



Influence of Monomer Concentration on Capability of Voltammetric Polypyrrole Based Cation Sensor Using Modified Butler-Volmer Equation

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Abstract: In this work, a modified Butler-Volmer equation is used to determine capability of voltammetric ion sensor based on modified PPy/DBS electrode. This method shows a direct relationship between mid point reversible potential (E_R) and the logarithm of the electrolyte concentration. Slopes from Butler-Volmer equation include electron-transfer coefficient. Modified PPy/DBS electrode was successfully applied as voltammetric cation sensor. It was shown that the capability of the sensor depends on the quality of formed polypyrrole film which is dependent on the initial monomer concentration.

INTRODUCTION

The voltammetric sensors have some advantages when compared to ion-selective electrodes: they dispense with the need to prepare one electrode per ion; the current-time and potential-time curves provide more analytically useful information than single equilibrium potential curves obtained under potentiometric conditions; also, the reversible potential can be calculated from data obtained under dynamic conditions. For voltammetric ion sensors based on polymeric materials, linear relationships between potential and the logarithm of electrolyte concentration can be found. The voltammetric sensors are very attractive for practical applications because they are associated with small-size, portability, low energy consumption, and low cost (Wooster and Bond, 2003; Wooster, Bond and Honeychurch, 2003; Cano, Rodriguez-Amaro and Romero, 2008a, 2008b).

Electrically conducting polymers have also attracted much attention due to their many promising technological applications, as for example microelectronic devices, electroluminescence devices, electrochemomechanical devices, corrosion inhibitors and chemical sensors.

Application of conducting polymers in chemical sensors has been extensively studied since 1987. Among conducting polymers, polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh), are particularly attractive because of their simple synthesis, high conductivity and excellent environmental stability. These polymers offer great possibilities to improve the sensors selectivity, partly by changing the chemical structure of the polymer backbone, and partly because the many possible counterions or neutral molecules can be trapped inside the polymer (Aradilla, Estrany, Azambuja, *et. al.*, 2010; Inzelt, 2008; Jovanović, Stanković, Laninović *et. al.*, 2000; Wallace, Spinks, Kane-Maguire *et. al.*, 2009).

EXPERIMENTAL

Instruments

All electrochemical parameters were determined using Princeton Applied Research model PAR263A potentiostat/galvanostat connected to PowerCV software. A three-electrode cell was used with Pt disc electrode, an Ag/AgCl/KCl_(sat) reference electrode (+197 mV vs. SHE), and a Pt foil as counter electrode.

Reagents

Pyrrrole (Sigma-Aldrich, 99%) was double distilled under vacuum before use, and kept in the refrigerator, protected from light. Sodium dodecylbenzene sulfonate (DBS) (Sigma-Aldrich), LiClO₄, NaClO₄, KClO₄ and Al₂O₃ (Kemika, Zagreb), were used as received. All solutions were made using doubly distilled water.

Determination of the electrode surface

The "electrochemical surface" of a polished platinum electrode is determined by a chronoamperometry using the electrochemical reduction of complexed Fe(III) ions. The analysis uses the Cottrell equation which establishes the time evolution profile of the current versus the surface, the concentration and the diffusion coefficient of the species for a large potential step at planar electrode. The integration of the Cottrell equation establishes that the slope of I versus \sqrt{t} is directly proportional to the electroactive surface. The electroactive surface is calculated from chronoamperometric response of Pt electrode in 0.01 mol dm⁻³ solution of K₃[Fe(CN)₆] using Cottrell equation (Zoski, 2007):

$$I = nFAc_0(D/\pi t)^{-1/2} \quad (1)$$

where n is the number of electrons, A is the electrode area (cm²), D is the diffusion coefficient, F is the Faraday constant and c is the concentration (mol cm⁻³).

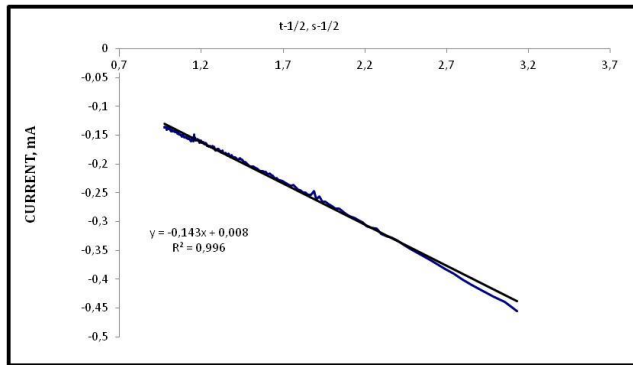


Figure 1: Chronoamperometric determination of electrode area

Using the slope from the chronoamperometric curve, calculated electrode surface of Pt disc electrode was 0.09866 cm².

Electrode immobilization

Pyrrrole electropolymerization and deposition over the bare Pt electrode (0.09866 cm²) was performed potentiostatically at 0.8 V vs. Ag/AgCl from an aqueous solution of three different concentrations of pyrrrole monomer (0.05 mol dm⁻³, 0.1 mol dm⁻³ and 1 mol dm⁻³) containing also 0.1 mol dm⁻³ DBS, in a three-electrode conventional cell using Pt foil as counter electrode. The amount of polypyrrole deposited can be controlled by choosing proper deposition times, or choosing the charge value. As reported in some previous papers, 0.3 C cm⁻² value of charge density showed good sensitivity, so the same value of charge density was chosen for the measurements (Goncles, Massafra, Benedetti *et al.*, 2009).

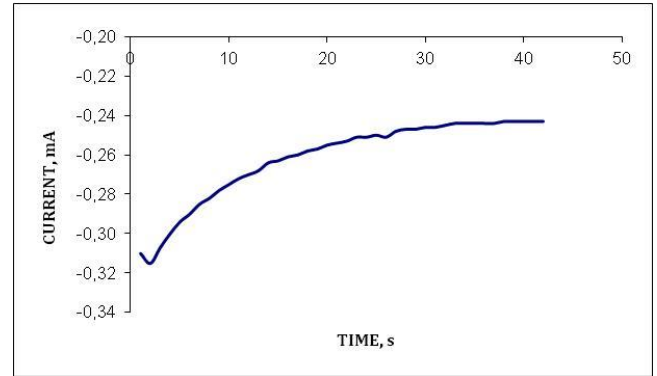


Figure 2: Chronoamperometric curve obtained during formation of modified PPY/DBS electrode

Modified Butler-Volmer equation

Nernst equation was used to characterize ion-selective electrodes. Bond *et al.* adapted the equation to voltammetric ion sensors (Wooster and Bond, 2003; Wooster, Bond and Honeychurch, 2003). Electromotive force (EMF) was changed with mid point reversible potential (E_R) and considering an activity coefficient close to unity.

These authors suggested equations 2 and 3 as followed:

$$E_R = E^0 + S \log[M_A^+] \quad (2)$$

$$E_R = E^0 - S \log[X^-] \quad (3)$$

These equations give direct relationship between E_R and the logarithm of the electrolyte concentration. S is the slope derived from the curve, which has positive or negative values for cationic or anionic exchanging, respectively. Moreover, ideally S will be equal to $2.303RT/nF$. E_R is the mid point reversible potential defined by:

$$E_R = \frac{E_p^{red} + E_p^{ox}}{2} \quad (4)$$

where E_p^{red} is the reduction peak potential and E_p^{ox} is the oxidation peak potential. Equations have also been successfully applied to check 7,7,8,8-tetracyanoquinodimethane (TCNQ) and tetrathiafulvalene (TTF) composite as ion selective electrode.

Romero *et al.* used equations reported by Bond *et al.* and modified them to get these equations:

$$E_R = H + 2,303 \frac{RT}{2\alpha_c n_s} \log[M^+] \quad (5)$$

$$E_R = H - 2,303 \frac{RT}{2\alpha_c n_s} \log[X^-] \quad (6)$$

where H is the intercept and α_c is the electron-transfer coefficient.

It can be shown, by comparing equations 2 and 3 with equations 5 and 6, that the only difference is in the slope and the intercept. As Romero *et. al.* demonstrated, the modified Butler-Volmer equation can be successfully applied to modified PPy/DBS electrodes tested as voltammetric cation sensors. Same authors showed that slopes deduced out of semilogarithmic curves were different from Nernstian values, because they included the electron-transfer coefficient (Cano, Rodriguez-Amaro and Romero, 2008a, 2008b).

RESULTS AND DISCUSSION

PPy/DBS modified electrode as a cation sensor

As explained above, modified Butler-Volmer equation gives a direct relationship between E_R and ion concentration.

Three different modified electrodes were immersed in aqueous solution of lithium, sodium and potassium perchlorate to test the capability of polypyrrole modified electrodes as voltammetric sensors.

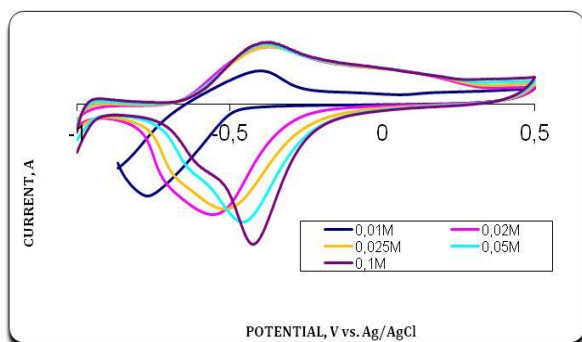


Figure 3: Voltammograms obtained at a scan rate of 10 mV s^{-1} when a PPy(0.1M)/DBS modified electrode was immersed in different concentrations of LiClO_4 aqueous solution

Three modified electrodes were PPy(0.05M)/DBS, PPy(0.1M)/DBS and PPy(1M)/DBS electrode. E_R values were calculated from voltammograms as shown in Figure 3 using equation 4, and a linear relationship between E_R and $\log [M^+]$ was obtained for all three cations studied. Example of calibration curve is shown in Figure 4.

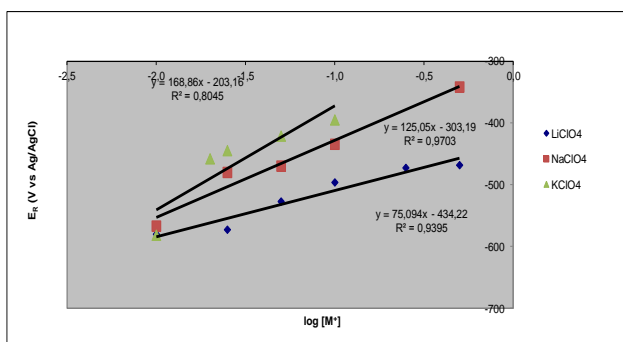


Figure 4: Calibration curves of E_R vs. $\log [M^+]$ for a modified PPy(0.1M)/DBS electrode in aqueous solution of $M^+\text{ClO}_4^-$

As can be seen from Figure 4 positive slopes are observed, which is in accordance with equations 2 and 5.

Table 1: Voltammetric parameters for the modified PPy(0.05M)/DBS electrode in aqueous solution of KClO_4 , NaClO_4 and LiClO_4

Cation	$S, \text{ mV dec}^{-1}$	α
Potassium	170.90	0.17
Sodium	122.93	0.24
Lithium	92.69	0.32

Table 2: Voltammetric parameters for the modified PPy(0.1M)/DBS electrode in aqueous solution of KClO_4 , NaClO_4 and LiClO_4

Cation	$S, \text{ mV dec}^{-1}$	α
Potassium	168.86	0.18
Sodium	125.05	0.24
Lithium	75.09	0.39

Table 3: Voltammetric parameters for the modified PPy(1M)/DBS electrode in aqueous solution of KClO_4 , NaClO_4 and LiClO_4

Cation	$S, \text{ mV dec}^{-1}$	α
Potassium	98.97	0.30
Sodium	137.42	0.22
Lithium	88.14	0.34

Data in Tables 1, 2 and 3 show that for all three tested electrodes a positive slope from the calibration curves can be derived. In all three cases slopes have the lowest value for lithium ion, and when 0.05 mol dm^{-3} and 0.1 mol dm^{-3} monomer concentration is used the highest value is shown for potassium ion. The only slope value differing from the others is when 1 mol dm^{-3} monomer concentration is used. Regarding the electron transfer coefficients, results show the highest value for lithium ion and the lowest for potassium ion, except again for the electrode made from 1 mol dm^{-3} monomer, when the value of electron transfer coefficient differs from the others.

CONCLUSIONS

Electrochemical synthesis of polypyrrole at a platinum electrode was successfully performed with all three concentrations of monomers. It is proved that the new method based on a modified Butler-Volmer equation can be successfully applied to determine the capability of voltammetric sensors. Modified PPy/DBS electrodes were sensitive to three cations analyzed. It was shown that the capability of the sensor depends on the quality of formed polypyrrole film which is dependent on the initial monomer concentration. In the application of modified PPy/DBS electrode the largest deviations were found when initial monomer concentration was 1 mol dm^{-3} of pyrrole, whereas the results when monomer concentration of 0.05 mol dm^{-3} and 0.1 mol dm^{-3} monomer were used agree with each other.

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Summary/Sažetak

U ovom radu je primijenjena modifikovana Butler-Volmer jednačina za određivanje kapaciteta voltametrijskog senzora zasnovanog na modifikovanoj elektrodi PPy/DBS. Ova metoda dovodi u direktnu vezu srednju vrijednost reverzibilnog potencijala i logaritma koncentracije elektrolita. Nagib Butler-Volmerove jednačine uključuje i koeficijent prenosa naboja. Modifikovana PPy/DBS elektroda je uspješno primijenjena kao voltametrijski katjon senzor. Dokazano je da polazna koncentracija monomera utiče na formiranje polipirrolnog filma, od čije kvalitete zavisi i kapacitet senzora.