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The Characterization of Poly (P-Phenylenediamine) using Scanning Electron Microscopy Cyclic Voltammetry and Rotating Disc Electrode

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Abstract

In this work, the electropolymerization of P-phenylenediamine at three-phase junction in acidic solution free monomer have been performed. Scanning Electron Microscopy (SEM) has been used to study the morphology of films formed. The characterization of films was done using cyclic voltammetry and rotating disk electrode techniques on Fe $(CN)_6^{4-/3-}$ Solution. Finally, the sensors fabricated have been applied on lead and cadmium detection. All the study stages Poly (p-phenylenediamine) formed at three-phase junction demonstrate much better performance than that obtained by usual electropolymerization.

Keywords: Electropolymerization, Poly (p-phenylenediamine), RDE, SEM, Three phase junction.

1. Introduction

In the last few years, the development of electronically conducting polymers has received much attention due to a new interesting properties in addition to their application potentials in different areas such as microelectronic devices [1], biomedical engineering[2], sensors and biosensors [3,4], corrosion protection [5].

Among the conducting polymers, polypyrrole [6], polyaniline [7] are the more intensively studied polymers, because of their environmental stability and their wide applications in different fields. Other aromatic compounds are containing one or two NH_2 groups or another functional groups, such as OH, have been used for preparation of polymeric film-coated electrodes. Typical compounds are m-, o-, and p-phenylenediamine [8-11], 1,5- and 1,8-diaminonaphtalene [12-16]. Ortho-aminophenol [17] have also some interesting properties like electro-chromic properties, redox activity, sensitivity to H^+, as well as their unique structures.

In recent studies [18-19], a new strategy of polymerization has been developed. It consists in incorporating p-phenylenediamine or 1-8-diaminonaphtalene into carbon paste electrode and performing electropolymerization

In the present work, the electrochemical behavior of poly (p-phynelenediamine) films prepared by different procedures has been characterized by SEM to study the morphology of films formed. A characterization of films was done also by cyclic voltammetry and rotating disk electrode techniques on Fe $(CN)_6^{4-/3-}$ Solution. As a result, the sensors fabricated have been applied to lead and cadmium detection.

2. Materials and methods

2.1. Apparatus

All the chemicals used were analytical reagent grade, used without further purification. The p-phenylenediamine has been obtained from (SIGMA), $k_4Fe(CN)_6/k_3Fe(CN)_6$ were commercialized by (FLUKA). Aqueous solutions were prepared with distilled water.

Cyclic voltammograms were recorded using the electrochemical measuring station AUTOLAB PGSTAT 10 Potentiostat (Ecochimie, Utrecht, Netherlands) controlled by GPES 4.8 software. The three electrode systems consist of the rotating disc electrode controlled by oxford motor (0, 0707 cm^2) as working electrode, a saturated electrode calomel (SEC) as the reference electrode and platinum wire as the counter electrode.

2.2. Preparation of carbon paste electrode (CPE)

The carbon paste electrode (CPE) was prepared by mixing 1g of graphite powder and 0,3ml of paraffin oil until a uniformly wetted paste was obtained. The paste was then inserted into the electrode cavity. A stainless steel wire provided the electrical contacts; the electrode surface could be renewed by simple extrusion of a small amount of paste from the tip of the electrode. Before each use, the CPE was rubbed with a piece of paper until a smooth surface was observed.

2.3. Modification of carbon past electrode

In the first procedure, the carbon paste electrode was prepared and immersed in a solution containing 5.10^{-3} M of p-phenylenediamine as monomer in 0,1 M of hydrochloride acid.

The second procedure consists on mixing a 0,01g of p-phenylenediamine dissolved in acetonitrile with 1g of graphite and an appropriate quantity of Nujol. Thereafter, the electrode was prepared as described in section 2.2 and immersed in the 0, 1 M of aqueous chloride solution free monomer.

3. Results and discussion

3.1. Electropolymerization conditions of p-phenylendiamine

In the first step, the p-phenylenediamine electropolymerization has been investigated by the cyclic voltammetry and the optimum conditions of electropolymerization were established. The choice of cyclic voltammetry method has been performed to better visualize the potential ranges of the monomer oxidation and the polymer. The potential cycling was performed at scan rate of 50mV/s. The voltammetric response of CPE shows that there is an initial oxidation of the monomer by formation of cation radical on the electrode surface. The peak of oxidation was around 0,65 V/ECS corresponding to amine group oxidation [18]. The current decrease in the second cycle, however after about 10 cycles it remains constant.

When the polymerization was conducted into carbon paste in acidic media without monomer, the current observed increase with successive cycles indicating that the polymer formed is conducting [18].

3.2. Characterization of poly (p-phenylendiamine) morphology by Scanning Electron Microscopy (SEM)

In order to facilitate a further direct comparison between synthesis of Poly (p-phenylenediamine) in solution and at three phase junction, the CPE modified by both of these methods were characterized by SEM. **Figure A_1** shows the morphologies of the CPE modified in surface by poly (p-phenylenediamine): the p-phenylenediamine is dissolved in the aqueous solution and the electropolymerized at CPE, While, **Figure B_1** shows the morphology of the CPE modified in bulk: p-phenylenediamine is incorporating in CPE matrix during the polymerization.

Figure B_1 reveals that the poly (p-phenylenediamine) film obtained by modification in volume has rod like morphology. The formation of poly (p-phenylenediamine) microrods is probably related to the self assembly of poly (p-phneylenediamine) through intermolecular $\pi-\pi$ interactions and the electrostatic repulsion interactions, which is similar to the previous report [8].

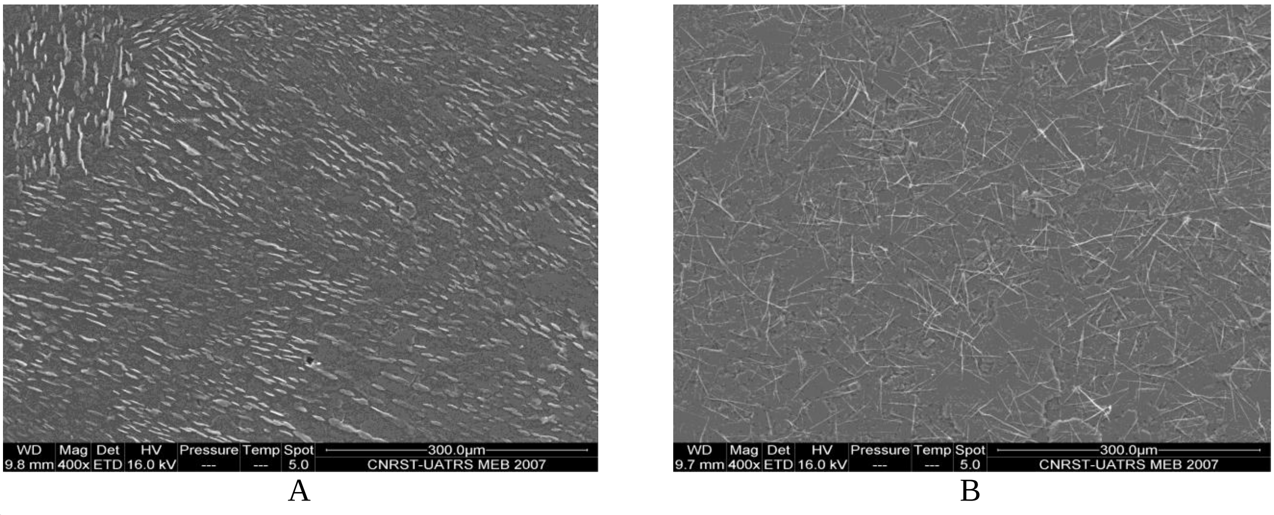

Figure 1: Morphology of CPE modified in surface (A) and CPE modified in volume (1% of p-phenylenediamine) (B)

3.3. Electrochemical behavior of poly (p-phenylenediamine) films coated CPE in presence of Fe (CN) $_6^{3-/4-}$

The cyclic voltammetry was used for evaluating the electrochemical characteristic of poly (p-phenylenediamine) films formed in presence of Fe $(CN)_6^{3-/4-}$ 10^{-3} M prepared in KCl 0.5 M. The **Figure 2** shows the Fe $(CN)_6^{3-/4-}$ redox couple response at the bare CPE, at the CPE modified in surface and at the CPE modified in volume et sweep rate of 50mV/s.

A simple comparison between the voltamograms obtained in **Figure 2** shows that the oxidation peak current of the bare CPE was fivefold lower than that of the CPE modified in volume, and higher than that modified in surface. In other hand, the electrochemical systems become more fast if we displace from the CPE modified in surface to this modified in volume. This result demonstrates that the poly (p-phenylenediamine) formed in volume had a catalytic effect in Fe $(CN)_6^{3-/4-}$ response. In contrary, the poly (p-phenylenediamine) modified in surface blocked the CPE surface due to the fact that the film is not vey conducting.

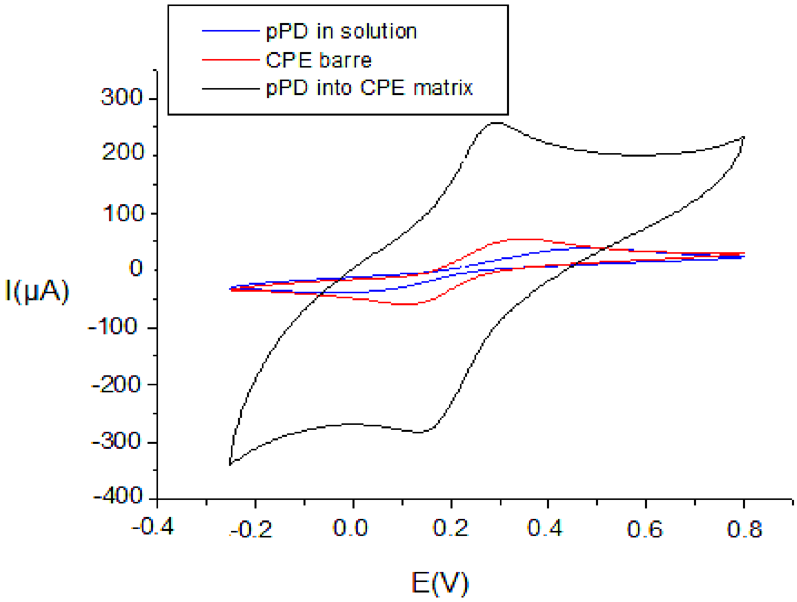

Figure 2 Cyclic voltammogram of Fe $(CN)_6^{3-/4-}$ obtained at bare CPE, at CPE modified in surface and at CPE modified in volume by 1% of p-phenylenediamine.

3.4. Diffusional character evaluation

In order to demonstrate the diffusional character of the mass transfer at an electrode modified in volume and in surface, the CPE and the modified CPE have been characterized by cyclic voltammetry ranging sweep rate from 10 to 1200 mV/s. **Table 1** shows the plots equations of the peak oxidation current against the squares root of sweep rate. The i_p-$v^{1/2}$ plots are linear passing through the origin, what is in agreement with the diffusional character of the mass transfer at modified electrode. In other hand, as we can concluded from **Table 1** that the oxidation peaks current of Fe $(CN)_6^{3-/4-}$ at the electrode modified in bulk are always much higher than that of the CPE modified in surface. We can explain this behavior by the “Three Phase Junction phenomenon” and the “Fractals theory”.

Table 1: The plots equations of the peak oxidation current against the squares root of sweep rate i_p (µA)-$v(mV/s)^{1/2}$ corresponding to Fe $(CN)_6^{3-/4-}$ oxidation obtained at bare CPE, at CPE modified in surface and at CPE modified in volume. Cyclic voltammetry experiments have been performed ranging sweep rate from 10 to 1200 mV/s.

Electrode	*Equations*	R^2
CPE modified in volume by 2% poly-pPD	*y = 43,7x*	*0,9986*
CPE modified in volume by 1% poly-pPD	*y = 35,5x*	*0,9938*
CPE modified in volume by 0.5% poly-pPD	*y = 26,7x*	*0,9931*
bare CPE	*y = 6,2x*	*0,9776*
CPE modified in surface by poly-pPD	*y = 4,1x*	*0,9606*

3.4.1. The three-phase junction phenomenon

The intrinsic property of the electrochemical process at three-phase junction is the coupling of two electrochemical steps, the electron transfer and the ion transfer reaction. The presence of the electroactive component (p-phenylenediamine) in the organic phase, duct to the electron transfer reaction at the working electrode|organic liquid (WE|OL) interface. As a consequence, the unbalanced electroneutrality of the organic phase, promoting an ion transfer reaction which has to occur across the organic liquid|aqueous electrolyte interface (OL|AQ). Although the ion transfer follows the electron transfer reaction, both of the electrochemical process proceeds simultaneously [20-24].

3.4.2. The fractals theory

The increasing current seen when the percentage of p-phenylenediamine incorporating in the CPE increases can be explained by the electrode surface augmentation (fractals theory). The same phenomena was observed and explained in case of poly (3, 4-ethylenedioxythophéne) in one of resent publication of Randriamahazaka and al [25]. In our case, all of the portions of poly (p-phenylenediamine) irregular surface showed in **Figure B_1** participate in reaction.

3.5. The electrochemical characterization of Poly (p-phenylenediamine) with rotating disk electrode in presence of Fe $(CN)_6^{3-/4}$

The Ferro/ferricyanide couple response was studied on rotating disk electrode at the bare CPE and at the CPE modified by poly (p-phenylenediamine) in volume (1%) and at the CPE modified in the surface. **Figure 3** demonstrates that the same electrochemical behavior has been observed for the bare CPE and the CPE modified in surface, and legers hysteresis for the CPE modified in volume. The current recorded on the modified electrode by poly (p-phenylenediamine) in volume are much higher indicating that the film is more conducting. This is in agreement with our previous results obtained by cyclic voltammetry.

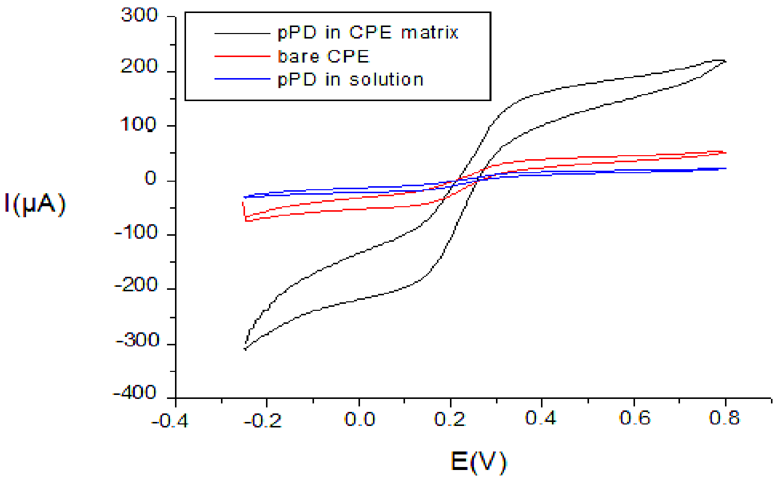

Figure 3 Ferro/ferricyanide couple response studied by cyclic voltammetry and rotating disk electrode at the bare CPE, at the CPE modified in volume (1%) by poly (p-phenylenediamine) and at CPE modified in surface. The rotation rate and the sweep rate used in this experience are 100 rpm and 10mV/s, respectively.

Thereafter, other experiences were realized against rotating rate, ranging from 100 rpm to 1200 rpm at 10 mV/s. **Figure 4** shows the $\mathbf{i_p}$-$\mathbf{\Omega^{1/2}}$ curves obtained at different electrodes (bare CPE and modified CPE) against rotating rate, varying rotating rate between 100 rpm to 1200 rpm and potential from -0.4 V/ECS to 0.8 V/ECS, with a sweep rate in order to 10 mV/s. These results showed that the response of the bare CPE is always very lower than that of the CPE modified in volume, and higher than that of the CPE modified in surface. The current increases with increasing the percentage of monomer in the carbon paste electrode.

The variation of current on a bare CPE, a CPE modified by poly (p-phenylenediamine) were measured on oxidation plateau E=0.5 V/ECS and analyzed below Levich model. The limiting current was given by Levich's law:

$$I_{lim} = 0.69nFD^{2/3}\,V^{1/6}\,A\,C\,\Omega^{1/2}$$

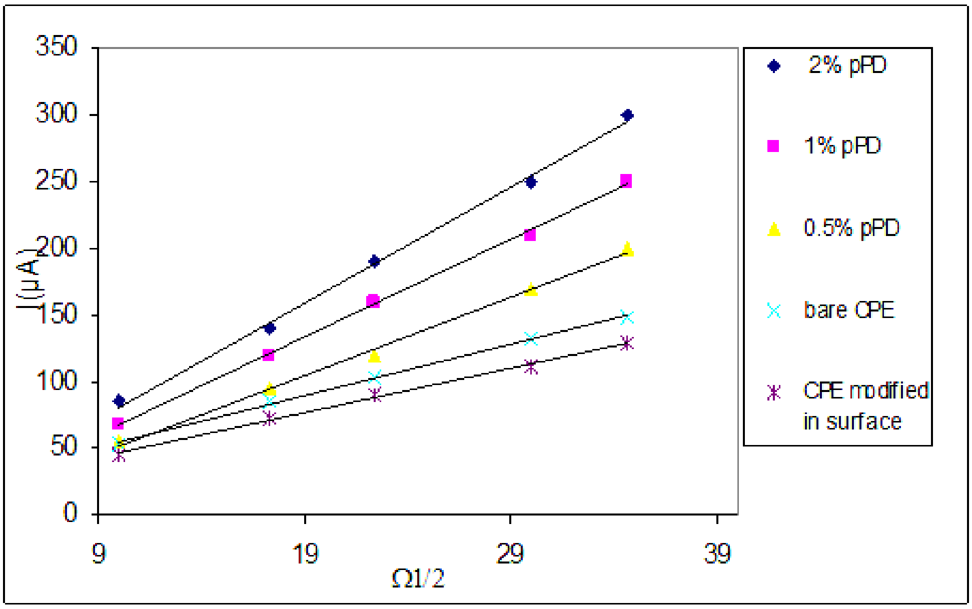

Figure 4 Levich plots (i_p-$\Omega^{1/2}$) obtained at different electrodes (bare CPE and modified CPEs), varying rotating rate between 100 rpm to 1200 rpm and potential from -0.4 V/ECS to 0.8 V/ECS, with a sweep rate in order to 10 mV/s.

3.6. The evaluation of Koutecky-Levich Law

The Koutecky-Levich criterion was applied at different electrodes. Eq. (1) assumes that the electroactive species dissolves into the polymer film with a partition equilibrium $\kappa = c_{pol}/c$ at the film | solution interface, where c_{pol} and c are the respective concentrations of the species in the polymer and the solution.

$$\frac{1}{I_{\lim}} = \frac{1}{I_k} + \frac{1}{I_d} = \frac{\phi}{nFA\kappa D_s c} + \frac{1}{0{,}62nFAD^{2/3}\nu^{-1/6}\Omega^{1/2}c} \qquad (1)$$

Were I is the measured current, I_k and I_d the kinetic and diffusion-limited currents, D_s and D are the diffusion coefficients of the electroactive species in the polymer and solution, ϕ is the film thickness of poly (p-phenylenediamine), c concentration of electroactive species and ν is the kinematic viscosity of the solution, n number of electron transferred per molecule, F faraday constant. **Tabe 2** show the plot equations of the inverse of oxidation peak current vs. of inverse of square rotating rate of electrode. The obtained curves no throwing origin, this result was in perfect agreement with Koutecky-Levich criteria Eq. (1).

Table 2: Koutecky-Levich plots equations of Fe $(CN)_6^{3-/4-}$ oxidation at bare CPE, at CPE modified in surface and at CPE modified in volume $(I(\mu A)^{-1}$ vs $\Omega(rad.s^{-1})^{-1/2})$

Electrode	*Equations*	*R^2*
CPE modified in volume by 2% poly-pPD	*y = 0,2059x + 0,0021*	*0,9996*
CPE modified in volume by 1% poly-pPD	*y = 0,1843x + 0,0019*	*0,9999*
CPE modified in volume by 0.5% poly-pPD	*y = 0,1726x + 0,0018*	*0,999*
bare CPE	*y = 0,1535x + 0,0014*	*0,9995*
CPE modified in surface by poly-pPD	*y = 0,1182x + 0,001*	*0,9977*

3.7. Analytical application of modified electrode for simultaneous detection of Cd^{2+} and Pb^{2+}

The results obtained from cyclic voltammetry experiments demonstrate that poly (p-phenylenediamine) formed in volume had a catalytic effect in Fe $(CN)_6^{3-/4-}$ response. In contrary, the poly (p-phenylenediamine) modified in surface blocked the CPE surface. The same phenomenon has been obtained on lead and cadmium detection in acidic medium, no response of cadmium and lead had detected in case of poly (p-phenylenediamine) modified in surface.

In 2005 our group has applied the p-phenylenediamine polymerized in volume to lead detection in aqueous solution [19]. The sensor developed (poly(p-phenylenediamine) modified in volume (1%)) in 2005 has been tested in this work under rotation electrode rate effect for Cd^{2+} and Pb^{2+} determination in acidic medium. **Figure 6** shows the voltammogram of 100 ppb of Cd^{2+} and Pb^{2+} at Carbone paste electrode modified in volume (1%) under 100 and 900 rpm rotation rate of electrode effect. The comparison between the two separate peaks indicates that the rotation rate has increased the sensor performance.

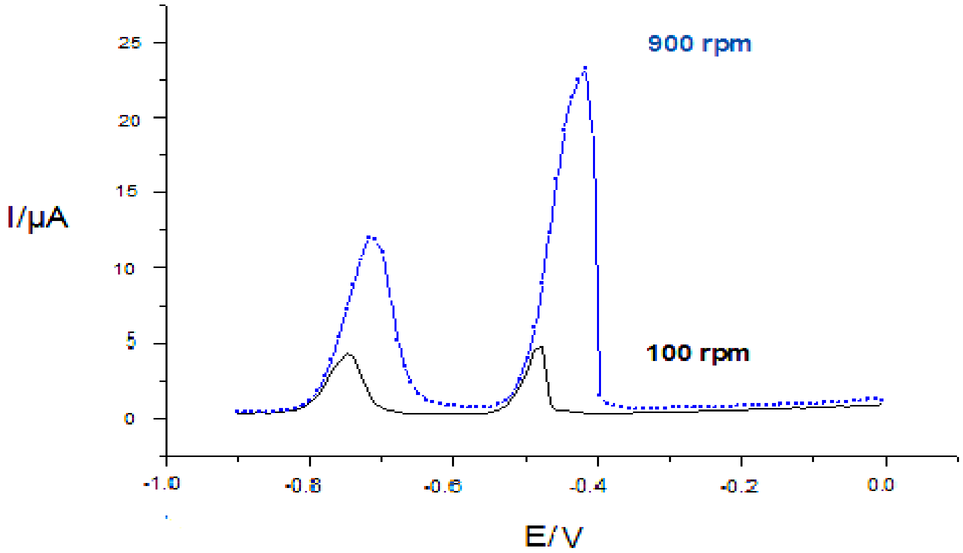

Figure 6: Voltammogram of 100 ppb of Cd^{2+} and Pb^{2+} determination at Carbone paste electrode modified in volume by poly (p-phenylenediamine), for two rotating rate 100 and 900 rpm. Condition: E_{dep} : –1.1V/ECS, t_{dep} : 120 s, t_{eq} de 30 s ; Electrolyte support : HCl 0.1 mol L^{-1}.

Conclusion

In this work, the electropolymerization of p-phenylediamine into carbon paste electrode has been studied and compared by the usual electropolymerization at the CPE surface. Polymers formed have been characterized by SEM, Cyclic voltammetry, and by Rotating Disk Electrode.

SEM Analysis demonstrates that the poly (p-phenylenediamine) film obtained by modification in volume has rod like morphology. The results obtained from cyclic voltammetry experiments demonstrate that poly (p-phenylenediamine) formed in volume had a catalytic effect in Fe $(CN)_6^{3-/4-}$ response. In contrary, the poly (p-phenylenediamine) modified in surface blocked the CPE surface.

The results obtained from the rotating disk electrode experiments show that the diffusion process of Fe $(CN)_6^{4-/3-}$ is in parfait agreement with the diffusional character of the mass transfer at modified electrode.

To conclude, that the oxidation peaks current of Fe $(CN)_6^{3-/4-}$ at the electrode modified in volume are always much higher than that of the CPE modified in surface. That is explained by the “Three Phase Junction phenomenon” and the “Fractals theory”. Levich and Koutecky-Levich plots was obtained using rotating disk. Plotting the reciprocal current (1/i) against the reciprocal square root of the angular rotation rate yields a straight line with an intercept equal to the reciprocal kinetic current ($1 / i_K$). The kinetic current is the current that would be observed in the absence of any mass transport limitations.

Finally, the electrode modified in volume has been tested (under the rotation of the electrode) for simultaneous detection of Cd^{2+} and Pb^{2+}.

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