pulse voltammetry experiments.

EXPERIMENTAL

In all experiments, ultrapure water with a resistance of 18.3 MΩ cm (Millipore Milli-Q purification system, Millipore



Scheme-I: Chemical structure of 4,4'-methylenedianiline

Corp. Bedford, MA, USA) was used for preparation of aqueous solutions, the cleaning of glassware and polishing of the electrodes. All chemicals of reagent grade were used as received. 4,4'-methylenedianiline, NBu₄BF₄ and CH₃CN were obtained from Fluka (Buchs SG, Switzerland) or Sigma-Aldrich (Buchs SG, Switzerland) chemical companies. Solutions were thoroughly deoxygenated by purging with purified argon gas (99.99 %) for 10 min prior to the electrochemical experiments.

Electrochemical measurements were performed with GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA from GAMRY Instruments (PA, USA), using a standard cell with three electrodes. The working electrode was a Pt electrode BAS model MF-2013. The reference electrodes an Ag/Ag⁺ (10 mM AgNO₃) (BAS Model MF-2042) for non-aqueous media and a Ag/AgCl/3 M KCl (BAS Model MF-2063) for aqueous media were used. Platinum wire (BAS Model MW-1032) was used as counter electrode.

The size of platinum working electrode was 1.6 mm dia. Prior to the surface modification, the platinum electrode was polished on a polishing cloth with wet alumina powders, starting with 0.3 μm particle size and then with finer grades down to 0.05 μm. It was then rinsed with ultrapure water and sonicated for 5 min⁸.

RESULTS AND DISCUSSION

The Pt working electrode surface was modified by using a solution of 1 mM 4,4'-methylenedianiline, in a non-aqueous media, in CH₃CN containing 100 mM NBu₄BF₄. Modification was performed in the range from 0.0 mV to +1600 mV at 100 mV s⁻¹ scan rate with 30 cycles (Fig. 1). Cyclic voltammogram of 4,4'-methylenedianiline shows two oxidation peaks at the Pt electrode surface. Anodic peaks are observed at 525.4 mV and 959.2 mV for 4,4'-methylenedianiline vs. Ag/Ag⁺ + electrode.

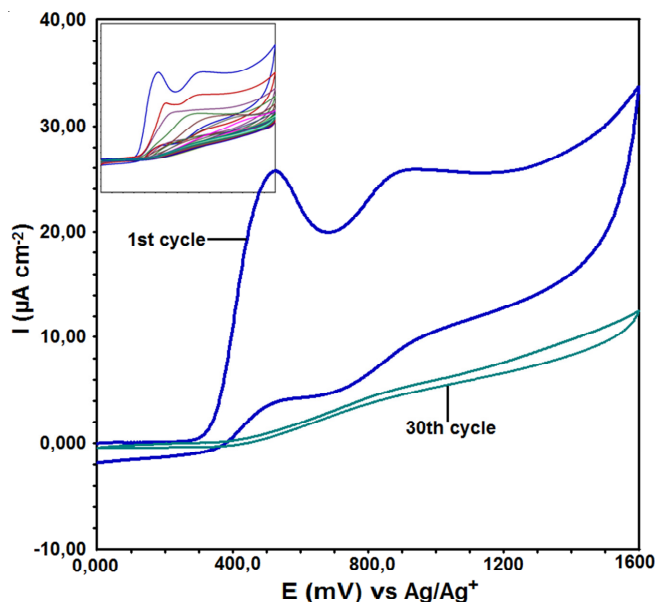


Fig. 1. Cyclic voltammogram of 1 mM 4,4'-methylenedianiline in CH₃CN containing 100 mM NBu₄BF₄ vs. Ag/Ag⁺ (10 mM AgNO₃) on a Pt working electrode. Potential range from +0.0 mV to +1600 mV, scan rate is 100 mV s⁻¹

Surface characterizations after the modification process were carried out by cyclic voltammetry and electrochemical impedance spectroscopy. In the characterizations with cyclic voltammetry, 1 mM ferrocene solution in 100 mM NBu₄BF₄ was carried out the potential range from -200 mV to +400 mV in non-aqueous media and 1 mM Fe(CN)₆³⁻ in Britton-Robinson (BR) buffer solution, pH 2, was performed the potential range from +500 mV to -100 mV in aqueous media at scan rate of 100 mV s⁻¹. Fig. 2A and 2B exhibits the voltammograms ferrocene and Fe(CN)₆³⁻, respectively. When the voltammogram obtained in ferrocene and Fe(CN)₆³⁻ is overlaid with the voltammogram obtained for bare Pt electrode, it is clear that the modified surfaces are not allow electron transfer.

Impedance measurements were carried out in 1 mM Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ mixture in 100 mM KCl in the range from 100.000 Hz to 0.05 Hz frequency by electrochemical impedance spectroscopy and the Nyquist plots were recorded (Fig. 3). The Nyquist plot of the modified electrode was compared with the electrochemical impedance spectroscopy data of bare Pt electrode. The bare Pt electrode exhibits a low frequency straight line with a very small semi-circle. 4,4'-Methylenedianiline/Pt electrode, there is a semi-circle at high frequency region, implying that modified Pt electrode surface depicts a blocking ability for electron transfer reaction.

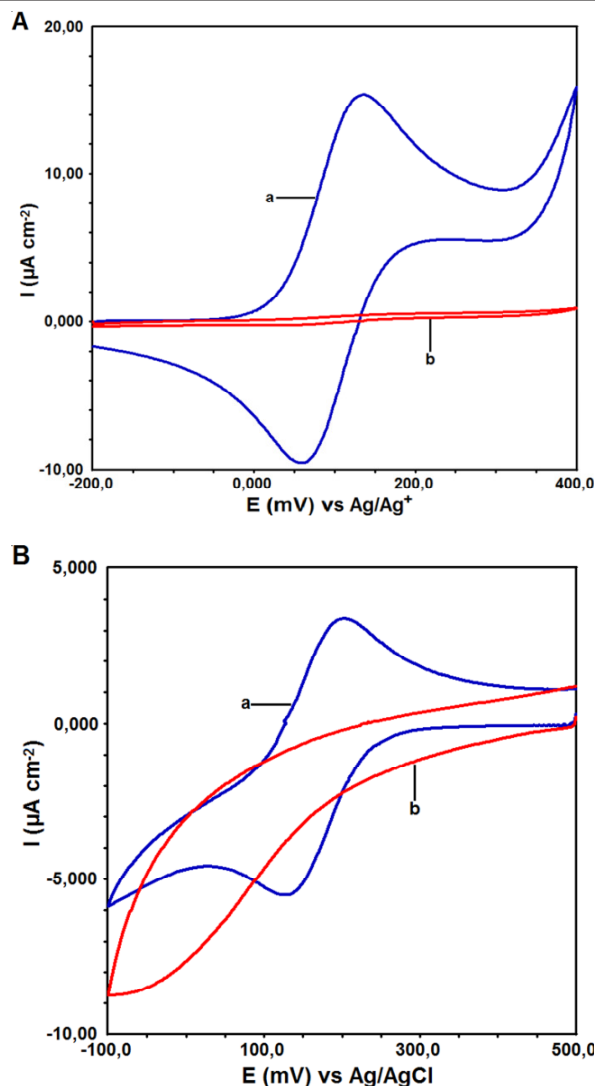


Fig. 2. Overlying cyclic voltammograms for (A) 1mM ferrocene redox probe solution vs. Ag/Ag⁺ (10 mM AgNO₃) in CH₃CN containing 100 mM NBu₄BF₄, (B) 1 mM Fe(CN)₆³⁻ redox probe solution vs. Ag/AgCl/3 M KCl reference electrode in BR buffer solution, pH = 2, with a Pt working electrode at 100 mV s⁻¹ scan rate (a, bare Pt; b, 4,4'-methylenedianiline/Pt)

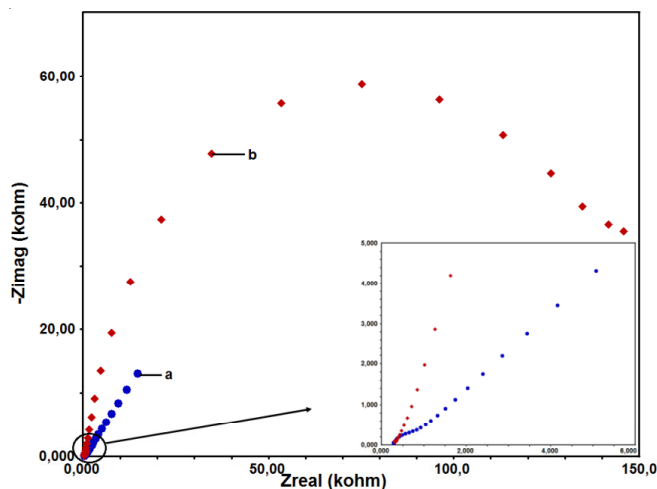


Fig. 3. Nyquist plots for electrochemical impedance spectra of 1 mM Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ redox couple solution in 100 mM KCl at the frequency range of 100.000-0.05 Hz at 10 mV wave amplitude, on a Pt working electrode (a, bare Pt; b, 4,4'-methylenedianiline/Pt)

In differential pulse voltammetry experiments, the potential range was from 0.0 mV to +1000 mV, the potential scan rate was 50 mV s^{-1} , the pulse amplitude was 25 mV, the pulse period was 0.05 s and the sample period was 1.0 s. The differential pulse voltammogram of the modified electrode was compared with the differential pulse voltammogram of bare Pt electrode. Anodic peaks are observed at 424.5 mV and 720.4 mV for 4,4'-methylenedianiline/Pt vs. Ag/Ag⁺ electrode in CH₃CN containing 100 mM NBu₄BF₄.

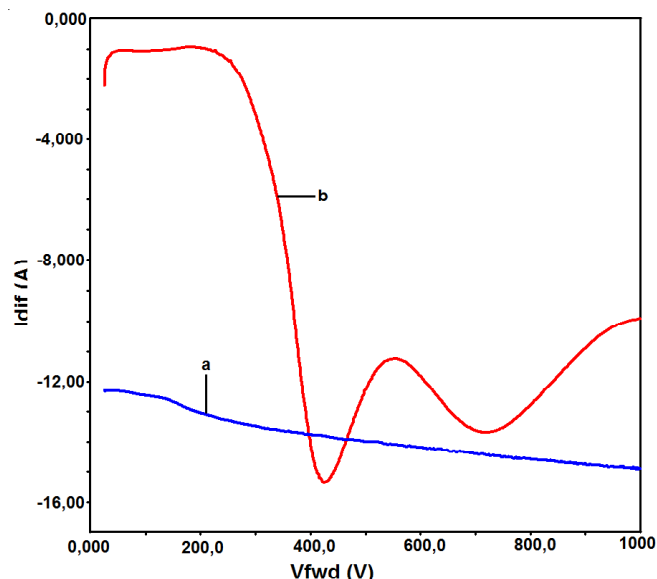


Fig. 4. Differential pulse voltammograms (scan rate 25 mV s^{-1}) of 1 mM 4,4'-methylenedianiline in CH₃CN containing 100 mM NBu₄BF₄ vs. Ag/Ag⁺/(10 mM AgNO₃) on a Pt working electrode (a, bare Pt; b, 4,4'-methylenedianiline/Pt)

Conclusion

An investigation was performed about the electrochemical and spectroelectrochemical properties of 4,4'-methylenedianiline

on Pt electrode. The molecule has two -NH₂ group attached one to each phenyl ring. From the voltammogram in Fig. 1 and the surface characterization process, it can be concluded that the molecule binds to the electrode surface through amine group simultaneously. First oxidation peak on Fig. 1 belongs to the oxidation of amine groups (2H^+ , 2e^- transfer) and second peak belongs to the binding of the molecule to the electrode surface through C-N covalent bonding. The binding reaction takes place over EC (Electrochemical and Chemical) mechanism. Differential pulse voltammetry voltammogram was taken after the modification process, shows that the molecule has binds to the electrode surface successfully. The next step of this study will be the synthesizing the diazonium salt of this molecule. Thus only one -NH₂ group will be converted to diazo group and the molecule will bind to the electrode surface by reduction through C-C covalent bond from diazo and an electroactive modified electrode will be obtained by having an unaffected -NH₂ group. The developed electrode will be able used as a chemical sensor electrode for proper molecules.

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